

Kinetics and Mechanisms of the Gas-Phase Reactions of the NO₃ Radical with Organic Compounds

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A substantial data base concerning the rate constants for the gas-phase reactions of the nitrate (NO₃) radical with organic compounds is now available, with rate constants having been determined using both absolute and relative rate methods. To date, the majority of these kinetic data have been obtained at room temperature using relative rate techniques utilizing both the reactions of the NO₃ radical with other organic compounds and the equilibrium constant for the NO₃ + NO₂ ⇌ N₂O₅ reactions as the reference reaction. In this article, the literature kinetic and mechanistic data for the gas-phase reactions of the NO₃ radical with organic compounds (through late 1990) have been tabulated, reviewed and evaluated. While this available data base exhibits generally good agreement and self-consistency, further absolute rate data are needed, preferably as a function of temperature. Most importantly, mechanistic and product data for the reactions of the NO₃ radical with organic compounds need to be obtained.

Key words: atmospheric chemistry; nitrate radical; organic compounds; reaction kinetics; reaction mechanisms.

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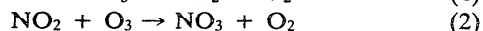
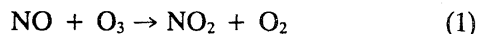
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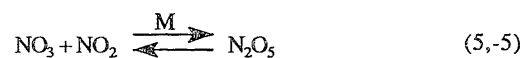
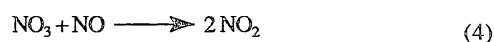
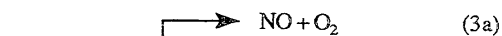
1. Introduction

Measurements made during the 13 years have shown the nitrate (NO_3) radical to be present in the nighttime stratosphere¹⁻¹⁰ and troposphere.¹¹⁻²⁰ In the lower troposphere over continental areas the reported NO_3 radical mixing ratios range from <2 parts-per-trillion (ppt) [$\leq 5 \times 10^7$ molecule cm^{-3}]¹⁶ up to 430 ppt [$\sim 1.0 \times 10^{10}$ molecule cm^{-3}].¹⁸ The NO_3 radical mixing ratios in marine air masses in the troposphere are low, with upper limits of <0.5 ppt being reported by Platt and Perner²¹ at Loop Head, Ireland and a mixing ratio of 0.25 ± 0.1 ppt being measured by Noxon¹⁵ at 3 km altitude in the free troposphere from Mauna Loa, Hawaii.

NO_3 radicals are formed in the troposphere and stratosphere from NO and NO_2 by the reaction sequence,



with rate constants k_1 and k_2 of $k_1 = 1.8 \times 10^{-12} e^{-1370/T}$ cm^3 molecule⁻¹s⁻¹ and $k_2 = 1.2 \times 10^{-13} e^{-2450/T}$ cm^3 molecule⁻¹s⁻¹.²² The following reactions lead to the removal and/or temporary storage of NO_3 radicals,



with $k_4 = 1.6 \times 10^{-11} e^{150/T}$ cm^3 molecule⁻¹s⁻¹, $k_5 = 2.0 \times 10^{-12} (T/300)^{0.2}$ cm^3 molecule⁻¹s⁻¹ at the high pressure limit and $J_3 = 0.2$ s⁻¹ at the earth's surface for a zenith angle of 0° ($J_{3b}/J_3 = 0.9$).²² While, as discussed below, there are significant uncertainties concerning the equilibrium constant $K_5 (= k_5/k_{-5})$ for the $\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5$ reactions,²²⁻²⁴ the thermal decomposition lifetime of N_2O_5 is ~ 20 s at 298 K and 760 Torr total pressure of air.²²

Because of the rapid photolysis of the NO_3 radical and its rapid reactions with NO and O_3 (and the rapid reaction of NO with O_3),^{22,23} ambient atmospheric NO_3 radical concentrations are low during daylight hours. For example, under lower tropospheric conditions characteristic of "rural" areas, with NO, NO_2 and O_3 concentrations (in molecule cm^{-3} units) of: NO, $\leq 1 \times 10^{10}$; NO_2 , 2.4×10^{10} ; and O_3 , 7×10^{11} , a daytime NO_3 radical concentration of $\sim (1-2) \times 10^6$ molecule cm^{-3} is calculated from consideration of reactions (2), (3), (4) and (5). NO_3 radical concentrations are expected to build up during the early evening and nighttime hours, due to the absence of photolysis [reaction (3)] and the low nighttime concentrations of NO. In addition to the gas-phase inorganic reactions shown above, NO_3 radicals can also be removed and/or transformed in the lower troposphere by reactions with organic compounds and by dry and/or wet deposition of the NO_3 radical and/or N_2O_5 .^{13,16,25-33}

While direct measurements have shown that the homogeneous gas-phase reaction of N_2O_5 with water vapor



has an upper limit to the rate constant of $k_6 < 1.5 \times 10^{-21}$ cm^3 molecule⁻¹s⁻¹ at room temperature,³⁴⁻³⁷ this upper limit to the rate constant is not sufficiently low to exclude this gas-phase reaction as a contributor to NO_3 radical/ N_2O_5 removal and acid formation.^{25,30-32} However, it is expected that wet and dry deposition of NO_3 radicals and/or N_2O_5 dominates over reaction (6).^{32,33} The gas-phase reactions of the NO_3 radical with organic compounds have been the subject of numerous studies over the past 16 years, and the reactions of the NO_3 radical with alkenes (including the monoterpenes),^{28,38,39} organosulfur compounds,²⁸ aldehydes^{26,40,41} and hydroxyaromatics⁴² can be important in the removal of oxides of nitrogen and/or the organic compounds^{26,28,38-42} and the formation of acids^{26,40} in the lower troposphere.

Despite numerous kinetic and product studies of the gas-phase reactions of the NO_3 radical with organic compounds and the importance of these reactions in the chemistry of the lower troposphere, to date the available NO_3 radical rate constant data have not been critically evaluated. This is carried out in this review article, and

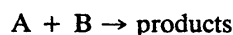
the kinetic and mechanistic recommendations made will be of use to chemical modelers of the lower troposphere and of urban air pollution. Another review, dealing with the spectroscopy and photochemistry of the NO_3 radical, the kinetics and mechanisms of its gas- and aqueous-phase reactions with inorganic and organic species, ambient atmospheric NO_3 radical concentrations, and the role of the NO_3 radical in the chemistry of the atmosphere, has recently been published⁴³ through the auspices of the Commission of the European Communities.

1.1. Experimental Techniques

Rate constants for the gas-phase reactions of the NO_3 radical with organic compounds have been obtained using two general methods, namely absolute and relative rate techniques. The salient features of the experimental methods used to date are briefly discussed below.

1.1.a. Absolute Rate Measurements

In the majority of the absolute rate constant determinations carried out, the pseudo-first order decay rate of one of the reactants (the NO_3 radical or the organic compound) has been measured in the presence of a known excess concentration of the other reactant,

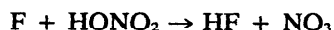


and hence,

$$-d \ln[A]/dt = k[B]$$

where k is the rate constant for the reaction of the NO_3 radical with the organic compound. For the more reactive alkenes and alkynes, Canosa-Mas *et al.*⁴⁴ have also conducted kinetic measurements under conditions where the full second-order kinetic data analysis was necessary. Absolute rate measurements have been carried out using both low pressure (≤ 10 Torr total pressure) flow techniques⁴⁴⁻⁴⁸ and higher pressure (≥ 20 Torr total pressure) pulsed or modulated photolysis systems under slow flow conditions.⁴⁹⁻⁵²

In the low pressure flow method, NO_3 radicals have been generated by the reaction of F atoms (generated by the dissociation of F_2 in a microwave discharge) with nitric acid^{44,45,47,48}



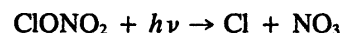
and by the thermal dissociation of N_2O_5 at 400–425 K^{45,46}



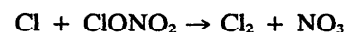
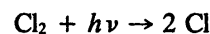
NO_3 radicals have been detected and/or quantified by optical absorption at 662 nm,^{44,45} laser induced fluorescence with excitation at 662 nm,^{45,46} mass spectrometry,^{47,48,53} and chemical titration with NO or 2,3-dimethyl-2-butene.^{48,54} The detection limits for NO_3 radicals using these methods have been reported as being $\sim 1 \times 10^8$ molecule cm^{-3} using laser induced fluorescence⁴⁶ and ~ 5

$\times 10^{11}$ molecule cm^{-3} using either optical absorption^{44,45} or mass spectrometry.⁵³ In the experimental studies carried out in which the pseudo-first order decays of the NO_3 radical were monitored, the initial NO_3 radical concentrations employed (in molecule cm^{-3} units) have typically been $(0.5-40) \times 10^{10}$ using laser induced fluorescence,^{45,46} $(0.7-5) \times 10^{13}$ using optical absorption,^{44,45} and $(1.5-3) \times 10^{12}$ using mass spectrometry.⁵³ Using mass spectrometry, Rahman *et al.*,⁴⁷ Benter and Schindler⁵³ and Poulet and Le Bras⁴⁸ have also determined rate constants by monitoring the decay of the organic reactant in the presence of excess concentrations of NO_3 radicals.

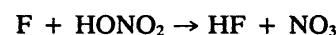
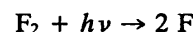
In the higher pressure pulsed or modulated photolysis systems, NO_3 radicals have been generated by the photolysis of ClONO_2 at wavelengths > 180 nm,⁵¹



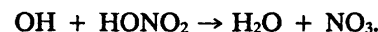
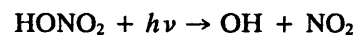
the photolysis of $\text{Cl}_2 - \text{ClONO}_2$ mixtures at wavelength > 280 nm,^{49,51}



the photolysis of $\text{F}_2 - \text{HONO}_2$ mixtures at wavelength > 180 nm⁵¹ or 310–400 nm,⁴⁹



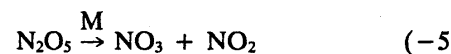
and by the photolysis of HONO_2 at ~ 250 nm^{50,52}



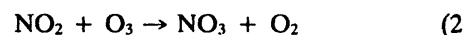
In these pulsed or modulated photolysis studies, NO_3 radicals were monitored by optical absorption at 627 nm^{49,50} or 662 nm.^{51,52} The initial NO_3 radical concentrations in the flash and laser photolysis studies of Wallington *et al.*^{51,56} and Daykin and Wine⁵² were $\sim (2-5) \times 10^7$ molecule cm^{-3} and $(0.4-2) \times 10^{12}$ molecule cm^{-3} , respectively, and the steady state NO_3 radical concentrations in the modulated photolysis study of Tyndall *et al.*⁵ were $(4-40) \times 10^{10}$ molecule cm^{-3} . Total pressures using these flash, laser and modulated photolysis techniques ranged from 19–500 Torr.^{49-52,56,57}

1.1.b. Relative Rate Measurements

Two distinct relative rate methods have been used to date. In both cases, NO_3 radicals are generated from either the thermal decomposition of N_2O_5



or the reaction of NO_2 with O_3 ,



which is followed by the reaction of NO_3 radicals with NO_2 to generate N_2O_5 and the subsequent decomposition of N_2O_5 [reactions (5), (-5)].

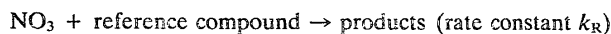
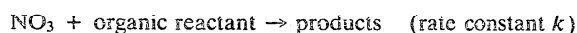
In the method first described and used by Morris and Niki⁵⁸ and subsequently employed by Japar and Niki,³⁸ Wilkinson *et al.*,³⁹ Cantrell *et al.*,^{40,41,59} Hjorth *et al.*⁶⁰ and Andersson and Ljungström,⁶¹ the enhanced decay rates of N_2O_5 in the presence of known excess concentrations of the organic reactant are monitored. Under conditions where NO_3 radicals, NO_2 and N_2O_5 are in equilibrium, $[\text{NO}_2] \gg [\text{N}_2\text{O}_5]_{\text{initial}}$ and $K_5[\text{NO}_2] \gg 1$, then the N_2O_5 decays in the presence of the organic reactant are exponential³⁹ and

$$\text{enhanced } \text{N}_2\text{O}_5 \text{ decay rate} = k[\text{organic}]/K_5[\text{NO}_2],$$

where k is the rate constant for the reaction of NO_3 radicals with the organic reactant. Under conditions where the initial N_2O_5 concentration is of a similar magnitude to the NO_2 concentration, then the NO_2 concentration may change during the reaction and exponential decays of N_2O_5 are no longer observed.³⁸ The individual references should be consulted for further details of the studies carried out.

This technique may be subject to the occurrence of secondary reactions removing N_2O_5 ,^{39,62,63} and this would be most likely to be the case for organic compounds which react with NO_3 radicals to form products which are more reactive towards NO_3 radicals than is the parent organic compound. The rate constants determined in this manner are relative to the equilibrium constant K_5 for the $\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5$ reactions, and this equilibrium constant is not accurately known (see below) and is also very temperature dependent (with K_5 increasing by $\sim 10\%$ for a 1 K temperature decrease at ~ 298 K).²²⁻²⁴

In the second, and most used method to date, the relative rates of consumption of two or more organic compounds, including one (the reference organic) for which the NO_3 radical reaction rate constant is reliably known, are monitored in the presence of NO_3 radicals.^{39,42,62-66} NO_3 radicals have been generated by the thermal decomposition of N_2O_5 ,^{39,62-66} or from the reaction of O_3 with NO_2 .⁴² In many studies, several additions of N_2O_5 to the reaction mixtures have been necessary, and any dilution must then be allowed for.^{39,67} If the organic compounds are removed only by reaction with the NO_3 radical,



then,

$$\ln \left\{ \frac{[\text{organic reactant}]_t}{[\text{organic reactant}]_0} \right\} - D_t = \frac{k}{k_R} \left[\ln \left\{ \frac{[\text{reference compound}]_t}{[\text{reference compound}]_0} \right\} - D_t \right]$$

where $[\text{organic reactant}]_0$ and $[\text{reference compound}]_0$ are the concentrations of the organic reactant and the

reference compound, respectively, at time t_0 , $[\text{organic reactant}]_t$ and $[\text{reference compound}]_t$ are the corresponding concentrations at time t , and D_t is the amount of dilution at time t . NO_2 has generally been added to the reactant mixtures to lengthen the reaction times^{38,39} and to minimize secondary reactions⁶⁷⁻⁶⁹ [possibly involving OH radicals].⁶⁷ The rate constant ratios k/k_R obtained can then be placed on an absolute basis by use of the known rate constant k_R .

The relative rate experiments conducted to date have employed static reaction vessels of 50–6400 liters in volume, and experiments have been carried out at room temperature and 700–750 Torr total pressure. The organic reactants have been monitored during the reactions by Fourier transform infrared (FT-IR) absorption spectroscopy^{38-41,58,60,61} or gas chromatography,^{39,42,62-67} while N_2O_5 has been monitored when necessary by FT-IR absorption spectroscopy. The individual references should again be consulted for further details of the studies carried out.

1.2. Product Studies

Product studies of the gas-phase reactions of the NO_3 radical with organic compounds have generally been carried out in much the same manner as the relative rate constant studies, using FT-IR absorption spectroscopy and/or chromatographic techniques to identify and quantify the products formed in $\text{N}_2\text{O}_5 - \text{NO}_2 - \text{organic} - \text{air}$ or irradiated $\text{NO}_x - \text{organic} - \text{air}$ mixtures.^{40,41,58,66,70-77} The individual references should be consulted for details.

2. Kinetic, Mechanistic, and Product Data Obtained

In the following sections, the reactions of the NO_3 radical with the various classes of organic compounds (alkanes, haloalkanes, alkenes, haloalkenes, alkynes, oxygen-, sulfur-, nitrogen-, phosphorus-, selenium- and silicon-containing organics, aromatic compounds and organic radicals) are discussed separately. The available rate constant data are tabulated, with those rate data obtained relative to the rate constant for the reaction of the NO_3 radical with a reference organic being re-evaluated on the basis of the recommended rate constants for the reference reactions at the temperatures employed.

While many relative rate studies have obtained NO_3 radical reaction rate constants relative to the equilibrium constant K_5 for the $\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5$ reactions, the value of K_5 is not well known.^{19,22-24,78-82} In order to place these relative rate constant determinations on an absolute basis in this article, the equilibrium constant K_5 has been evaluated by use of the recent direct experimental studies of Tuazon *et al.*,⁸⁰ Burrows *et al.*⁸² and Cantrell *et al.*²⁴ [which is judged to supersede the earlier study of Perner *et al.*¹⁹ from this research group] and the evaluation of Kircher *et al.*⁸¹ using the rate constants for reactions (5) and (-5).

A value of $K_5 = 3.41 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ at 298 K is obtained from a unit-weighted average of the reported [or interpolated from the cited temperature expression²⁴] equilibrium constants (in units of $10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$) of 3.44,⁸⁰ 3.26,⁸¹ 2.50⁸² and 4.45.²⁴ (An essentially identical value is obtained from a unit-weighted average of the experimentally measured equilibrium constants of Tuazon *et al.*,⁸⁰ Burrows *et al.*,⁸² and Cantrell *et al.*²⁴) Similarly, a temperature dependence of $B = 11275 \text{ K}$ in the expression $K_5 = A e^{B/T}$ is obtained from a unit-weighted average of the temperature dependencies (B) of 11050 K [for the temperature range 256–357 K ($1000/T \text{ (K)} = 2.8 - 3.9$)],⁸¹ 11960 K⁸² and 10815 K.²⁴ These literature data^{24,80-82} are plotted in Arrhenius form in Fig. 1, together with the recommended expression of

$$K_5 = 1.26 \times 10^{-27} e^{11275/T} \text{ cm}^3 \text{ molecule}^{-1}$$

resulting from the above 298 K value and temperature dependence. It should be noted that this analysis neglects both the uncertainties in the visible absorption cross-section for the NO_3 radical²² and the differences in the absorption cross-sections used in the three direct studies^{24,80,82} considered. This evaluation of K_5 is in good agreement with the recent IUPAC²² and NASA²³ evaluations, which yield values of K_5 at 298 K of $2.90 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ [derived from the rate constants for reactions (5) and (-5)] and $3.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$, respectively.

The value of K_5 at any given temperature over the restricted range of ~ 255 – 355 K has an estimated overall uncertainty of a factor of ~ 1.5 . Accordingly, rate constants for the reactions of the NO_3 radical with organic compounds determined relative to the equilibrium constant K_5 are given less weight in the evaluations.

In the rate constant tabulations, the experimental techniques used are denoted by abbreviations such as DF-A, where the first letters denote the following: DF, discharge flow (NO_3 radicals formed by the reaction of F atoms, generated in a microwave discharge, with HONO_2); F, flow system (NO_3 radicals generated from the thermal decomposition of N_2O_5); FP, flash photolysis; LP, laser photolysis; MP, modulated photolysis; and S, static system; and the second set of letters denote the detection method: A, optical absorption; LIF, laser induced fluorescence; and MS, mass spectrometry. The relative rate studies are denoted by RR and the reference reactions and the reference compound rate constant or equilibrium constant (K_5) used is noted. For those reactions for which a temperature dependence can be recommended, the temperature dependence of the rate constant, k , is given by either the Arrhenius expression, $k = A e^{-B/T}$, or, if curvature in the Arrhenius plot is evident, by the modified Arrhenius expression, $k = CT^2 e^{-D/T}$.

2.1 Alkanes

2.1.a. Kinetics and Mechanisms

The literature rate constant data for the gas-phase reactions of the NO_3 radical with alkanes are given in Table

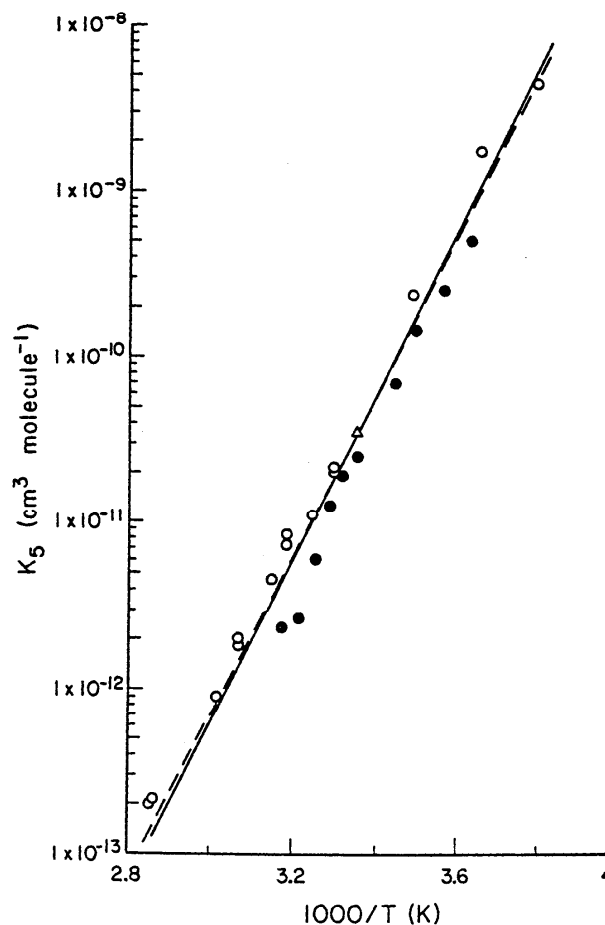


FIG. 1. Plot of the logarithm of the equilibrium constant K_5 for the $\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5$ reactions against $1/T \text{ (K)}$ over the temperature range 260–355 K. (Δ) Tuazon *et al.*,⁸⁰ (---) Kirch *et al.*,⁸¹ (\bullet) Burrows *et al.*,⁸² (\circ) Cantrell *et al.*,²⁴ (—) recommendation, see text.

1. All of the rate constants have been obtained at room temperature, mainly from relative rate measurement. Only for methane, *n*-butane, 2,3-dimethylbutane and *n* heptane have more than a single study been carried out and there are obvious discrepancies between the absolute⁵¹ and relative⁶² rate determinations for *n*-butane.

(1) Methane

Only upper limits to the room temperature rate constant have been determined.^{49,51,59} Based on the data from these studies^{49,51,59} and the correlation of NO_3 radical abstraction rate constants with OH radical abstraction rate constants (see below), an upper limit to the rate constant of

$$k(\text{methane}) < 1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K is recommended.

(2) 2,3-Dimethylbutane

Two kinetic studies have been carried out,^{62,67} with the room temperature rate constant being determined relative to the equilibrium constant K_5 ⁶² and to the rate constants for the reactions of the NO_3 radical with *n*-heptane⁶² and *trans*-2-butene.⁶⁷ The rate constants obtained are in reasonable agreement. Since a lower weight is given to the rate data obtained relative to the equilibrium constant K_5 , the recommendation is based upon the most recent rate constant study of Atkinson *et al.*,⁶⁷ leading to

$$k(2,3\text{-dimethylbutane}) = 4.08 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$$

at 296 K, with an estimated overall uncertainty of a factor of 1.5. Assuming a preexponential factor in the Arrhenius expression of $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$, the rate constant for 2,3-dimethylbutane at 298 K is then $4.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$.

(3) *n*-Heptane

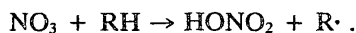
Rate constants at room temperature have been determined relative to the equilibrium constant K_5 ⁶² and to the rate constant for the reaction of the NO_3 radical with *trans*-2-butene.⁶⁷ The agreement is excellent, and the recommendation is based upon the most recent and precise study of Atkinson *et al.*,⁶⁷ leading to

$$k(n\text{-heptane}) = 1.37 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$$

at 296 K, with an estimated overall uncertainty of a factor of 1.5. Assuming a preexponential factor of $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$ in the Arrhenius expression leads to a rate constant at 298 K of $1.45 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$.

(4) Other Alkanes

No explicit recommendations are made for the other alkanes for which rate constant data have been reported. However, an assessment of the general validity of the rate constants given in Table 1 and of the relative reactivities of the differing C—H bonds in the alkanes can be made. The NO_3 radical reactions with the alkanes proceed by H-atom abstraction from the various —CH₃, —CH₂— and >CH— groups.



As discussed previously for the reactions of the OH radical with alkanes,^{83,84} the rate constants for H-atom abstraction correlate with the C—H bond dissociation energy, increasing with decreasing bond dissociation energy. Hence the NO_3 radical reaction rate constants for H-atom abstraction (per equivalent C—H bond) should correlate with the corresponding OH radical reaction

rate constants. Since the bond dissociation energies are not known accurately for all of the C—H bonds in the alkanes, Atkinson^{85,86} developed an estimation technique in which the OH radical reaction rate constants are calculated from the —CH₃, —CH₂— and >CH— group rate constants. These group rate constants depend on the identity of the substituents, with

$$k(\text{CH}_3\text{—}X) = k^{\text{prim}} F(X),$$

$$k(X\text{—CH}_2\text{—}Y) = k^{\text{sec}} F(X) F(Y)$$

and

$$k\left(X\text{—CH} \begin{array}{l} \diagup Y \\ \diagdown Z \end{array}\right) = k^{\text{tert}} F(X) F(Y) F(Z),$$

where k^{prim} , k^{sec} and k^{tert} are the rate constants per —CH₃, —CH₂— and >CH— group for a standard substituent, respectively, X , Y , and Z are the substituent groups, and $F(X)$, $F(Y)$ and $F(Z)$ are the corresponding substituent factors. The standard substituent group was chosen to be $X = Y = Z = \text{—CH}_3$, with $F(\text{—CH}_3) = 1.00$ by definition.⁸⁵ The values of the group rate constants and substituent factors at 298 K for the OH radical abstraction reactions have been evaluated⁸⁶ and are:

$$k_{\text{OH}}^{\text{prim}} = 1.44 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1},$$

$$k_{\text{OH}}^{\text{sec}} = 8.38 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1},$$

$$k_{\text{OH}}^{\text{tert}} = 1.83 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1},$$

and

$$F_{\text{OH}}(\text{—CH}_2\text{—}) = F_{\text{OH}}(>\text{CH—}) = F_{\text{OH}}(>\text{C}<) = 1.29,$$

with the temperature dependence of the substituent factors being given in the form $F(X) = e^{E_X/T}$.

A correlation of the H-atom abstraction rate constants per equivalent C—H bond for the room temperature reactions of NO_3 and OH radicals with a series of alkanes and aldehydes is shown in Fig. 2. (The OH radical rate constants for acetaldehyde, 2,3-dimethylbutane and 2-methylpropane⁸⁷ were corrected⁸⁶ to take into account the minor amount of H-atom abstraction from the —CH₃ groups, and the rate constant for H-atom abstraction from *n*-heptane is that for a —CH₂— group bonded to two other —CH₂— groups, $k[\text{CH}_2(\text{CH}_2)_2]$. For the NO_3 radical reactions, H-atom abstraction from the —CH₃ groups was neglected, and lower and upper limits for the rate constant for a secondary C—H bond in a —CH₂— group bonded to two other —CH₂— groups in *n*-heptane of $1.4 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$ and $2.3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$, respectively, were derived by assuming that (a) all the secondary C—H bonds were equivalent and (b) the two —CH₂— groups bonded to one —CH₃ group and one —CH₂— group contributed negligibly. A preferred H-atom abstraction rate constant of $k[\text{CH}_2(\text{CH}_2)_2] = 2.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$ was used in the correlation).

TABLE 1. Rate constants k for the gas-phase reactions of the NO_3 radical with alkanes

Alkane	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
Methane	$< 4 \times 10^{-16}$	298	MP-A	Burrows <i>et al.</i> ⁴⁹
	$\leq 2 \times 10^{-17}$	298 ± 2	FP-A	Wallington <i>et al.</i> ⁵¹
	$< 6 \times 10^{-21}$	a	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 3.41 \times 10^{-11}$] ^b	Cantrell <i>et al.</i> ⁵⁹
Ethane	$\leq 4 \times 10^{-18}$	298 ± 2	FP-A	Wallington <i>et al.</i> ⁵¹
<i>n</i> -Butane	$(6.6 \pm 1.7) \times 10^{-17}$	296 ± 2	RR [relative to $k(n\text{-heptane})$ $= 1.37 \times 10^{-16}$] ^b	Atkinson <i>et al.</i> ⁶²
	$\leq 2 \times 10^{-17}$	298 ± 2	FP-A	Wallington <i>et al.</i> ⁵¹
2-Methylpropane	$(9.8 \pm 2.1) \times 10^{-17}$	296 ± 2	RR [relative to $k(2,3\text{-dimethylbutane})$ $= 4.08 \times 10^{-16}$] ^b	Atkinson <i>et al.</i> ⁶²
<i>n</i> -Pentane	$(8.1 \pm 1.7) \times 10^{-17}$	296 ± 2	RR [relative to $k(n\text{-heptane})$ $= 1.37 \times 10^{-16}$] ^b	Atkinson <i>et al.</i> ⁶²
<i>n</i> -Hexane	$(1.05 \pm 0.20) \times 10^{-16}$	296 ± 2	RR [relative to $k(n\text{-heptane})$ $= 1.37 \times 10^{-16}$] ^b	Atkinson <i>et al.</i> ⁶²
2,3-Dimethylbutane	$(5.34 \pm 1.11) \times 10^{-16}$	296 ± 2	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 4.40 \times 10^{-11}$] ^b	Atkinson <i>et al.</i> ⁶²
	$(4.04 \pm 0.18) \times 10^{-16}$	296 ± 2	RR [relative to $k(n\text{-heptane})$ $= 1.37 \times 10^{-16}$] ^b	Atkinson <i>et al.</i> ⁶²
	$(4.08 \pm 0.32) \times 10^{-16}$	296 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.89 \times 10^{-13}$] ^b	Atkinson <i>et al.</i> ⁶⁷
Cyclohexane	$(1.35 \pm 0.25) \times 10^{-16}$	296 ± 2	RR [relative to $k(2,3\text{-dimethylbutane})$ $= 4.08 \times 10^{-16}$] ^b	Atkinson <i>et al.</i> ⁶²
<i>n</i> -Heptane	$(1.34 \pm 0.37) \times 10^{-16}$	296 ± 2	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 4.40 \times 10^{-11}$] ^b	Atkinson <i>et al.</i> ⁶²
	$(1.37 \pm 0.14) \times 10^{-16}$	296 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.89 \times 10^{-13}$] ^b	Atkinson <i>et al.</i> ⁶⁷
<i>n</i> -Octane	$(1.82 \pm 0.22) \times 10^{-16}$	296 ± 2	RR [relative to $k(n\text{-heptane})$ $= 1.37 \times 10^{-16}$] ^b	Atkinson <i>et al.</i> ⁶²
<i>n</i> -Nonane	$(2.41 \pm 0.29) \times 10^{-16}$	296 ± 2	RR [relative to $k(n\text{-heptane})$ $= 1.37 \times 10^{-16}$] ^b	Atkinson <i>et al.</i> ⁶²

^a Room temperature, not reported; 298 K has been assumed.

^b From present recommendations (see text).

The correlation is excellent, and a least-squares analysis leads to (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ units)

$$\ln k_{\text{NO}_3} = 6.498 + 1.611 \ln k_{\text{OH}}$$

Use of this equation and the OH radical group rate constants given above⁸⁶ leads to

$$k_{\text{NO}_3}^{\text{prim}} = 7.0 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

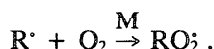
$$k_{\text{NO}_3}^{\text{sec}} = 1.5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

and

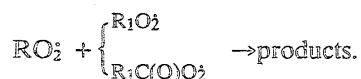
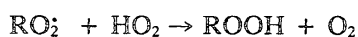
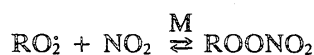
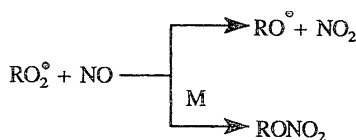
$$k_{\text{NO}_3}^{\text{tert}} = 8.2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

all at 298 K. Since $F_{\text{NO}_3}(X) = [F_{\text{OH}}(X)]^{1.611}$, $F_{\text{NO}_3}(\text{—CH}_2\text{—}) = F_{\text{NO}_3}(>\text{CH—}) = 1.5$ at 298 K. Using these parameters, the calculated 298 K rate constants for the reactions of the NO_3 radical with the alkanes studied to date (Table 1) are (in units of $10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): ethane, 0.014; propane, 0.17; *n*-butane, 0.47; 2-methylpropane, 0.85; *n*-pentane, 0.81; *n*-hexane, 1.15; cyclohexane, 2.0; 2,3-dimethylbutane, 2.5; *n*-heptane, 1.5; *n*-octane, 1.8; and *n*-nonane, 2.0. These calculated rate constants are in generally good agreement with the experimental data (Table 1), with the possible exception of *n*-butane. The assumption that H-atom abstraction by the NO_3 radical from the —CH_3 groups can be neglected is confirmed, and this assumption is also consistent with the correlations recently presented by Sabljic and Gusten.⁸⁸

These group rate constants and substituent factors can be used to calculate the overall rate constants for the reactions of the NO_3 radical with alkanes at room temperature and the distributions of the various alkyl radicals formed in these NO_3 radical reactions. The subsequent reactions of the alkyl ($\text{R}\cdot$) radicals formed under tropospheric conditions have been discussed in detail in the literature,^{22,89} and involve rapid initial reaction with O_2 to form the corresponding alkyl peroxy (RO_2) radicals



These alkyl peroxy radicals then undergo reactions with NO , NO_2 , HO_2 radicals, and/or other organic peroxy radicals.^{22,89}



These reactions have been reviewed and evaluated elsewhere,^{22,89} and these references should be consulted for details.

2.2. Haloalkanes

2.2.a. Kinetics and Mechanisms

The only rate constants available for the reactions of the NO_3 radical with haloalkanes are for trichloromethane, and these data are given in Table 2. Since this is the only study for this haloalkane, no recommendation is made. The reported rate expression⁹⁰ leads to an extrapolated rate constant of $k(\text{trichloromethane}) = 6.7 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. This reaction is expected to occur by H-atom abstraction. However, based upon the correlation shown in Fig. 2 and the room temperature rate constant for the reaction of the OH radical with CHCl_3 ,⁸⁷ the rate constant for the reaction of the NO_3 radical with CHCl_3 at 298 K is estimated to be $\sim 8 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. An essentially identical rate constant is predicted from the value of $k_{\text{NO}_3}^{\text{tert}}$ derived in Sec. 2.1 above and $F_{\text{NO}_3}(\text{Cl}) = [F_{\text{OH}}(\text{Cl})]^{1.611} (= 0.21)$.⁸⁶ This apparent discrepancy of two orders of magnitude indicates that further studies are necessary.

2.3. Alkenes

2.3.a. Kinetics

The available rate constant data are given in Tables 3 (acyclic monoalkenes), 4 (acyclic di- and trienes) and 5 (cyclic alkenes).

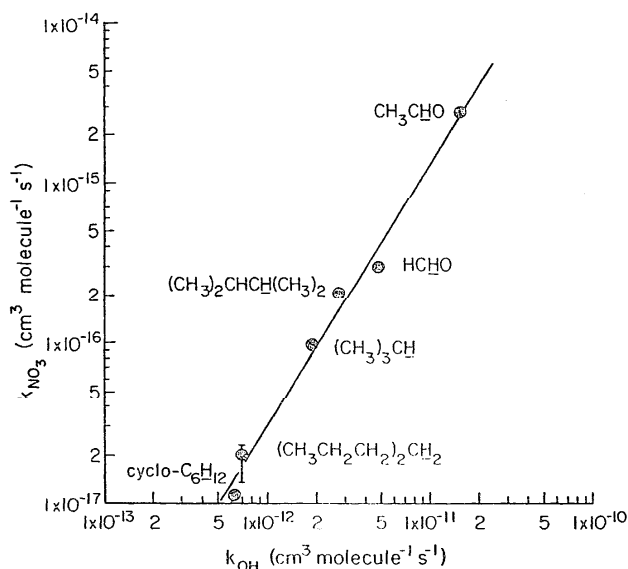


FIG. 2. Plot of the rate constants for H-atom abstraction per equivalent C—H bond (underlined) from a series of alkanes (2-methylpropane, cyclohexane, 2,3-dimethylbutane and *n*-heptane) and aldehydes (formaldehyde and acetaldehyde) by NO_3 radicals against the corresponding OH radical reaction rate constants. [OH radical reaction rate constants from Atkinson^{86,87} (see text)] (—) least-squares regression.

TABLE 2. Rate constants k and temperature-dependent parameters, $k = A e^{-B/T}$, for the gas-phase reactions of the NO_2 radical with haloalkane

Haloalkane	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
Trichloro- methane	$0.85^{+0.64}_{-0.37}$	2815 ± 241	2.6×10^{-16}	323	DF-A	Canosa-Mas <i>et al.</i> ⁹⁰
			$(4.3 \pm 1.2) \times 10^{-16}$	373		
			$(1.20 \pm 0.014) \times 10^{-15}$	423		
			$(2.17 \pm 0.48) \times 10^{-15}$	473		
			$(3.88 \pm 0.73) \times 10^{-15}$	523		

(1) Ethene

The available rate constant data of Japar and Niki,³⁸ Atkinson *et al.*,^{39,62,67} Canosa-Mas *et al.*,^{44,91} Andersson and Ljungström⁶¹ and Barnes *et al.*⁶⁶ are given in Table 3 and are plotted in Arrhenius form in Fig. 3. The sole temperature dependence arises from the absolute rate study of Canosa-Mas *et al.*⁹¹ The room temperature rate constant of Japar and Niki³⁸ is an order of magnitude higher than the other room temperature rate constants,^{39,44,61,62,66,67} all of which are in reasonable agreement (covering a range of a factor of 1.8). The good agreement at room temperature between the low pressure (2–5 Torr total pressure) rate constant of Canosa-Mas *et al.*⁴⁴ and the atmospheric pressure rate constants of Atkinson *et al.*,^{39,62,67} Andersson and Ljungström⁶¹ and Barnes *et al.*⁶⁶ indicates that the rate constant is independent of total pressure above ~ 2 Torr at ~ 298 K. The rate constants obtained by Atkinson *et al.*,³⁹ Andersson and Ljungström⁶¹ and Barnes *et al.*⁶⁶ are subject to significant uncertainties due to uncertainties in the equilibrium constant K_s ,^{39,61} uncertainties in the rate constant for 2-methylpropane⁶⁶ (only a single rate constant is available and no recommendation is made) or due to the small amounts of ethene consumed by reaction.³⁹ The absolute rate constants of Canosa-Mas *et al.*^{44,91} and the relative rate constant of Atkinson *et al.*⁶⁷ (which supercedes the earlier data of Atkinson *et al.*⁶²) are used in the evaluation of this rate constant. As seen from Fig. 3, a small amount of curvature is evident in the Arrhenius plot. Using the expression $k = CT^2 e^{-D/T}$, a unit-weighted least-squares analysis of these data^{44,67,91} yields the recommendation of

$$k(\text{ethene}) = (4.88^{+1.78}_{-1.31}) \times 10^{-18} T^2 e^{-(2282 \pm 113)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 295–523 K, where the error limits are two least-squares standard deviations, and

$$k(\text{ethene}) = 2.05 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of a factor of 1.5. Using the Arrhenius expression, a unit-weighted least-squares analysis of these data^{44,67,91} yields

$$k(\text{ethene}) = (5.43^{+2.92}_{-1.90}) \times 10^{-12} e^{-(3041 \pm 156)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

where the error limits are again two least-squares standard deviations, and

$$k(\text{ethene}) = 2.01 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

(2) Propene and Propene- d_6

The available rate constant data of Morris and Niki,⁵ Japar and Niki,³⁸ and Atkinson *et al.*^{39,67} are given in Table 3. These rate constants were all derived from relative rate studies carried out at room temperature. The agreement is reasonably good, and the most recent and precise rate constant study of Atkinson *et al.*⁶⁷ is used to recommend that

$$k(\text{propene}) = 9.45 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty of $\pm 40\%$. The data of Japar and Niki³⁸ show that the room temperature rate constant for propene- d_6 is within 20% of that for propene- h_6 , indicating no significant isotope effect.

(3) 1-Butene

The available rate constant data of Japar and Niki,³ Atkinson *et al.*,^{39,67} Andersson and Ljungström⁶¹ and Barnes *et al.*⁶⁶ are given in Table 3. Again, all of these were relative rate studies carried out at room temperature. The agreement is excellent, and a unit-weighted average of the rate constant data of Atkinson *et al.*^{39,67} and Barnes *et al.*⁶⁶ leads to the recommendation of

$$k(1\text{-butene}) = 1.25 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty of $\pm 40\%$.

(4) 2-Methylpropene

The available rate constant data of Japar and Niki,³ Atkinson *et al.*,³⁹ Ravishankara and Mauldin,⁴⁵ Rahman *et al.*,⁴⁷ Canosa-Mas *et al.*⁴⁴ and Barnes *et al.*⁶⁶ are given in Table 3. All of these studies were carried out at room temperature, with those of Ravishankara and Mauldin,⁴ Rahman *et al.*⁴⁷ and Canosa-Mas *et al.*⁴⁴ being absolute rate constant measurements. The rate constants of Atkinson *et al.*,³⁹ Ravishankara and Mauldin,⁴⁵ Rahman *et al.*,⁴⁷ Canosa-Mas *et al.*⁴⁴ and Barnes *et al.*⁶⁶ are in excellent

TABLE 3. Rate constants k and temperature-dependent parameters, $k = A e^{-B/T}$, for the gas-phase reactions of the NO_3 radical with acyclic monoalkenes

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference	
Ethene			$(1.90 \pm 0.21) \times 10^{-15}$	300	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 2.65 \times 10^{-11} \text{ s}^{-1}$] ^a	Japar and Niki ³⁸	
			$(1.35 \pm 0.44) \times 10^{-16}$	298 ± 1	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 3.41 \times 10^{-11} \text{ s}^{-1}$] ^a	Atkinson <i>et al.</i> ³⁹	
			$(1.23 \pm 0.57) \times 10^{-16}$	298 ± 1	RR [relative to $k(\text{propene})$ $= 9.45 \times 10^{-15} \text{ s}^{-1}$] ^a	Atkinson <i>et al.</i> ³⁹	
			$(2.04 \pm 0.20) \times 10^{-16}$	296 ± 2	RR [relative to $k(n\text{-heptane})$ $= 1.37 \times 10^{-16} \text{ s}^{-1}$] ^a	Atkinson <i>et al.</i> ⁶²	
			$(1.85 \pm 0.24) \times 10^{-16}$	295 ± 2	DF-A	Canosa-Mas <i>et al.</i> ⁴⁴	
			$(4.0 \pm 1.0) \times 10^{-16}$	323 ± 3	DF-A	Canosa-Mas <i>et al.</i> ⁹¹	
			$(1.41 \pm 0.24) \times 10^{-15}$	373 ± 3			
			$(3.72 \pm 0.66) \times 10^{-15}$	423 ± 3			
			$(8.91 \pm 1.12) \times 10^{-15}$	473 ± 3			
		$6.29_{-2.0}^{+2.9}$	3103 ± 145	$(1.83 \pm 0.18) \times 10^{-14}$	523 ± 3		
				$(2.16 \pm 0.20) \times 10^{-16}$	296 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.89 \times 10^{-13} \text{ s}^{-1}$] ^a	Atkinson <i>et al.</i> ⁶⁷
				$(1.43 \pm 0.54) \times 10^{-16}$	296 ± 1	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 4.40 \times 10^{-11} \text{ s}^{-1}$] ^a	Andersson and Ljungström ⁶¹
Propene			$(1.74 \pm 0.37) \times 10^{-16}$	298 ± 2	RR [relative to $k(2\text{-methylpropane})$ $= 9.8 \times 10^{-17} \text{ s}^{-1}$] ^b	Barnes <i>et al.</i> ⁶⁶	
			$(6.4 \pm 1.6) \times 10^{-15}$	300	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 2.65 \times 10^{-11} \text{ s}^{-1}$] ^a	Morris and Niki ⁵⁸	
			$(1.08 \pm 0.07) \times 10^{-14}$	300	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 2.65 \times 10^{-11} \text{ s}^{-1}$] ^a	Japar and Niki ³⁸	
			$(7.57 \pm 1.54) \times 10^{-15}$	298 ± 1	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 3.41 \times 10^{-11} \text{ s}^{-1}$] ^a	Atkinson <i>et al.</i> ³⁹	
			$(7.41 \pm 1.95) \times 10^{-15}$	298 ± 1	RR [relative to $k(\text{trans-2-butene})$ $= 3.90 \times 10^{-13} \text{ s}^{-1}$] ^a	Atkinson <i>et al.</i> ³⁹	
			$(9.45 \pm 0.47) \times 10^{-15}$	296 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.89 \times 10^{-13} \text{ s}^{-1}$] ^a	Atkinson <i>et al.</i> ⁶¹	
	Propene- d_6			$(1.20 \pm 0.09) \times 10^{-14}$	300	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 2.65 \times 10^{-11} \text{ s}^{-1}$] ^a	Japar and Niki ³⁸
				$(1.59 \pm 0.17) \times 10^{-14}$	300	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 2.65 \times 10^{-11} \text{ s}^{-1}$] ^a	Japar and Niki ³⁸

TABLE 3. Rate constants k and temperature-dependent parameters, $k = A e^{-B/T}$, for the gas-phase reactions of the NO_3 radical with acyclic monoalkenes — Continued

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
			$(1.23 \pm 0.02) \times 10^{-14}$	298 ± 1	RR [relative to $k(\text{propene})$ $= 9.45 \times 10^{-15} \text{ J}^a$	Atkinson <i>et al.</i> ³⁹
			$(1.24 \pm 0.07) \times 10^{-14}$	296 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.89 \times 10^{-13} \text{ J}^a$	Atkinson <i>et al.</i> ⁶⁷
			$(1.50 \pm 0.08) \times 10^{-14}$	296 ± 1	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 4.40 \times 10^{-11} \text{ J}^a$	Andersson and Ljungström ⁶¹
			$(1.27 \pm 0.19) \times 10^{-14}$	298 ± 2	RR [relative to $k(\text{propene})$ $= 9.45 \times 10^{-15} \text{ J}^a$	Barnes <i>et al.</i> ⁶⁶
2-Methylpropene			$(2.24 \pm 0.21) \times 10^{-13}$	300	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 2.65 \times 10^{-11} \text{ J}^a$	Japar and Niki ³⁸
			$(3.15 \pm 0.02) \times 10^{-13}$	298 ± 1	RR [relative to $k(\text{trans-2-butene})$ $= 3.90 \times 10^{-13} \text{ J}^a$	Atkinson <i>et al.</i> ³⁹
			$(3.38 \pm 0.43) \times 10^{-13}$	298	DF-A	Ravishankara and Mauldin ⁴⁵
			$(3.3 \pm 0.5) \times 10^{-13}$	298	DF-MS	Rahman <i>et al.</i> ⁴⁷
			$(3.4 \pm 0.7) \times 10^{-13}$	295 ± 2	DF-A	Canosa-Mas <i>et al.</i> ⁴⁴
			$(3.35 \pm 0.51) \times 10^{-13}$	298 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.90 \times 10^{-13} \text{ J}^a$	Barnes <i>et al.</i> ⁶⁶
<i>cis</i> -2-Butene			$(3.67 \pm 0.41) \times 10^{-13}$	300	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 2.65 \times 10^{-11} \text{ J}^a$	Japar and Niki ³⁸
			$(3.50 \pm 0.02) \times 10^{-13}$	298 ± 1	RR [relative to $k(\text{trans-2-butene})$ $= 3.90 \times 10^{-13} \text{ J}^a$	Atkinson <i>et al.</i> ³⁹
<i>trans</i> -2-Butene			$(2.85 \pm 0.21) \times 10^{-13}$	300	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 2.65 \times 10^{-11} \text{ J}^a$	Japar and Niki ³⁸
			$(3.83 \pm 0.33) \times 10^{-13}$	298 ± 1	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 3.41 \times 10^{-11} \text{ J}^a$	Atkinson <i>et al.</i> ³⁹
			$(3.78 \pm 0.41) \times 10^{-13}$	298	DF-A/F-LIF	Ravishankara and Mauldin ⁴⁵
			$(3.46 \pm 0.42) \times 10^{-13}$	204	F-LIF	Dlugokencky and Howard ⁹²
			$(3.43 \pm 0.42) \times 10^{-13}$	206		
			$(3.31 \pm 0.40) \times 10^{-13}$	213		
			$(3.27 \pm 0.40) \times 10^{-13}$	223		
			$(3.35 \pm 0.41) \times 10^{-13}$	243		
			$(3.55 \pm 0.43) \times 10^{-13}$	267		
			$(3.96 \pm 0.48) \times 10^{-13}$	298		
			$(4.37 \pm 0.53) \times 10^{-13}$	337		
			$(4.99 \pm 0.60) \times 10^{-13}$	378		
	$[1.78 \pm 0.36$ $+ 0.0128 \pm 0.0026$	530 ± 100 $- 570 \pm 110]$				

TABLE 3. Rate constants k and temperature-dependent parameters, $k = A e^{-B/T}$, for the gas-phase reactions of the NO_3 radical with acyclic monoalkenes — Continued

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
Methyl-2-butene			$(1.12 \pm 0.11) \times 10^{-11}$	300	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 2.65 \times 10^{-11} \text{ s}^{-1}$ ^a	Japar and Niki ³⁸
			$(9.52 \pm 2.73) \times 10^{-12}$	298 ± 1	RR [relative to $k(\text{trans-2-butene})$ $= 3.90 \times 10^{-13} \text{ s}^{-1}$ ^a	Atkinson <i>et al.</i> ³⁹
			$(1.04 \pm 0.10) \times 10^{-11}$	295 ± 1	RR [relative to $k(\text{trans-2-butene})$ $= 3.88 \times 10^{-13} \text{ s}^{-1}$ ^a	Atkinson <i>et al.</i> ⁶⁵
			$(9.37 \pm 0.47) \times 10^{-12}$	296 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.89 \times 10^{-13} \text{ s}^{-1}$ ^a	Atkinson <i>et al.</i> ⁶⁷
2,3-Dimethyl-2-butene			$(7.54 \pm 1.02) \times 10^{-11}$	300	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 2.65 \times 10^{-11} \text{ s}^{-1}$ ^a	Japar and Niki ³⁸
			$(5.72 \pm 0.15) \times 10^{-11}$	298 ± 1	RR [relative to $k(2\text{-methyl-2-butene})$ $= 9.37 \times 10^{-12} \text{ s}^{-1}$ ^a	Atkinson <i>et al.</i> ³⁹
			$(5.74 \pm 0.15) \times 10^{-11}$	295 ± 1	RR [relative to $k(2\text{-methyl-2-butene})$ $= 9.37 \times 10^{-12} \text{ s}^{-1}$ ^a	Atkinson <i>et al.</i> ⁶⁵
			$(3.84 \pm 0.38) \times 10^{-11}$	298	DF-MS	Rahman <i>et al.</i> ⁴⁷
			$(5.72 \pm 0.32) \times 10^{-11}$	296 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.89 \times 10^{-13} \text{ s}^{-1}$ ^a	Atkinson <i>et al.</i> ⁶⁷
			$(4.5 \pm 0.4) \times 10^{-11}$	298	DF-MS	Poulet and Le Bras ⁴⁸

^a From present recommendations (see text).^b From the rate constant given in Table 1.

agreement, with the rate constant obtained by Japar and Niki³⁸ relative to the equilibrium constant K_5 being ~35% lower. The room temperature rate constant appears to be independent of total pressure over the range ~1–750 Torr. A unit-weighted average of the absolute rate constants of Ravishankara and Mauldin,⁴⁵ Rahman *et al.*⁴⁷ and Canosa-Mas *et al.*⁴⁴ and the relative rate constants of Atkinson *et al.*³⁹ and Barnes *et al.*⁶⁶ yields the recommendation of

$$k(2\text{-methylpropene}) = 3.32 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of $\pm 30\%$.

(5) *cis*-2-Butene

The rate constants of Japar and Niki³⁸ and Atkinson *et al.*,³⁹ both obtained from relative rate studies carried out at room temperature, are given in Table 3. The agree-

ment is excellent. The rate constant of Japar and Niki³⁸ was determined relative to the equilibrium constant K_5 and is hence subject to significant uncertainties. Therefore, the rate constant of Atkinson *et al.*³⁹ is used to yield the recommendation of

$$k(\text{cis-2-butene}) = 3.50 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of $\pm 35\%$.

(6) *trans*-2-Butene

The available rate constant data of Japar and Niki,³⁸ Atkinson *et al.*,³⁹ Ravishankara and Mauldin⁴⁵ and Dlugokencky and Howard⁹² are given in Table 3 and are plotted in Arrhenius form in Fig. 4. The sole temperature dependence study is that of Dlugokencky and Howard.⁹² At room temperature the agreement between the relative rate constant of Atkinson *et al.*³⁹ and the absolute data of

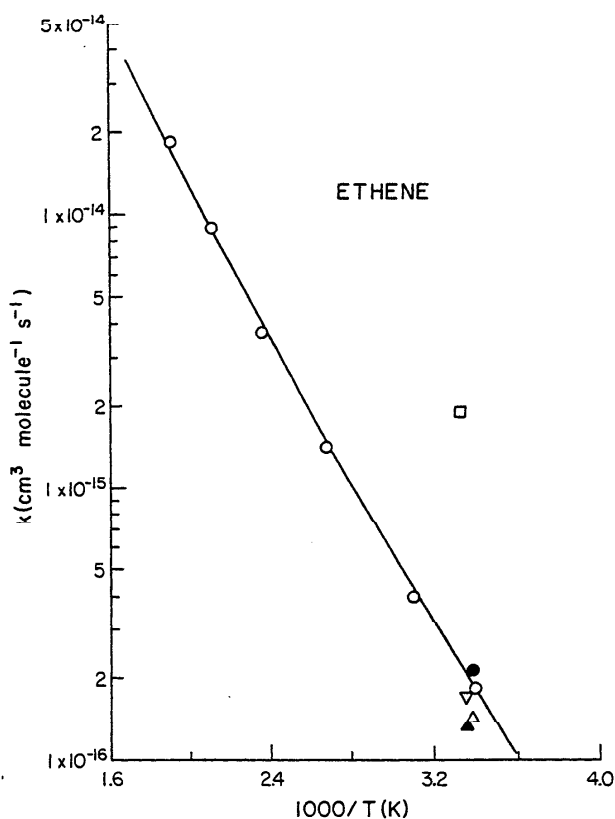


FIG 3. Arrhenius plot of rate constants for the gas-phase reaction of the NO_3 radical with ethene. (\square) Japar and Niki;³⁸ (\blacktriangle) Atkinson *et al.*,³⁹ relative to the equilibrium constant K_s ; (\circ) Canosa-Mas *et al.*;^{44,91} (\bullet) Atkinson *et al.*;⁶⁷ (\triangle) Anderson and Ljungström;⁶¹ (∇) Barnes *et al.*;⁶⁶ (—) recommendation, see text.

Ravishankara and Mauldin⁴⁵ and Dlugokencky and Howard⁹² is excellent, with the relative rate constant of Japar and Niki³⁸ being 25–30% lower. In this case, both of the relative rate constants^{38,39} were determined relative to the equilibrium constant K_s . Again, there is no evidence for a pressure dependence of the room temperature rate constant over the total pressure range 0.44–740 Torr. The Arrhenius plot is clearly curved, and Dlugokencky and Howard⁹² fit their data with the rate constant being the sum of two exponentials. Although empirical, a modified Arrhenius expression, $k = CT^2e^{-D/T}$, has been used in this evaluation, and a unit-weighted least-squares analysis of the data of Atkinson *et al.*,³⁹ Ravishankara and Mauldin⁴⁵ and Dlugokencky and Howard⁹² yields the recommendation of

$$k(\text{trans-2-butene}) = (1.22_{-0.13}^{+0.15}) \times 10^{-18} T^2 e^{(382 \pm 28)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 204–378 K, where the error limits are two least-squares standard deviations, and

$$k(\text{trans-2-butene}) = 3.90 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 30\%$. The temperature dependence assumed, of $k = CT^2e^{-D/T}$ appears to give a somewhat lesser degree of curvature in the Arrhenius plot than observed (Fig. 4), and hence the above recommendation should not be used outside of the temperature range 200–380 K.

(7) 2-Methyl-2-butene

The available rate constants of Japar and Niki³⁸ and Atkinson *et al.*,^{39,65,67} all obtained from relative rate studies carried out at room temperature, are given in Table 3. The agreement is excellent, and the most recent study of Atkinson *et al.*⁶⁷ is used to recommend that

$$k(\text{2-methyl-2-butene}) = 9.37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of $\pm 35\%$.

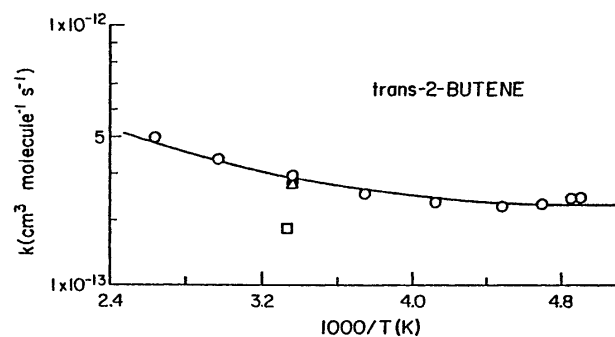


FIG 4. Arrhenius plot of rate constants for the gas-phase reaction of the NO_3 radical with *trans*-2-butene. (\square) Japar and Niki;³⁸ (\bullet) Atkinson *et al.*;³⁹ (\triangle) Ravishankara and Mauldin;⁴⁵ (\circ) Dlugokencky and Howard;⁹² (—) recommendation, see text.

(8) 2,3-Dimethyl-2-butene

The available rate constant data of Japar and Niki,³⁸ Atkinson *et al.*,^{39,65,67} Rahman *et al.*⁴⁷ and Poulet and L Bras,⁴⁸ all obtained at room temperature, are given in Table 3. These room temperature rate constants^{38,39,47,48,65,67} cover a range of a factor of 2. The most recent relative rate study of Atkinson *et al.*⁶⁷ is used to recommend that

$$k(\text{2,3-dimethyl-2-butene}) = 5.72 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of a factor of 1.1. [This recommended rate constant is within 4% of the unit-weighted average of the entire rate constant data set^{38,39,47,48,65,67}.]

(9) 1,3-Butadiene

The available rate constant data of Atkinson *et al.*,³⁹ Rahman *et al.*,⁴⁷ Benter and Schindler,⁵³ Canosa-Mas *et al.*,⁴⁴ Andersson and Ljungström,⁶¹ Barnes *et al.*⁶⁶ and

Poulet and Le Bras,⁴⁸ all obtained at room temperature, are given in Table 4. In this case, the measured rate constants range over a factor of 2.2, with no obvious pattern. Thus, the relative rate constants of Atkinson *et al.*⁶⁵ and Andersson and Ljungström⁶¹ and the absolute rate constant of Poulet and Le Bras⁴⁸ are in agreement, with a rate constant of $1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, while the absolute rate constants of Rahman *et al.*,⁴⁷ Benter and Schindler⁵³ and Canosa-Mas *et al.*⁴⁴ and the relative rate constant of Barnes *et al.*⁶⁶ are a factor of 2 higher at $(1.7-2.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. While the reasons for these discrepancies are not presently understood, the relative rate constants of Atkinson *et al.*⁶⁵ and Andersson and Ljungström⁶¹ and the absolute rate constant of Poulet and Le Bras⁴⁸ are used to tentatively recommend that

$$k(1,3\text{-butadiene}) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty of a factor of 3.

(10) 2-Methyl-1,3-butadiene (isoprene)

The available rate constant data of Atkinson *et al.*,⁶⁵ Benter and Schindler,⁵³ Dlugokencky and Howard,⁹² Barnes *et al.*⁶⁶ and Poulet and Le Bras⁴⁸ are given in Table 4 and are plotted in Arrhenius form in Fig. 5. As for 1,3-butadiene, there are significant discrepancies between the various studies. Thus, at room temperature the relative constant of Atkinson *et al.*⁶⁵ and the absolute rate constants of Dlugokencky and Howard⁹² and Poulet and Le Bras⁴⁸ are in reasonable agreement, with a rate constant of $(5.9-8.3) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, while the absolute and relative rate studies of Benter and Schindler⁵³ and Barnes *et al.*,⁶⁶ respectively, are in agreement with a rate constant of $(1.2-1.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. While the reasons for these discrepancies are not presently understood, a unit-weighted least-squares analysis of the absolute rate constants of Dlugokencky and Howard,⁹² using the Arrhenius expression, has been carried out to yield the recommendation of

$$k(2\text{-methyl-1,3-butadiene}) = (3.03^{+0.66}_{-0.54}) \times 10^{-12} e^{-(446 \pm 60)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 251–381 K, where the error limits are the two least-squares standard deviations, and

$$k(2\text{-methyl-1,3-butadiene}) = 6.78 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of a factor of 2. This recommended rate constant at 298 K is in good agreement with the relative and absolute rate constants of Atkinson *et al.*⁶⁵ and Poulet and Le Bras,⁴⁸ respectively.

It is of interest to note that the two alkenes for which significant discrepancies occur are both conjugated dienes of relatively low reactivity towards the NO_3 radical [compare with the much more reactive 1,3-cyclohexadiene for which the relative and absolute rate constants of

Atkinson *et al.*⁶⁵ and Benter and Schindler,⁵³ respectively, are in agreement (Table 5)].

(11) 2,3-Dimethyl-1,3-butadiene

The available absolute rate constants of Benter and Schindler⁵³ and Poulet and Le Bras⁴⁸ are given in Table 4. The room temperature rate constants from these studies are in good agreement, and a unit-weighted average of these rate constants^{48,53} yields the recommended rate constant at 298 K of

$$k(2,3\text{-dimethyl-1,3-butadiene}) = 2.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

with an estimated overall uncertainty of a factor of 2.

(12) 1,3- and 1,4-Cyclohexadiene

The available relative and absolute rate constants of Atkinson *et al.*⁶⁵ and Benter and Schindler,⁵³ respectively, are given in Table 5. For each cyclohexadiene the rate constants from these room temperature studies are in good (1,3-cyclohexadiene) or reasonably good (1,4-cyclohexadiene) agreement. Unit-weighted averages of these rate constants of Atkinson *et al.*⁶⁵ and Benter and Schindler⁵³ lead to the recommended rate constants at 298 K of

$$k(1,3\text{-cyclohexadiene}) = 1.16 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k(1,4\text{-cyclohexadiene}) = 6.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

each with estimated overall uncertainties of a factor of 1.5.

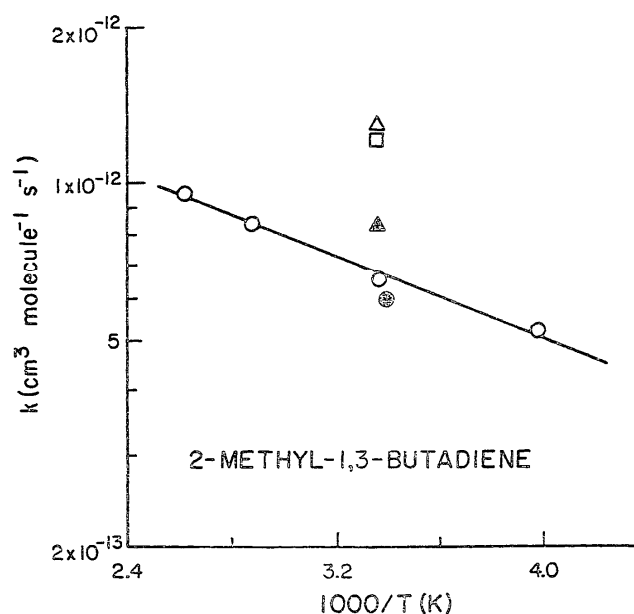


FIG 5. Arrhenius plot of rate constants for the gas-phase reaction of the NO_3 radical with 2-methyl-1,3-butadiene (isoprene). (●) Atkinson *et al.*,⁶⁵ (Δ) Benter and Schindler,⁵³ (○) Dlugokencky and Howard,⁹² (□) Barnes *et al.*⁶⁶ (Δ) Poulet and Le Bras,⁴⁸ (—) recommendation, see text.

TABLE 4. Rate constants k and temperature-dependent parameters, $k = A e^{-B/T}$, for the gas-phase reactions of the NO_3 radical with acyclic di- and trialkenes

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
1,3-Butadiene			$(9.82 \pm 0.24) \times 10^{-14}$	295 ± 1	RR [relative to $k(\text{trans-2-butene})$ $= 3.88 \times 10^{-13}]^a$	Atkinson <i>et al.</i> ⁶⁵
			$(1.7 \pm 0.3) \times 10^{-13}$	298	DF-MS	Rahman <i>et al.</i> ⁴⁷
			$(2.1 \pm 0.4) \times 10^{-13}$	298	DF-MS	Benter and Schindler ⁵³
			$(2.2 \pm 0.6) \times 10^{-13}$	295 ± 2	DF-A	Canosa-Mas <i>et al.</i> ⁴⁴
			$(1.03 \pm 0.15) \times 10^{-13}$	296 ± 1	RR [relative to $K_3(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 4.40 \times 10^{-11}]^a$	Andersson and Ljungström ⁶
			$(1.95 \pm 0.39) \times 10^{-13}$	298 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.90 \times 10^{-13}]^a$	Barnes <i>et al.</i> ⁶⁶
2-Methyl-1,3-butadiene			$(5.94 \pm 0.16) \times 10^{-13}$	295 ± 1	RR [relative to $k(\text{trans-2-butene})$ $= 3.88 \times 10^{-13}]^a$	Atkinson <i>et al.</i> ⁶⁵
			$(1.3 \pm 0.14) \times 10^{-12}$	298	DF-MS	Benter and Schindler ⁵³
			$(5.22 \pm 0.63) \times 10^{-13}$	251	F-LIF	Dlugokencky and Howard ⁹²
			$(6.52 \pm 0.78) \times 10^{-13}$	297		
			$(8.37 \pm 1.01) \times 10^{-13}$	347		
		3.03 ± 0.45	450 ± 70	$(9.55 \pm 1.15) \times 10^{-13}$	381	
2,3-Dimethyl-1,3-butadiene			$(1.21 \pm 0.20) \times 10^{-12}$	298 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.90 \times 10^{-13}]^a$	Barnes <i>et al.</i> ⁶⁶
			$(8.26 \pm 0.60) \times 10^{-13}$	298	DF-MS	Poulet and Le Bras ⁴⁸
			$(2.3 \pm 0.3) \times 10^{-12}$	298	DF-MS	Benter and Schindler ⁵³
3-Methyl-7-methyl-1,6-octadiene (myrcene)			$(1.96 \pm 0.20) \times 10^{-12}$	298	DF-MS	Poulet and Le Bras ⁴⁸
			$(1.06 \pm 0.02) \times 10^{-11}$	294 ± 2	RR [relative to $k(\text{2-methyl-2-butene})$ $= 9.37 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ⁹³
3,7-Dimethyl-1,3,6-octatriene (<i>cis</i> - and <i>trans</i> -ocimene) ^b			$(2.23 \pm 0.06) \times 10^{-11}$	294 ± 2	RR [relative to $k(\text{2-methyl-2-butene})$ $= 9.37 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ⁹³

^a From present recommendations (see text).^b Rate constants for the *cis*- and *trans*-isomers identical to within 8%.⁹³

TABLE 5. Rate constants k and temperature-dependent parameters, $k = Ae^{-B/T}$, for the gas-phase reactions of the NO_3 radical with cyclic alkenes.

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
Cyclopentene			$(4.64 \pm 0.04) \times 10^{-13}$	298 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.90 \times 10^{-13}]^a$	Atkinson <i>et al.</i> ⁹⁴
Cyclohexene			$(5.28 \pm 0.12) \times 10^{-13}$	295 ± 1	RR [relative to $k(\text{trans-2-butene})$ $= 3.88 \times 10^{-13}]^a$	Atkinson <i>et al.</i> ⁶⁵
1,3-Cyclohexadiene			$(1.23 \pm 0.11) \times 10^{-11}$	295 ± 1	RR [relative to $k(2\text{-methyl-2-butene})$ $= 9.37 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ⁶⁵
			$(1.1 \pm 0.1) \times 10^{-11}$	298	DF-MS	Benter and Schindler ⁵³
1,4-Cyclohexadiene			$(5.32 \pm 0.20) \times 10^{-13}$	295 ± 1	RR [relative to $k(\text{trans-2-butene})$ $= 3.88 \times 10^{-13}]^a$	Atkinson <i>et al.</i> ⁶⁵
			$(7.8 \pm 0.7) \times 10^{-13}$	298	DF-MS	Benter and Schindler ⁵³
Cycloheptene			$(4.84 \pm 0.16) \times 10^{-13}$	298 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.90 \times 10^{-13}]^a$	Atkinson <i>et al.</i> ⁹⁴
1,3-Cycloheptadiene			$(6.47 \pm 0.09) \times 10^{-12}$	295 ± 1	RR [relative to $k(2\text{-methyl-2-butene})$ $= 9.37 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ⁶⁵
1,3,5-Cycloheptatriene			$(1.19 \pm 0.05) \times 10^{-12}$	298 ± 2	RR [relative to $k(2\text{-methyl-2-butene})$ $= 9.37 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ⁹⁴
Bicyclo[2.2.1]- 2-heptene			$(2.47 \pm 0.02) \times 10^{-13}$	298 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.90 \times 10^{-13}]^a$	Atkinson <i>et al.</i> ⁹⁴
Bicyclo[2.2.1]- 2,5-heptadiene			$(1.02 \pm 0.01) \times 10^{-12}$	298 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.90 \times 10^{-13}]^a$	Atkinson <i>et al.</i> ⁹⁴
Bicyclo[2.2.2]- 2-octene			$(1.45 \pm 0.06) \times 10^{-13}$	298 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.90 \times 10^{-13}]^a$	Atkinson <i>et al.</i> ⁹⁴
α -Pinene ^b			$(5.82 \pm 0.16) \times 10^{-12}$	295 ± 1	RR [relative to $k(2\text{-methyl-2-butene})$ $= 9.37 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ⁶⁵
			$(7.88 \pm 0.95) \times 10^{-12}$	261	F-LIF	Dlugokencky and Howard ⁹²
			$(6.26 \pm 0.75) \times 10^{-12}$	297		
			$(6.10 \pm 0.73) \times 10^{-12}$	297		
			$(5.19 \pm 0.62) \times 10^{-12}$	338		
			$(4.24 \pm 0.51) \times 10^{-12}$	384		
	1.19 ± 0.31	-490 ± 70	$(6.56 \pm 0.94) \times 10^{-12}$	298 ± 2	RR [relative to $k(2\text{-methyl-2-butene})$ $= 9.37 \times 10^{-12}]^a$	Barnes <i>et al.</i> ⁶⁶
β -Pinene ^b			$(2.36 \pm 0.11) \times 10^{-12}$	295 ± 1	RR [relative to $k(2\text{-methyl-2-butene})$ $= 9.37 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ⁶⁵
			$(2.37 \pm 0.06) \times 10^{-12}$	296 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.89 \times 10^{-13}]^a$	Atkinson <i>et al.</i> ⁶⁷

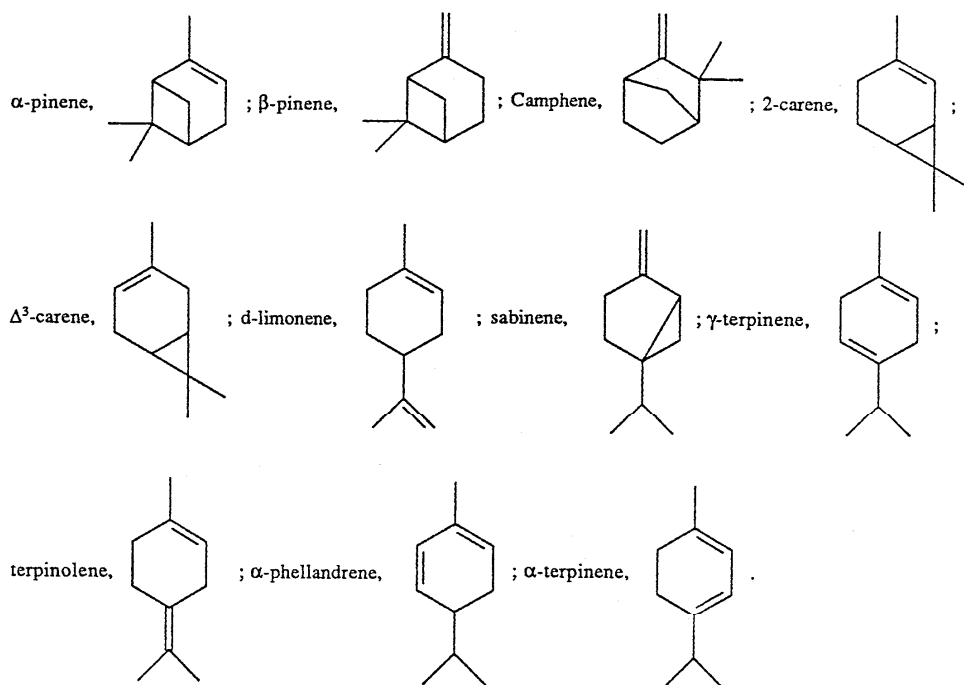
TABLE 5. Rate constants k and temperature-dependent parameters, $k = A e^{-B/T}$, for the gas-phase reactions of the NO_3 radical with cyclic alkenes - Continued

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
			$(1.6 \pm 0.6) \times 10^{-12}$	c	RR [relative to $K_3(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 1.26 \times 10^{-27}$ $e^{11275/T} \text{ s}^{-1}$]	Kotzias <i>et al.</i> ⁹⁵
			$(2.81 \pm 0.47) \times 10^{-12}$	298 ± 2	RR [relative to $k(2\text{-methyl-2-butene})$ $= 9.37 \times 10^{-12} \text{ s}^{-1}$]	Barnes <i>et al.</i> ⁶⁶
Camphene ^b			$(6.57 \pm 0.16) \times 10^{-13}$	296 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.89 \times 10^{-13} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁹⁶
2-Carene ^b			$(1.87 \pm 0.12) \times 10^{-11}$	295 ± 2	RR [relative to $k(2\text{-methyl-2-butene})$ $= 9.37 \times 10^{-12} \text{ s}^{-1}$]	Corchnoy and Atkinson ⁹⁷
			$(2.16 \pm 0.37) \times 10^{-11}$	295 ± 2	RR [relative to $k(2,3\text{-dimethyl-2-butene})$ $= 5.72 \times 10^{-11} \text{ s}^{-1}$]	Corchnoy and Atkinson ⁹⁷
Δ^3 -Carene ^b			$(1.01 \pm 0.02) \times 10^{-11}$	295 ± 1	RR [relative to $k(2\text{-methyl-2-butene})$ $= 9.37 \times 10^{-12} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁶⁵
			$(8.15 \pm 1.22) \times 10^{-12}$	298 ± 2	RR [relative to $k(2\text{-methyl-2-butene})$ $= 9.37 \times 10^{-12} \text{ s}^{-1}$]	Barnes <i>et al.</i> ⁶⁶
<i>d</i> -Limonene ^b			$(1.31 \pm 0.04) \times 10^{-11}$	295 ± 1	RR [relative to $k(2\text{-methyl-2-butene})$ $= 9.37 \times 10^{-12} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁶⁵
			$(1.12 \pm 0.17) \times 10^{-11}$	298 ± 2	RR [relative to $k(2\text{-methyl-2-butene})$ $= 9.37 \times 10^{-12} \text{ s}^{-1}$]	Barnes <i>et al.</i> ⁶⁶
Sabinene ^b			$(1.01 \pm 0.03) \times 10^{-11}$	296 ± 2	RR [relative to $k(2\text{-methyl-2-butene})$ $= 9.37 \times 10^{-12} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁹⁶
γ -Terpinene ^b			$(2.94 \pm 0.05) \times 10^{-11}$	294 ± 2	RR [relative to $k(2\text{-methyl-2-butene})$ $= 9.37 \times 10^{-12} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁹³
Terpinolene ^b			$(9.67 \pm 0.52) \times 10^{-11}$	295 ± 2	RR [relative to $k(2,3\text{-dimethyl-2-butene})$ $= 5.72 \times 10^{-11} \text{ s}^{-1}$]	Corchnoy and Atkinson ⁹⁷
α -Phellandrene ^b			$(8.52 \pm 0.63) \times 10^{-11}$	294 ± 2	RR [relative to $k(2,3\text{-dimethyl-2-butene})$ $= 5.72 \times 10^{-11} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁹³
α -Terpinene ^b			$(1.82 \pm 0.08) \times 10^{-10}$	294 ± 2	RR [relative to $k(2,3\text{-dimethyl-2-butene})$ $= 5.72 \times 10^{-11} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁹³

^aFrom present recommendations (see text).

Footnote to Table 5.

Structures:



¹ Room temperature, not reported.

² Equilibrium constant of Graham and Johnston⁷⁸ used,⁹⁵ with a value of $K_S = 1.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ being cited.⁹⁵ This value of K_S corresponds to a temperature of 299.6 K.⁷⁸

(13) α -Pinene

The available rate constant data of Atkinson *et al.*,⁶⁵ Dlugokencky and Howard⁹² and Barnes *et al.*⁶⁶ are given in Table 5 and are plotted in Arrhenius form in Fig. 6. The room temperature relative rate constants of Atkinson *et al.*⁶⁵ and Barnes *et al.*⁶⁶ are in excellent agreement with the absolute rate constant measured by Dlugokencky and Howard.⁹² The Arrhenius plot (Fig. 6) shows no evidence of curvature, and a unit-weighted least-squares analysis of these rate constants of Atkinson *et al.*,⁶⁵ Dlugokencky and Howard⁹² and Barnes *et al.*,⁶⁶ using the Arrhenius expression, yields the recommendation of

$$k(\alpha\text{-pinene}) = (1.19_{-0.33}^{+0.45}) \times 10^{-12} e^{(490 \pm 97)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 261–384 K, where the error limits are the two least-squares standard deviations, and

$$k(\alpha\text{-pinene}) = 6.16 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 30\%$.

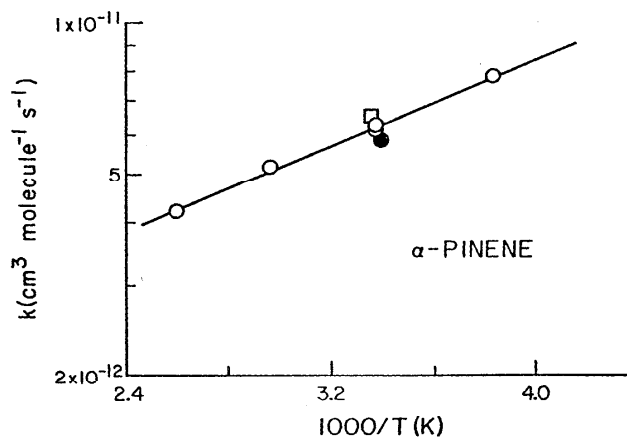


FIG. 6. Arrhenius plot of rate constants for the gas-phase reaction of the NO_3 radical with α -pinene. (●) Atkinson *et al.*,⁶⁵ (○) Dlugokencky and Howard,⁹² (□) Barnes *et al.*,⁶⁶ (—) recommendation, see text.

(14) β -Pinene

The available rate constants of Atkinson *et al.*,^{65,67} Kotzias *et al.*⁹⁵ and Barnes *et al.*,⁶⁶ all obtained from rela-

tive rate studies carried out at room temperature, are given in Table 5. These rate constants^{65-67,95} are in reasonable agreement. However, there are uncertainties in re-evaluating the rate constant of Kotzias *et al.*⁹⁵ since the temperature was not specified; the equilibrium constant K_5 used was from Graham and Johnston⁷⁸ with the cited value of $1.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ corresponding to a temperature of 299.6 K, $\sim 4\text{--}5$ K higher than previous studies from this group.^{36,60} Accordingly, a unit-weighted average of the rate constants of Atkinson *et al.*^{65,67} and Barnes *et al.*⁶⁶ leads to the recommendation of

$$k(\beta\text{-pinene}) = 2.51 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty of $\pm 40\%$.

(15) Δ^3 -Carene and *d*-Limonene

The available rate constants of Atkinson *et al.*⁶⁵ and Barnes *et al.*,⁶⁶ obtained from relative rate studies carried out at room temperature, are given in Table 5. The agreement is good, and unit-weighted averages of these rate constants of Atkinson *et al.*⁶⁵ and Barnes *et al.*⁶⁶ lead to the recommendations of

$$k(\Delta^3\text{-carene}) = 9.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ and}$$

$$k(d\text{-limonene}) = 1.22 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

both at 298 K and with estimated overall uncertainties of $\pm 35\%$.

(16) Other Dienes, Trienes and Cycloalkenes

Only single experimental studies are available, and hence no recommendations are made.

2.3.b. Mechanism

The rate constants at room temperature for the reactions of the NO_3 radical with the alkenes and cycloalkenes span 6 orders of magnitude, from $2 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for ethene to $1.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for α -terpinene. Apart from ethene and the 1-alkenes, the room temperature rate constants are $\geq 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and rate constants of this magnitude are too high to explain by an H-atom abstraction reaction pathway. For the acyclic alkenes, the room temperature rate constants increase with the degree of alkyl substitution around the $>\text{C}=\text{C}<$ bond, analogous to the case for the corresponding OH radical reactions,⁸⁵⁻⁸⁷ which proceed essentially totally by OH radical addition to the $>\text{C}=\text{C}<$ bond(s).⁸⁷ Furthermore, Japar and Niki³⁸ showed that for propene there is no significant deuterium isotope effect, again indicating that the NO_3 radical reaction proceeds by addition. A correlation of the room temperature NO_3 and OH radical rate constants for reaction with alkenes and cycloalkenes contain-

ing only a single $>\text{C}=\text{C}<$ bond is shown in Fig. 7. A reasonable correlation is evident, with that for the acyclic alkenes (filled circles) being good.

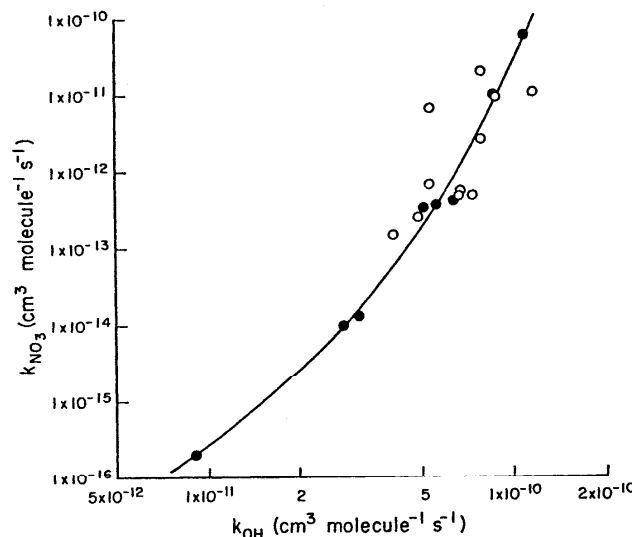
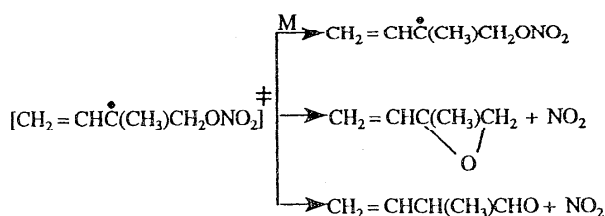
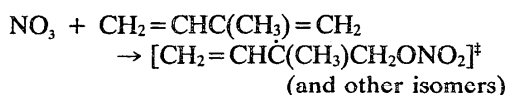


FIG. 7. Plot of rate constants for gas-phase reactions of the NO_3 radical with acyclic and cyclic monoalkenes against the rate constants for the corresponding gas-phase OH radical reactions (taken from Atkinson⁸⁷). (●) Acyclic monoalkenes; (○) cyclic monoalkenes; (—) trend of correlation for acyclic monoalkenes.

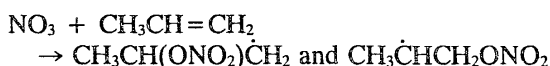
As discussed above for the individual alkenes, in all cases for which data are available the measured room temperature rate constants are independent of the total pressure over the range $\sim 1\text{--}750$ Torr, and show no evidence for fall-off behavior, in contrast to the corresponding reactions of the OH radical.⁸⁷ Thus, the rate constant for the reaction of the OH radical with ethene is in the fall-off regime at and below ~ 750 Torr total pressure of air at room temperature⁸⁷ and that for propene is in the fall-off regime below ~ 30 Torr total pressure.⁸⁷ Addition of the NO_3 radical to the alkenes to form the β -nitroalkyl radical is exothermic by $\sim 22 \text{ kcal mol}^{-1}$ ($\sim 11 \text{ kcal mol}^{-1}$ less exothermic than the corresponding OH radical addition reaction⁹⁸). The observed lack of a pressure dependence on the measured rate constants can be due to decomposition and/or isomerization of the initially energy-rich β -nitroalkyl radical to products other than the reactants. That this process occurs is shown by the NO_2 formation yield data obtained by Dlugokencky and Howard⁹² for the reactions of the NO_3 radical with *trans*-2-butene, 2-methyl-1,3-butadiene and α -pinene at total pressures of 0.5–4.1 Torr of He, O_2 or N_2 diluent. The NO_2 formation yields were observed to decrease with increasing total pressure, decreasing temperature, the complexity of the alkene and the third body efficiency of the diluent gas,⁹² with the NO_2 formation yields at 298 K from the reaction of the NO_3 radical with *trans*-2-butene being > 0.9 at total pressures of helium diluent of ≤ 4 Torr,⁹ decreasing to 0.84 and 0.70 at 1.0 and 2.0 Torr total pressures, respectively, of O_2 diluent.⁹²

Poulet and Le Bras⁴⁸ have observed the formation of epoxides and/or aldehydes from the reactions of the NO₃ radical with 2,3-dimethyl-2-butene, 1,3-butadiene, 2-methyl-1,3-butadiene and 2,3-dimethyl-1,3-butadiene at 0.5–2.5 Torr total pressure and 298 K, using mass spectrometry. The epoxide was identified from the reaction of the NO₃ radical with 2,3-dimethyl-2-butene,⁴⁸ while aldehydes were identified from the 2-methyl-1,3-butadiene and 2,3-dimethyl-1,3-butadiene reactions (epoxides could also have been formed⁴⁸). At room temperature and total pressures of ~1 Torr, the NO₃ radical reactions with the simple alkenes and dienes then proceed by (taking 2-methyl-1,3-butadiene as an example)



For the (CH₃)₂ĊC(CH₃)₂ONO₂ radical initially formed from NO₃ radical addition to 2,3-dimethyl-2-butene, the H atom migration and decomposition pathway cannot occur, and epoxide formation occurs (in competition with stabilization), as observed.⁴⁸

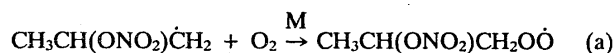
Thus, the NO₃ radical reactions with the alkenes proceed by initial addition. For example, for propene



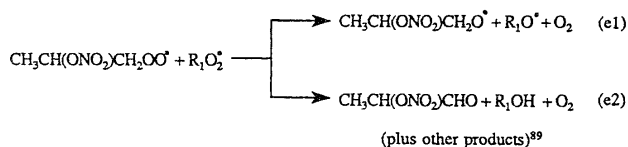
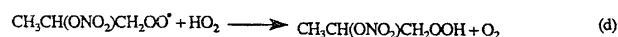
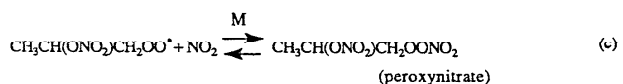
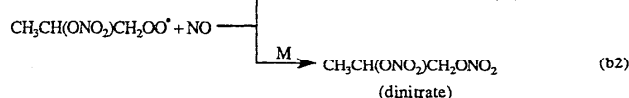
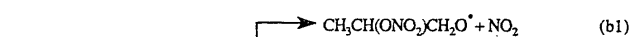
with these β-nitratoalkyl radicals being initially energy-rich. As discussed above, at low total pressures these β-nitratoalkyl radicals can decompose to form NO₂ and other products, with the importance of this decomposition route decreasing with increasing pressure, decreasing temperature and increasing complexity of the alkene.⁹² Under tropospheric conditions, these initially energy-rich β-nitratoalkyl radicals will be rapidly thermalized. However, it should be noted that, analogous to the situation for the OH radical reactions with the alkenes and aromatic hydrocarbons,⁸⁷ thermal decomposition of the thermalized radicals back to the reactants will become important at temperatures > 400 K unless other reaction pathways dominate. Since the decomposition reaction(s) of the β-nitratoalkyl radicals to form NO₂ dominates over thermal decomposition back to the reactants at low total pressures,⁹² it is expected that at elevated temperatures this will be the preferred decomposition path of the initially formed β-nitratoalkyl radicals, even at atmospheric pressure. Hence a rapid de-

crease in the measured high pressure reaction rate constants above ~400 K, as observed for the OH radical reactions with the simple alkenes above ~500–700 K,⁸⁷ is not expected for the NO₃ radical reactions with the alkenes.

Under tropospheric conditions, the β-nitratoalkyl radicals will rapidly add O₂ to form a peroxy (RO₂) radical, for example

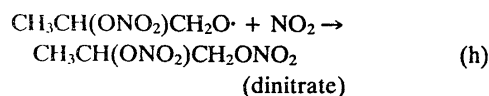
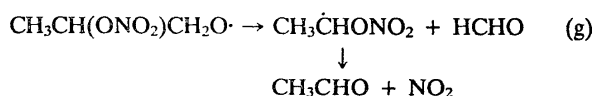
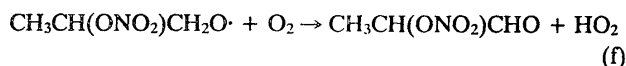


and this peroxy radical can then react with NO and NO₂ and HO₂, organic peroxy (R₁O₂) and acylperoxy (R₁C(O)OO·) radicals,⁸⁹ with the NO, NO₂ and HO₂ radical reactions being expected to be the most important in the lower troposphere.



The peroxynitrates formed in reaction (c) are expected to undergo rapid thermal decomposition (with a lifetime of ~1 s at room temperature⁸⁹), and hence the peroxynitrate acts as a temporary reservoir for the peroxy radicals, with the peroxy radicals ultimately reacting to form, at least in part, the corresponding alkoxy radicals.

The β-nitratoalkoxy radicals are expected to react with O₂, undergo thermal decomposition or react with NO₂ [reactions (f)-(h)].⁸⁹



Under conditions typical of the product studies of Bandow *et al.*,⁷² Shepson *et al.*⁷⁴ and Barnes *et al.*,⁶⁶ utilizing the dark reactions of NO₃ radicals with alkenes, with the NO₃ radicals being generated from the thermal de-

composition of N_2O_5 ,^{66,72} or from the reaction of NO_2 with O_3 ,⁷⁴ NO is absent and the relevant reactions are then expected to be reactions (c), (d) and (e), followed by reactions (f), (g) and (h) of the β -nitroalkoxy radicals. Since the dinitrate is formed from reaction (h), its yield is expected to increase with increasing NO_2 concentration, consistent with the data of Bandow *et al.*⁷² and Shepson *et al.*⁷⁴

This sequence of reactions is in accord with the product data of Hoshino *et al.*,⁷⁰ Akimoto *et al.*,⁷¹ Bandow *et al.*,⁷² Shepson *et al.*⁷⁴ and Barnes *et al.*,⁶⁶ with the most definitive data arising from the studies of Shepson *et al.*⁷⁴ and Barnes *et al.*⁶⁶ The expected products are then, in addition to the initial formation of the thermally labile intermediate peroxyxynitrate(s),^{66,72} the carbonyls arising from the β -nitroalkoxy radical decomposition reactions [reaction (g)] and the β -nitrocarbonyls formed from the reactions of the β -nitroalkoxy radicals with O_2 [reaction (f)] and, possibly, from the reactions of the β -nitroalkyl peroxy radicals with organic peroxy radicals [reaction (e2)]. These are the major products observed,^{66,74} together with small amounts of dinitrates formed from reaction (h). The molar product yields observed at room temperature and atmospheric pressure from the reactions of the NO_3 radical with propene, 1-butene, 2-methylpropene and *trans*-2-butene are: from propene: HCHO , 0.08–0.14;^{66,74} CH_3CHO , 0.11–0.12;^{66,74} $\text{CH}_3\text{COCH}_2\text{ONO}_2$, 0.22;⁷⁴ total nitratocarbonyls, ~ 0.58 ;⁶⁶ from 1-butene: HCHO , 0.11;⁶⁶ $\text{CH}_3\text{CH}_2\text{CHO}$, 0.12;⁶⁶ total nitratocarbonyls, ~ 0.60 ;⁶⁶ from 2-methylpropene: HCHO , 0.80;⁶⁶ CH_3COCH_3 , 0.85;⁶⁶ total nitratocarbonyls, ~ 0.25 ;⁶⁶ from *trans*-2-butene: CH_3CHO , 0.70;⁶⁶ $\text{CH}_3\text{COCH}(\text{ONO}_2)\text{CH}_3$, 0.55.⁶⁶ These product yields indicate that at room temperature and atmospheric pressure reactions (f) and (g) are of comparable importance, with the relative importance of these reactions depending on the particular alkene.

The available, and limited, product data for the conjugated dienes⁶⁶ and the monoterpenes^{66,95} suggest that the formation of nitratocarbonyl and/or nitrate-containing products dominates.

2.4. Haloalkenes

2.4.a. Kinetics and Mechanisms

The available kinetic data are given in Table 6. Only for vinyl chloride has more than a single study been carried out.

(1) Vinyl chloride

The rate constants of Atkinson *et al.*⁹⁹ and Andersson and Ljungström,⁶¹ both obtained from relative rate studies carried out at room temperature, are given in Table 6. The agreement is reasonable. The rate constant of Andersson and Ljungström⁶¹ was determined relative to the equilibrium constant K_5 , and hence is subject to significant uncertainties (in addition to those in the experimen-

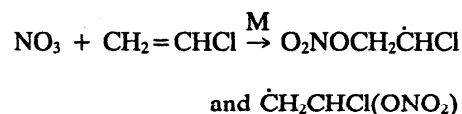
tal measurement of k/K_5). Accordingly, the rate constant of Atkinson *et al.*⁹⁹ is used to recommend that

$$k(\text{vinyl chloride}) = 4.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty of a factor of 2

No recommendations are made for the other haloalkenes studied and, because of the low reactivity of the compounds towards the NO_3 radical and the potential production of Cl atoms from the more chlorinated haloalkenes (analogous to the situation for the analogous OH radical reactions^{100,101}), the rate constants given Table 6 may be subject to significant uncertainties.

Analogous to the reactions of the OH radical with 1 haloalkenes, the NO_3 radical reactions are anticipated proceed by addition. For example, for vinyl chloride,



2.5. Alkynes

2.5.a. Kinetics and Mechanisms

The available kinetic data are given in Table 7. Only for acetylene and propyne have more than a single study been carried out.

(1) Acetylene

The rate constants, or upper limits thereof, of Atkinson *et al.*⁹⁹ and Canosa-Mas *et al.*^{44,91} are given in Table 7. The upper limit to the rate constant obtained by Atkinson *et al.*⁹⁹ at 298 K is lower than the rate constant determined by Canosa-Mas *et al.*⁴⁴ at 295 K (although it overlaps within the large uncertainties of the data Canosa-Mas *et al.*⁴⁴). An upper limit to the rate constant of

$$k(\text{acetylene}) < 5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K is recommended. This recommendation is consistent with the value of $k(\text{acetylene}) = 4 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature estimated by Sabl and Gsten⁸⁸ from the observed correlation of the rate constants with the vertical ionization energies.

(2) Propyne

The available rate constants of Atkinson *et al.*⁹⁹ and Canosa-Mas *et al.*^{44,91} are given in Table 7 and are plotted in Arrhenius form in Fig. 8. The relative⁹⁹ and absolute room temperature rate constants are in reasonable agreement, and a unit-weighted least-squares analysis of the data of Atkinson *et al.*⁹⁹ and Canosa-Mas *et al.*,^{44,91} using the Arrhenius expression, yields the recommendation

$$k(\text{propyne}) = (1.63_{-1.23}^{+4.97}) \times 10^{-11} \text{ e}^{-(3328 \pm 486)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

TABLE 6. Rate constants k for the gas-phase reactions of the NO_3 radical with haloalkenes

Haloalkene	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
Vinyl Chloride	$(4.26 \pm 0.19) \times 10^{-16}$	298 ± 2	RR [relative to $k(\text{ethene}) = 2.05 \times 10^{-16}$] ^a	Atkinson <i>et al.</i> ⁹⁹
	$(3.30 \pm 1.66) \times 10^{-16}$	296 ± 1	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 4.40 \times 10^{-11}$] ^a	Andersson and Ljungström ⁶¹
1,1-Dichloroethene	$(1.23 \pm 0.15) \times 10^{-15}$	298 ± 2	RR [relative to $k(\text{ethene}) = 2.05 \times 10^{-16}$] ^a	Atkinson <i>et al.</i> ⁹⁹
<i>cis</i> -1,2-Dichloroethene	$(1.39 \pm 0.13) \times 10^{-16}$	298 ± 2	RR [relative to $k(\text{ethene}) = 2.05 \times 10^{-16}$] ^a	Atkinson <i>et al.</i> ⁹⁹
<i>trans</i> -1,2-Dichloroethene	$(1.07 \pm 0.11) \times 10^{-16}$	298 ± 2	RR [relative to $k(\text{ethene}) = 2.05 \times 10^{-16}$] ^a	Atkinson <i>et al.</i> ⁹⁹
Trichloroethene	$(2.81 \pm 0.17) \times 10^{-16}$	298 ± 2	RR [relative to $k(\text{ethene}) = 2.05 \times 10^{-16}$] ^a	Atkinson <i>et al.</i> ⁹⁹
Tetrachloroethene	$< 5.2 \times 10^{-17}$	298 ± 2	RR [relative to $k(\text{ethene}) = 2.05 \times 10^{-16}$] ^a	Atkinson <i>et al.</i> ⁹⁹
3-Chloro-1-propene (allyl chloride)	$(5.35 \pm 0.21) \times 10^{-16}$	298 ± 2	RR [relative to $k(\text{ethene}) = 2.05 \times 10^{-16}$] ^a	Atkinson <i>et al.</i> ⁹⁹

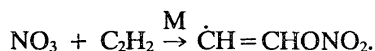
^a From present recommendations (see text).

over the temperature range 295–473 K, where the indicated error limits are two least-squares standard deviations, and

$$k(\text{propyne}) = 2.30 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of a factor of 2.

For the other alkynes, no recommendations are made. Analogous to the OH radical reactions with the alkynes,⁸⁷ the room temperature rate constants increase with the degree of alkyl substitution around the carbon-carbon triple bond. These NO_3 radical reactions are expected to proceed by initial NO_3 radical addition



2.6. Oxygen-Containing Organic Compounds

2.6.a. Kinetics and Mechanisms

The available rate constant data are given in Table 8. Only for formaldehyde, acetaldehyde and methanol have more than a single kinetic study been carried out.

(1) Formaldehyde

The available rate constants of Atkinson *et al.*,³⁹ Cantrell *et al.*⁴⁰ and Hjorth *et al.*,⁶⁰ all obtained at room temperature, are given in Table 8. The rate constants of

Atkinson *et al.*³⁹ and Hjorth *et al.*⁶⁰ were determined relative to the equilibrium constant K_5 . Although Hjorth *et al.*⁶⁰ stated that they used the equilibrium constant of Graham and Johnston,⁷⁸ the value of K_5 cited⁶⁰ ($1.88 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$) does not agree with that calculated from the expression of Graham and Johnston⁷⁸ ($3.43 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ at 295 K), and hence the re-evaluated rate constant of Hjorth *et al.*⁶⁰ (which assumes the use of the Graham and Johnston⁷⁸ equilibrium constant and a temperature of 295 K) is highly uncertain.

In addition to determining a rate constant relative to the equilibrium constant K_5 , Cantrell *et al.*⁴⁰ monitored directly the NO_3 radical concentration in several experiments, and hence an absolute rate constant can also be obtained from this study of Cantrell *et al.*⁴⁰ (Table 8). The rate constants of Atkinson *et al.*³⁹ and Cantrell *et al.*⁴⁰ are in reasonable agreement, especially the relative rate constant of Atkinson *et al.*³⁹ and the absolute value of Cantrell *et al.*⁴⁰. Based upon the relative and absolute rate constants of Atkinson *et al.*³⁹ and Cantrell *et al.*,⁴⁰ respectively, a rate constant of

$$k(\text{formaldehyde}) = 5.8 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

is recommended, with an estimated overall uncertainty of a factor of 2. This recommendation is identical or essentially identical to the recent IUPAC²² and NASA²³ evaluations of $k(\text{formaldehyde}) = 6 \times 10^{-16} \text{ cm}^3$

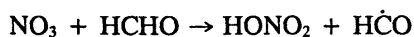
TABLE 7. Rate constants k and temperature-dependent parameters, $k = Ae^{-B/T}$, for the gas-phase reactions of the NO_3 radical with alkyne

Alkyne	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
Acetylene			$\leq 2.9 \times 10^{-17}$	298 ± 2	RR [relative to $k(\text{ethene})$ $= 2.05 \times 10^{-16}$] ^a	Atkinson <i>et al.</i> ⁹⁹
			$(5.1 \pm 3.5) \times 10^{-17}$	295 ± 2	DF-A	Canosa-Mas <i>et al.</i> ⁴⁴
			$(1.9 \pm 1.2) \times 10^{-16}$	348 ± 3	DF-A	Canosa-Mas <i>et al.</i> ⁹¹
			$(5.4 \pm 3.4) \times 10^{-16}$	423 ± 3		
			$(3.3 \pm 1.9) \times 10^{-15}$	523 ± 3		
	$0.49^{+1.6}_{-0.4}$	2742 ± 542				
Propyne			$(1.74 \pm 0.15) \times 10^{-16}$	298 ± 2	RR [relative to $k(\text{ethene})$ $= 2.05 \times 10^{-16}$] ^a	Atkinson <i>et al.</i> ⁹⁹
			$(2.66 \pm 0.32) \times 10^{-16}$	295 ± 2	DF-A	Canosa-Mas <i>et al.</i> ⁴⁴
			$(6.8 \pm 2.1) \times 10^{-16}$	323 ± 3	DF-A	Canosa-Mas <i>et al.</i> ⁹¹
			$(1.68 \pm 0.60) \times 10^{-15}$	373 ± 3		
			$(5.38 \pm 2.1) \times 10^{-15}$	423 ± 3		
	$14.7^{+40.0}_{-11.0}$	3284 ± 494	$(1.80 \pm 0.18) \times 10^{-14}$	473 ± 3		
1-Butyne			$(4.55 \pm 0.46) \times 10^{-16}$	295 ± 2	DF-A	Canosa-Mas <i>et al.</i> ⁴⁴
			$(4.48 \pm 1.24) \times 10^{-15}$	373 ± 3	DF-A	Canosa-Mas <i>et al.</i> ⁹¹
			$(1.03 \pm 0.33) \times 10^{-14}$	423 ± 3		
	$32.1^{+50.0}_{-20.0}$	3320 ± 349	$(3.26 \pm 0.72) \times 10^{-14}$	473 ± 3		
2-Butyne			$(6.70 \pm 1.50) \times 10^{-14}$	295 ± 2	DF-A	Canosa-Mas <i>et al.</i> ⁴⁴
1-Pentyne			$(7.54 \pm 0.75) \times 10^{-16}$	295 ± 2	DF-A	Canosa-Mas <i>et al.</i> ⁴⁴
			$(1.40 \pm 0.14) \times 10^{-15}$	323 ± 3	DF-A	Canosa-Mas <i>et al.</i> ⁹¹
			$(4.64 \pm 0.76) \times 10^{-15}$	373 ± 3		
			$(1.54 \pm 0.16) \times 10^{-14}$	423 ± 3		
			$(3.58 \pm 0.45) \times 10^{-14}$	473 ± 3		
	$29.8^{+25.0}_{-14.0}$	3212 ± 217				
1-Hexyne			$(1.60 \pm 0.19) \times 10^{-15}$	295 ± 2	DF-A	Canosa-Mas <i>et al.</i> ⁴⁴
			$(3.91 \pm 0.97) \times 10^{-15}$	333 ± 3	DF-A	Canosa-Mas <i>et al.</i> ⁹¹
			$(7.53 \pm 1.80) \times 10^{-15}$	373 ± 3		
			$(1.94 \pm 0.19) \times 10^{-14}$	423 ± 3		
			$(3.83 \pm 0.61) \times 10^{-14}$	473 ± 3		
	$8.95^{+5.1}_{-3.2}$	2598 ± 169				

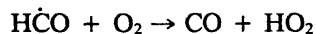
^a From present recommendations (see text).

molecule⁻¹s⁻¹ and $5.8 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively, both at 298 K.

This reaction of the NO_3 radical with HCHO proceeds by H-atom abstraction^{39,40}



with the $\dot{\text{C}}\text{O}$ radical reacting rapidly with O_2 to yield CO and the HO_2 radical^{22,23}



Use of the $-\text{CH}_2-$ group rate constant derived above (Sec. 2.1.), combined with a substituent factor of

$F_{\text{NO}_3(=\text{O})} = [F_{\text{OH}(=\text{O})}]^{1.61} = 33$,⁸⁶ leads to an estimate rate constant for the reaction of the NO_3 radical with HCHO of $5.0 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, in excellent agreement with the recommendation.

(2) Acetaldehyde

The available rate constant data of Morris and Niki Atkinson *et al.*,³⁹ Cantrell *et al.*⁴¹ and Dlugokencky and Howard⁹² are given in Table 8 and are plotted in Arrhenius form in Fig. 9. The agreement between the room temperature relative rate data of Morris and Niki Atkinson *et al.*³⁹ and Cantrell *et al.*⁴¹ and the absolute

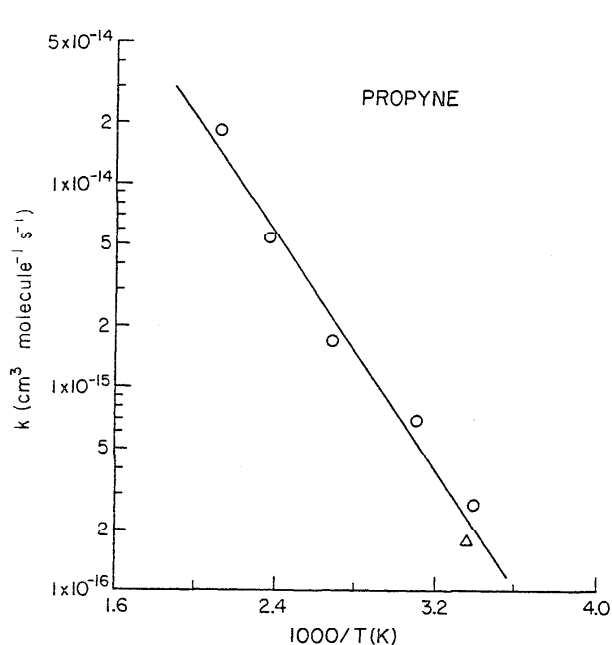


FIG 8. Arrhenius plot of rate constants for the gas-phase reaction of the NO_3 radical with propyne. (Δ) Atkinson *et al.*;⁹⁹ (\circ) Canosa-Mas *et al.*;^{44,91} (—) recommendation, see text.

room temperature rate constant of Dlugokencky and Howard⁹² is good. Since the relative rate data^{39,41,58} are subject to significant uncertainties due to uncertainties in the equilibrium constant K_5 , a unit-weighted least-squares analysis of the absolute rate constants of Dlugokencky and Howard,⁹² using the Arrhenius expression, has been carried out to yield the recommendation of

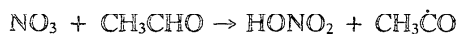
$$k(\text{acetaldehyde}) = (1.44^{+0.15}_{-0.14}) \times 10^{-12} \text{ e}^{-(1862 \pm 30)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 264–374 K, where the indicated errors are the two least-squares standard deviations, and

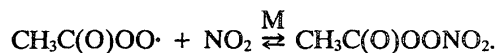
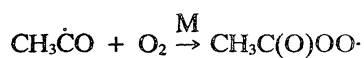
$$k(\text{acetaldehyde}) = 2.78 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 35\%$. This recommendation is essentially identical to the recent IUPAC²² and NASA²³ evaluations of $k(\text{acetaldehyde}) = 1.4 \times 10^{-12} \text{ e}^{-1860/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $1.4 \times 10^{-12} \text{ e}^{-1900/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively.

The observed formation of HONO_2 and peroxyacetyl nitrate (PAN, $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$) during the reaction of CH_3CHO in $\text{N}_2\text{O}_5 - \text{NO}_3 - \text{NO}_2 - \text{O}_2 - \text{N}_2$ (or Ar) mixtures^{41,58} shows that, as expected, the reaction of the NO_3 radical with CH_3CHO proceeds by H-atom abstraction from the $-\text{CHO}$ group,



followed by the reactions^{39,41,58,89}



Use of the $>\text{CH}-$ group rate constant derived in Sec. 2.1. above and the substituent factor $F_{\text{NO}_3}(=\text{O}) = 33$ (see Sec. 2.6.a.(1) above) leads to a calculated rate constant for this reaction at 298 K of $2.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in excellent agreement with the recommendation.

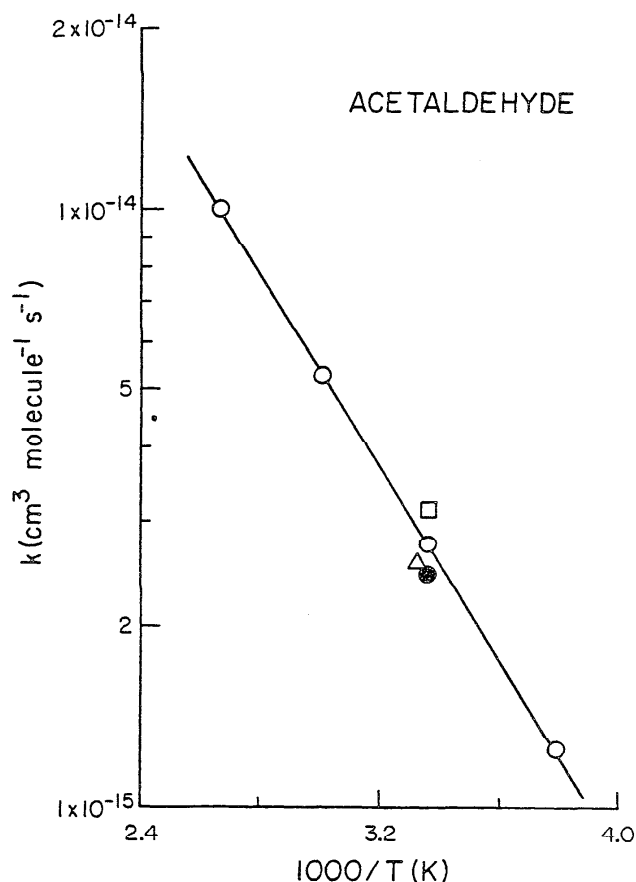


FIG 9. Arrhenius plot of rate constants for the gas-phase reaction of the NO_3 radical with acetaldehyde. (Δ) Morris and Niki;⁵⁸ (\bullet) Atkinson *et al.*;³⁹ (\square) Cantrell *et al.*;⁴¹ (\circ) Dlugokencky and Howard;⁹² (—) recommendation, see text.

(3) Methanol

The available rate constant data of Wallington *et al.*⁵⁷ and Canosa-Mas *et al.*⁹⁰ are given in Table 8. The upper limit to the rate constant determined by Wallington *et al.*⁵⁷ at 298 K is consistent with the room temperature rate constant of Canosa-Mas *et al.*⁹⁰ The reaction of the NO_3 radical with methanol will proceed by H-atom abstraction, with this H-atom abstraction being expected to occur essentially totally from the $-\text{CH}_3$ group.

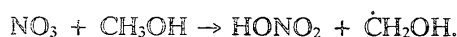


TABLE 8. Rate constants k and temperature-dependent parameters, $k = Ae^{-B/T}$, for the gas-phase reactions of the NO₃ radical with oxygen containing organic compounds

Oxygenate	$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	B (K)	k (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
Formaldehyde			$(5.89 \pm 0.48) \times 10^{-16}$	298 ± 1	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 3.41 \times 10^{-11} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ³⁹
			5.6×10^{-16}	298 ± 2	S-A	Cantrell <i>et al.</i> ⁴⁰
			$(8.7 \pm 0.6) \times 10^{-16}$	298 ± 2	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 3.41 \times 10^{-11} \text{ s}^{-1}$]	Cantrell <i>et al.</i> ⁴⁰
			$(7.9 \pm 1.7) \times 10^{-16b}$	295 ± 2	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 5.00 \times 10^{-11} \text{ s}^{-1}$]	Hjorth <i>et al.</i> ⁶⁰
Acetaldehyde			$(2.54 \pm 0.64) \times 10^{-15}$	300	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 2.65 \times 10^{-11} \text{ s}^{-1}$]	Morris and Niki ²⁸
			$(2.44 \pm 0.52) \times 10^{-15}$	298 ± 1	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 3.41 \times 10^{-11} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ³⁹
			$(3.15 \pm 0.60) \times 10^{-15}$	299 ± 1	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 3.00 \times 10^{-11} \text{ s}^{-1}$]	Cantrell <i>et al.</i> ⁴¹
			$(1.26 \pm 0.16) \times 10^{-15}$	264	F-LIF	Dlugokencky and Howar
			$(2.74 \pm 0.33) \times 10^{-15}$	298		
			$(5.27 \pm 0.63) \times 10^{-15}$	332		
		$(1.00 \pm 0.12) \times 10^{-14}$	374			
	1.44 ± 0.18	1860 ± 300				
Acrolein			$(1.11 \pm 0.17) \times 10^{-15}$	298 ± 2	RR [relative to $k(\text{ethene})$ $= 2.05 \times 10^{-16} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁹⁹
Crotonaldehyde			$(5.12 \pm 0.17) \times 10^{-15}$	298 ± 2	RR [relative to $k(\text{propene})$ $= 9.45 \times 10^{-15} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁹⁹
Methanol			$\leq 6 \times 10^{-16}$	298 ± 2	FP-A	Wallington <i>et al.</i> ⁵⁷
			$(2.1 \pm 1.1) \times 10^{-16}$	294	DF-A	Canosa-Mas <i>et al.</i> ⁹⁰
			$(4.61 \pm 0.92) \times 10^{-16}$	323		
			$(6.8 \pm 2.7) \times 10^{-16}$	348		
			$(1.29 \pm 0.49) \times 10^{-15}$	373		
			$(3.11 \pm 0.84) \times 10^{-15}$	423		
			$(2.51 \pm 0.45) \times 10^{-15}$	428		
			$(6.32 \pm 1.35) \times 10^{-15}$	473		
	$1.25^{+1.16}_{-0.61}$	2562 ± 241				
Ethanol			$< 9 \times 10^{-16}$	298 ± 2	FP-A	Wallington <i>et al.</i> ⁵⁷
2-Propanol			$\leq 2.3 \times 10^{-15}$	298 ± 2	FP-A	Wallington <i>et al.</i> ⁵⁷
Dimethyl ether			$\leq 3 \times 10^{-15}$	298 ± 2	FP-A	Wallington <i>et al.</i> ⁵⁶
Tetrahydrofuran			$(4.90 \pm 0.28) \times 10^{-15}$	296 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.89 \times 10^{-13} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁶⁷
Furan			$(1.44 \pm 0.02) \times 10^{-12}$	295 ± 1	RR [relative to $k(\text{trans-2-butene})$ $= 3.88 \times 10^{-13} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ¹⁰²

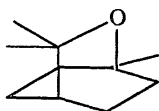
TABLE 8. Rate constants k and temperature-dependent parameters, $k = Ae^{-B/T}$, for the gas-phase reactions of the NO_3 radical with oxygen-containing organic compounds — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
1,8-Cineole ^c			$(1.75 \pm 1.07) \times 10^{-16}$	295 ± 2	RR [relative to $k(2,3\text{-dimethylbutane}) = 4.08 \times 10^{-16}$] ^a	Corchnoy and Atkinson ⁹⁷

^a From present recommendations (see text).

^b Reevaluation uncertain; see text.

^c Structure:



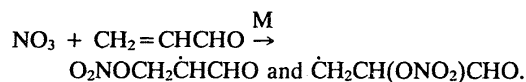
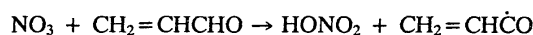
Based on the correlation shown in Fig. 2 and also on the $-\text{CH}_3$ group rate constant and the substituent factor $F_{\text{NO}_3}(-\text{OH}) = [F_{\text{OH}}(-\text{OH})]^{1.61} = 7.2$,⁸⁶ the estimated room temperature rate constant for the reaction of the NO_3 radical with methanol is $\sim(0.5-1.4) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in reasonable agreement with the room temperature rate constant of $3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ estimated by Sabljic and Gsten⁸⁸ from the observed correlation of the NO_3 radical reaction rate constants with the vertical ionization energies. These estimated room temperature rate constants are an order of magnitude lower than that measured by Canosa-Mas *et al.*⁹⁰

(4) Other Oxygen Containing Organic Compounds

For the other oxygen-containing organic compounds for which rate data are available (Table 8), only single studies have been carried out and hence no recommendations are made. The NO_3 radical reactions with ethanol, 2-propanol, dimethyl ether, tetrahydrofuran and 1,8-cineole will proceed by H-atom abstraction. The observed room temperature rate constants (or upper limits to the rate constants) for these reactions^{56,57,67,97} are reasonably consistent with those calculated from the group rate constants and substituent factors (calculated from the corresponding OH radical substituent factors⁸⁶), of (in units of $10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): ethanol, 1.1; 2-propanol, 5.9; dimethyl ether, 0.05 (0.14 from the correlation shown in Fig. 2); tetrahydrofuran, 8.8; and 1,8-cineole, 4.1. Interestingly, while the room temperature rate constants estimated by Sabljic and Gsten⁸⁸ from the observed correlation of the NO_3 radical reaction rate constants with the vertical ionization energies for ethanol and 2-propanol are in good agreement with the present estimates, that for dimethyl ether⁸⁸ of $2.9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is two orders of magnitude higher than the above estimate, and is just consistent with the upper limit to the rate constant determined by Wallington *et al.*⁵⁶

The NO_3 radical reaction with furan is expected to proceed by initial NO_3 radical addition to the $>\text{C}=\text{C}<$ bonds,¹⁰² and those with acrolein and crotonaldehyde can

proceed by both H-atom abstraction from the $-\text{CHO}$ group and/or NO_3 radical addition to the $>\text{C}=\text{C}<$ bond⁹⁹



Assuming that the rate constant for H-atom abstraction for the $-\text{CHO}$ group in the α,β -unsaturated aldehydes at room temperature is similar to that for acetaldehyde, then it appears that the H-atom abstraction pathway dominates for acrolein and that both the H-atom abstraction and NO_3 radical addition pathways are operable for crotonaldehyde.⁹⁹

2.7. Sulfur-Containing Organic Compounds

2.7.a. Kinetics

The available rate constant data are given in Table 9, and multiple studies have been carried out for four of the seven organosulfur compounds for which rate data are available.

(1) Methanethiol

The available rate constant data of Mac Leod *et al.*,¹⁰³ Wallington *et al.*,⁵⁶ Rahman *et al.*⁴⁷ and Dlugokencky and Howard⁴⁶ are given in Table 9 and are plotted in Arrhenius form in Fig. 10. At room temperature and below, these relative¹⁰³ and absolute^{46,47,56} rate constants are in reasonable agreement, being in the range $(0.77-1.12) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature. No effect of total pressure over the range 0.45-740 Torr on the room temperature rate constant is evident.^{46,47,56,103} The rate constant of Wallington *et al.*⁵⁶ at 350 K is a factor of 2 lower than that of Dlugokencky and Howard,⁴⁶ and the rate constants of Wallington *et al.*⁵⁶ are consistently lower than those of Dlugokencky and Howard⁴⁶ over the temperature range 280-350 K.

A unit-weighted average of the room temperature rate constants of Mac Leod *et al.*,¹⁰³ Wallington *et al.*,⁵⁶

Rahman *et al.*⁴⁷ and Dlugokencky and Howard,⁴⁶ combined with the zero temperature dependence determined by Dlugokencky and Howard,⁴⁶ yields the recommendation of

$$k(\text{methanethiol}) = 9.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

independent of temperature over the range 254–367 K, with an estimated overall uncertainty of a factor of 1.5 over this temperature range. This recommendation is essentially identical to the recent IUPAC evaluation²² of $k(\text{methanethiol}) = 9.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 250–370 K, and is similar to the NASA evaluation²³ of $k(\text{methanethiol}) = 4.4 \times 10^{-13} e^{210/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

(2) Dimethyl sulfide

The available rate constant data of Atkinson *et al.*,⁶⁴ Tyndall *et al.*,⁵⁰ Wallington *et al.*,^{51,56} Dlugokencky and Howard⁴⁶ and Daykin and Wine⁵² are given in Table 9 and are plotted in Arrhenius form in Fig. 11. At room temperature, the relative rate constant of Atkinson *et al.*⁶⁴ and the absolute rate constants of Tyndall *et al.*⁵⁰ and Dlugokencky and Howard⁴⁶ are in excellent agreement, but are ~25% higher than the absolute rate constants of Wallington *et al.*^{51,56} and 20–25% lower than the absolute rate constant of Daykin and Wine.⁵² As for CH₃SH, at ~298 K the rate constant is independent of total pressure over the range 0.5–740 Torr.

The rate constants of Wallington *et al.*^{51,56} for CH₃SH, CH₃SCH₃ and CH₃SSCH₃ are consistently lower than the absolute rate constants of Dlugokencky and Howard⁴⁶ and are lower than the relative rate constants of Mac Leod *et al.*¹⁰³ for CH₃SH and Atkinson *et al.*⁶⁴ for CH₃SCH₃, and it is possible that the rate data of Wallington *et al.*^{51,56} are systematically low by ~25%.

A unit-weighted least-squares analysis of the absolute rate constant data of Tyndall *et al.*,⁵⁰ Dlugokencky and Howard⁴⁶ and Daykin and Wine⁵² and the relative rate constant of Atkinson *et al.*,⁶⁴ using the Arrhenius expression, yields the recommendation of

$$k(\text{dimethyl sulfide}) = (1.87_{-0.66}^{+1.03}) \times 10^{-13} e^{(519 \pm 128)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 256–376 K, where the indicated errors are the two least-squares standard deviations, and

$$k(\text{dimethyl sulfide}) = 1.07 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty at 298 K of ±40%. This recommendation is essentially identical to the recent IUPAC²² and NASA²³ evaluations of $k(\text{dimethyl sulfide}) = 1.9 \times 10^{-13} e^{500/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–380 K.

(3) Dimethyl disulfide

The available absolute rate constant data of Wallington *et al.*⁵⁶ and Dlugokencky and Howard⁴⁶ are given in Table 9 and are plotted in Arrhenius form in Fig. 12. In addition to these two studies,^{46,56} Mac Leod *et al.*¹⁰³ carried out a relative rate study, and obtained an apparent room temperature rate constant an order of magnitude lower than the absolute values.^{46,56} A subsequent investigation by Atkinson *et al.*¹⁰⁵ showed that reliable rate constant data could not be obtained from these relative rate studies^{103,105} because of chemical complexities in the reaction system, and hence the data of Mac Leod *et al.*¹⁰³ are not included in Table 9 nor in the evaluation of the rate constant for this reaction.

As for CH₃SH and CH₃SCH₃, the rate constants of Wallington *et al.*⁵⁶ are lower than those of Dlugokencky and Howard.⁴⁶ Based mainly on the data of Dlugokencky and Howard,⁴⁶ a rate constant of

$$k(\text{dimethyl disulfide}) = 7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

independent of temperature over the range ~300–380 K is recommended, with an overall uncertainty of a factor of 2 over this temperature range. This recommendation is identical to the recent IUPAC evaluation²² and is similar to the NASA evaluation²³ of $k(\text{dimethyl disulfide}) = 1.2 \times 10^{-12} e^{-270/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

(4) Thiophene

The available rate constants of Atkinson *et al.*,^{67,102,10} all obtained from relative rate studies, are given in Table 9. The rate constant appears to be essentially independent of temperature over the restricted range of 272–296 K,^{67,102,104} and the rate constant of Atkinson *et al.*⁶⁷ at 296 K is used to recommend that

$$k(\text{thiophene}) = 3.93 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

independent of temperature over the range 272–296 K with an estimated overall uncertainty of ±35% over this temperature range.

(5) Ethanethiol

The sole rate constant of Mac Leod *et al.*¹⁰³ at 297 K (Table 9) is essentially identical to that for methanethiol indicating no effect of the alkyl group on the rate constant. Since only a single study has been carried out, no recommendation is made.

2.7.b. Mechanism

The magnitude of the rate constants and the zero or negative temperature dependencies of the rate constant for the reactions of the NO₃ radical with the thiol (RSH), sulfides (RSR) and disulfides (RSSR) indicate that these reactions proceed by initial addition of the

TABLE 9. Rate constants k and temperature-dependent parameters, $k = A e^{-B/T}$, for the gas-phase reactions of the NO_3 radical with sulfur-containing organic compounds

Organosulfur	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
Methanethiol [CH_3SH]			$(1.00 \pm 0.22) \times 10^{-12}$	297 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.89 \times 10^{-13}]^a$	Mac Leod <i>et al.</i> ¹⁰³
			$(8.0 \pm 1.4) \times 10^{-13}$	280	FP-A	Wallington <i>et al.</i> ⁵⁶
			$(8.1 \pm 0.6) \times 10^{-13}$	298		
			$(5.4 \pm 0.7) \times 10^{-13}$	350		
	$0.10^{+0.26}_{-0.07}$	-600 ± 400	$(7.7 \pm 0.5) \times 10^{-13}$	298	DF-MS	Rahman <i>et al.</i> ⁴⁷
Ethanethiol [$\text{C}_2\text{H}_5\text{SH}$]			$(1.11 \pm 0.17) \times 10^{-12}$	254	F-LIF	Dlugokencky and Howard ⁴⁶
			$(1.12 \pm 0.17) \times 10^{-12}$	296		
			$(1.12 \pm 0.17) \times 10^{-12}$	367		
	1.09 ± 0.17	0 ± 50				
Dimethyl sulfide [CH_3SCH_3]			$(1.21 \pm 0.28) \times 10^{-12}$	297 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.89 \times 10^{-13}]^a$	Mac Leod <i>et al.</i> ¹⁰³
			$(9.92 \pm 0.20) \times 10^{-13}$	296 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.89 \times 10^{-13}]^a$	Atkinson <i>et al.</i> ⁶⁴
			$(1.2 \pm 0.3) \times 10^{-12}$	278	MP-A	Tyndall <i>et al.</i> ⁵⁰
			$(9.9 \pm 3.5) \times 10^{-13}$	298		
			$(1.0 \pm 0.25) \times 10^{-12}$	318		
			$(7.5 \pm 0.5) \times 10^{-13}$	298 ± 2	FP-A	Wallington <i>et al.</i> ⁵¹
			$(8.8 \pm 1.2) \times 10^{-13}$	280	FP-A	Wallington <i>et al.</i> ⁵⁶
			$(8.1 \pm 1.3) \times 10^{-13}$	298		
			$(7.7 \pm 0.7) \times 10^{-13}$	350		
			$(1.40 \pm 0.21) \times 10^{-12}$	256	F-LIF	Dlugokencky and Howard ⁴⁶
Dimethyl sulfide- d_6 [CD_3SCD_3]			$(1.45 \pm 0.22) \times 10^{-12}$	257		
			$(1.21 \pm 0.19) \times 10^{-12}$	277		
			$(1.08 \pm 0.17) \times 10^{-12}$	297		
			$(1.04 \pm 0.16) \times 10^{-12}$	297		
			$(8.6 \pm 1.3) \times 10^{-13}$	337		
			$(7.4 \pm 1.2) \times 10^{-13}$	376		
			$(1.3 \pm 0.3) \times 10^{-12}$	298 ± 1	LP-A	Daykin and Wine ⁵²
			$(3.4 \pm 0.8) \times 10^{-13}$	298 ± 1	LP-A	Daykin and Wine ⁵²
			$(4.8 \pm 1.2) \times 10^{-12}$	298 ± 1	LP-A	Daykin and Wine ⁵²
			$(5.3 \pm 0.8) \times 10^{-13}$	280	FP-A	Wallington <i>et al.</i> ⁵⁶
Diethyl sulfide [$\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$]			$(4.9 \pm 0.8) \times 10^{-13}$	298		
			$(4.3 \pm 0.6) \times 10^{-13}$	350		
	0.19 ± 0.03	-290 ± 50	$(7.3 \pm 1.5) \times 10^{-13}$	334	F-LIF	Dlugokencky and Howard ⁴⁶
		$(7.5 \pm 1.5) \times 10^{-13}$	382			
	0.74 ± 0.15	0 ± 200				
Dimethyl disulfide [CH_3SSCH_3]			$(5.3 \pm 0.8) \times 10^{-13}$	280	FP-A	Wallington <i>et al.</i> ⁵⁶
			$(4.9 \pm 0.8) \times 10^{-13}$	298		
Thiophene			$(4.3 \pm 0.6) \times 10^{-13}$	350		
			$(7.3 \pm 1.5) \times 10^{-13}$	334	F-LIF	Dlugokencky and Howard ⁴⁶
Thiophene			$(3.57 \pm 0.90) \times 10^{-14}$	295 ± 1	RR [relative to $k(\text{trans-2-butene})$ $= 3.88 \times 10^{-13}]^a$	Atkinson <i>et al.</i> ¹⁰²
			$(3.91 \pm 0.09) \times 10^{-14}$	295 ± 1	RR [relative to $k(\text{propene})$ $= 9.45 \times 10^{-15}]^a$	Atkinson <i>et al.</i> ¹⁰²

TABLE 9. Rate constants k and temperature-dependent parameters, $k = A e^{-B/T}$, for the gas-phase reactions of the NO_3 radical with sulfur-containing organic compounds — Continued

Organosulfur	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) at T (K)	Technique	Reference	
			$(3.93 \pm 0.16) \times 10^{-14}$	296 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.89 \times 10^{-13} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁶⁷
			$(4.01 \pm 0.56) \times 10^{-14}$	272.4 ± 0.6	RR [relative to $k(\text{trans-2-butene})$ $= 3.68 \times 10^{-13} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ¹⁰⁴

^aFrom present recommendations (see text).

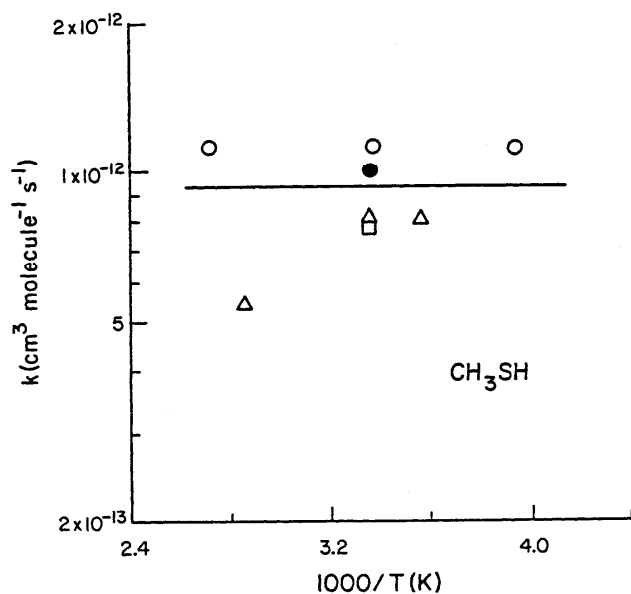


FIG 10. Arrhenius plot of rate constants for the gas-phase reaction of the NO_3 radical with methanethiol. (●) Mac Leod *et al.*;¹⁰³ (Δ) Wallington *et al.*;⁵⁶ (□) Rahman *et al.*;⁴⁷ (○) Dlugokencky and Howard;⁴⁶ (—) recommendation, see text.

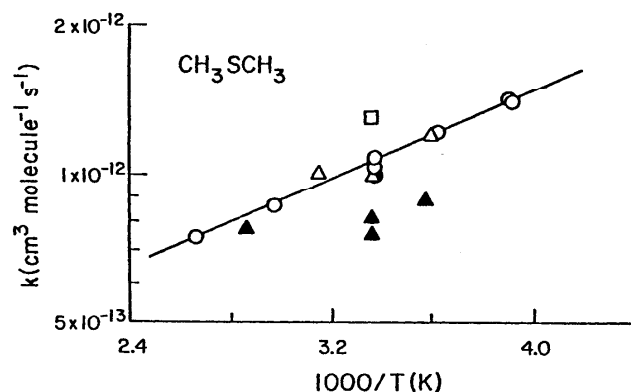
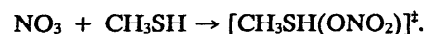


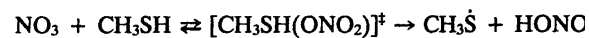
FIG 11. Arrhenius plot of rate constants for the gas-phase reaction of the NO_3 radical with dimethyl sulfide. (●) Atkinson *et al.*;⁶⁴ (Δ) Tyndall *et al.*;⁵⁰ (▲) Wallington *et al.*;^{51,56} (○) Dlugokencky and Howard;⁴⁶ (□) Daykin and Wine;⁵² (—) recommendation, see text.

NO_3 radical to the S atom.^{46,50,52,56,64,103} For example, methanethiol

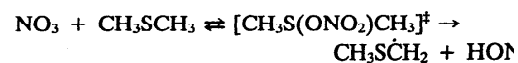


The subsequent reactions of these addition adducts are not totally understood. Decomposition of the adducts to generate NO_2 is not observed,^{46,50} with an NO_2 formation yield of <5% being reported for the NO_3 radical reactions with CH_3SH and CH_3SCH_3 at a total pressure of ~ 1 Torr.⁴⁶ Since the measured rate constants are independent of the total pressure for pressures > 1 Torr,^{46,47,50-52,56,64,103} this indicates that other decomposition pathways of the addition adduct, other than to regenerate reactants, occur.⁴⁶

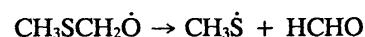
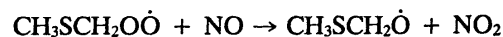
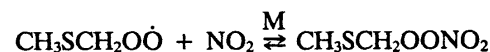
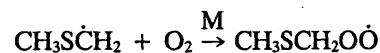
From a product study of the NO_3 radical reactions with CH_3SH , $\text{C}_2\text{H}_5\text{SH}$ and CH_3SSCH_3 conducted at room temperature and atmospheric pressure with FT-IR absorption spectroscopic detection of reactants and products, Mac Leod *et al.*¹⁰³ suggested the formation of $\text{CH}_3\dot{\text{S}}$ radicals from the reaction of the NO_3 radical with CH_3SH . The reaction sequence may then be,



where the addition adduct may decompose back to reactants as well as to $\text{CH}_3\dot{\text{S}}$ radicals and HONO_2 . The absolute room temperature rate constants determined by Daykin and Wine⁵² for the reactions of the NO_3 radical with CH_3SCH_3 , CD_3SCD_3 and $\text{C}_2\text{H}_5\text{SC}_2\text{H}_5$ show that the rate determining step involves H (or D) atom abstraction. These observations indicate that an analogous reaction mechanism occurs for the sulfides,⁵²



followed by reactions of the $\text{CH}_3\dot{\text{S}}\text{CH}_2$ radical to yield $\text{CH}_3\dot{\text{S}}$ radical⁵²



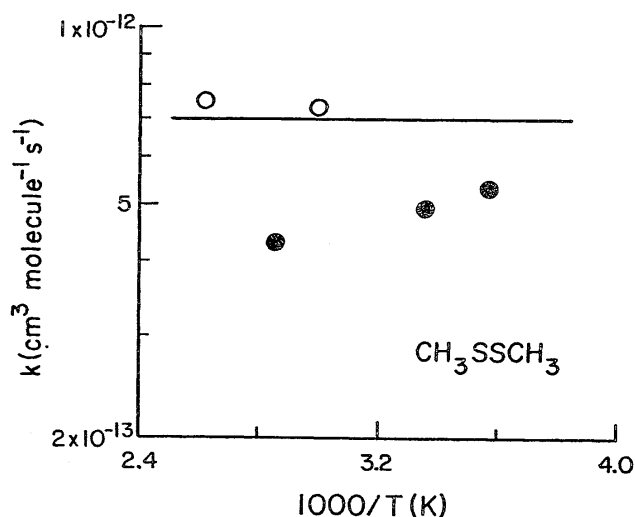
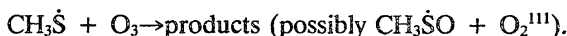
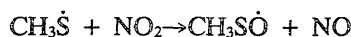
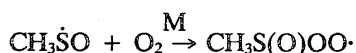
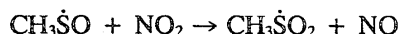


FIG 12. Arrhenius plot of rate constants for the gas-phase reaction of the NO_3 radical with dimethyl disulfide. (●) Wallington *et al.*,⁵⁶ (O) Dlugokencky and Howard;⁴⁶ (—) recommendation, see text.

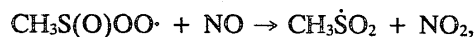
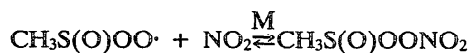
The subsequent reactions of the $\text{CH}_3\dot{\text{S}}$ radical must then form, among other products, SO_2 and HCHO .^{103,106} Kinetic and product studies of the gas-phase reactions of the $\text{CH}_3\dot{\text{S}}$ radical with NO ,^{107,108} NO_2 ,^{106,108-110} O_2 ,^{108,110} and O_3 ,¹¹¹ suggest that the important reactions of the $\text{CH}_3\dot{\text{S}}$ radical under atmospheric conditions are with NO_2 and O_3 ,



Under atmospheric conditions, the $\text{CH}_3\dot{\text{S}}\text{O}$ radical reacts with NO_2 ^{106,109,110} and O_2 ,¹⁰⁶



which is followed by¹⁰⁶



and possibly also with O_3 .¹¹¹ Reactions of the $\text{CH}_3\dot{\text{S}}\text{O}_2$ radical must then lead to the formation of SO_2 , HCHO (through the $\cdot\text{CH}_3$ radical), and $\text{CH}_3\text{SO}_3\text{H}$.¹⁰⁶

The reaction of the NO_3 radical with thiophene may occur by NO_3 radical addition to the $>\text{C}=\text{C}<$ bonds as well as by NO_3 radical addition to the S atom.

2.8. Nitrogen-Containing Organic Compounds

2.8.a. Kinetics and Mechanisms

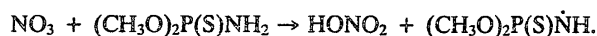
The available rate constant data are given in Table 10. Rate constants, or upper limits thereof, are available only

for acetonitrile⁵⁹ and pyrrole.¹⁰² No recommendations are made. The reaction of the NO_3 radical with pyrrole is expected to proceed by NO_3 radical addition to the $>\text{C}=\text{C}<$ bonds and/or to the N atom.

2.9. Phosphorus-Containing Organic Compounds

2.9.a. Kinetics and Mechanisms

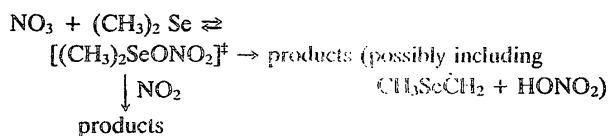
The available rate constant data are given in Table 11. Only single rate constant studies have been carried out for each organophosphorus compound, and only the dimethyl phosphorothioamidates were observed to react with the NO_3 radical,¹¹³ presumably by interaction of the NO_3 radical with the $-\text{N}(\text{CH}_3)_2$, $-\text{NHCH}_3$ and $-\text{NH}_2$ groups, possibly by overall H-atom abstraction from these substituent groups.¹¹³ For example,



2.10. Selenium-Containing Organic Compounds

2.10.a. Kinetics and Mechanisms

The only organoselenium compound studied to date¹¹⁵ has been dimethyl selenide, $(\text{CH}_3)_2\text{Se}$, and the room temperature rate constant extrapolated to zero NO_2 concentration is given in Table 11. The rate constant was determined relative to the rate constants for the reactions of the NO_3 radical with 2-methyl-2-butene and 2,3-dimethyl-2-butene¹¹⁵ and the measured rate constant increased linearly with increasing NO_2 concentration.¹¹⁵ The measured rate constant for the gas-phase reaction of the NO_3 radical with dimethyl selenide at 296 ± 2 K increased from 1.6×10^{-11} cm^3 molecule⁻¹ s⁻¹ at an NO_2 concentration of 1.2×10^{14} molecule cm^{-3} to 3.5×10^{-11} cm^3 molecule⁻¹ s⁻¹ at an NO_2 concentration of 1.2×10^{15} molecule cm^{-3} , with the rate constants at a given NO_2 concentration relative to 2-methyl-2-butene and 2,3-dimethyl-2-butene being in excellent agreement.¹¹⁵ The magnitude of this rate constant indicates that the reaction proceeds by addition of the NO_3 radical to the selenium atom.¹¹⁵ The reason for the observed increase in the measured rate constant with increasing NO_2 concentration and the detailed reaction mechanism is not understood at present, although the reaction sequence



can explain the observed kinetic behavior.

2.11. Silicon-Containing Organic Compounds

2.11.a. Kinetics and Mechanisms

The available kinetic data are given in Table 11. For all five organosilicon compounds studied, no reaction was

TABLE 10. Rate constants k for the gas-phase reactions of the NO_3 radical with nitrogen-containing organic compounds

Organic	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
Acetonitrile [CH_3CN]	$< 5 \times 10^{-19}$	a	RR [relative to $K_3(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 3.41 \times 10^{-11}$] ^b	Cantrell <i>et al.</i> ⁵⁹
Pyrrole	$(4.61 \pm 0.09) \times 10^{-11}$	295 ± 1	RR [relative to k (2-methyl-2-butene) $= 9.37 \times 10^{-12}$] ^b	Atkinson <i>et al.</i> ¹⁰²

^a Room temperature, not reported; 298 K assumed.

^b From present recommendations (see text).

TABLE 11. Rate constants k for the gas-phase reactions of the NO_3 radical with phosphorus-, selenium- and silicon- containing organic compounds

Organic	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
<i>Organophosphorus Compounds</i>				
$(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{SCH}_3$	$< 1.1 \times 10^{-15}$	298 ± 2	RR [relative to k (propene) $= 9.45 \times 10^{-15}$] ^a	Goodman <i>et al.</i> ¹¹²
	$< 1.6 \times 10^{-14}$	298 ± 2	RR [relative to k (<i>trans</i> -2-butene) $= 3.90 \times 10^{-13}$] ^a	Goodman <i>et al.</i> ¹¹²
$(\text{CH}_3\text{S})_2\text{P}(\text{O})\text{OCH}_3$	$\leq 2.4 \times 10^{-15}$	298 ± 2	RR [relative to k (propene) $= 9.45 \times 10^{-15}$] ^a	Goodman <i>et al.</i> ¹¹²
	$\leq 7.1 \times 10^{-14}$	298 ± 2	RR [relative to k (<i>trans</i> -2-butene) $= 3.90 \times 10^{-13}$] ^a	Goodman <i>et al.</i> ¹¹²
$(\text{CH}_3\text{O})_3\text{PS}$	$< 1.6 \times 10^{-14}$	298 ± 2	RR [relative to k (<i>trans</i> -2-butene) $= 3.90 \times 10^{-13}$] ^a	Goodman <i>et al.</i> ¹¹²
$(\text{CH}_3\text{O})_2\text{P}(\text{S})\text{SCH}_3$	$< 2.8 \times 10^{-14}$	298 ± 2	RR [relative to k (<i>trans</i> -2-butene) $= 3.90 \times 10^{-13}$] ^a	Goodman <i>et al.</i> ¹¹²
$(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{N}(\text{CH}_3)_2$	$< 3.6 \times 10^{-14}$	296 ± 2	RR [relative to k (<i>trans</i> -2-butene) $= 3.89 \times 10^{-13}$] ^a	Goodman <i>et al.</i> ¹¹³
$(\text{CH}_3\text{O})_2\text{P}(\text{S})\text{N}(\text{CH}_3)_2$	$(3.23 \pm 0.94) \times 10^{-14}$	296 ± 2	RR [relative to k (<i>trans</i> -2-butene) $= 3.89 \times 10^{-13}$] ^a	Goodman <i>et al.</i> ¹¹³
$(\text{CH}_3\text{O})_2\text{P}(\text{S})\text{NHCH}_3$	$(3.11 \pm 0.13) \times 10^{-13}$	296 ± 2	RR [relative to k (<i>trans</i> -2-butene) $= 3.89 \times 10^{-13}$] ^a	Goodman <i>et al.</i> ¹¹³
$(\text{CH}_3\text{O})_2\text{P}(\text{S})\text{NH}_2$	$(4.05 \pm 0.67) \times 10^{-13}$	296 ± 2	RR [relative to k (<i>trans</i> -2-butene) $= 3.89 \times 10^{-13}$] ^a	Goodman <i>et al.</i> ¹¹³
$(\text{CH}_3\text{O})_2\text{P}(\text{S})\text{Cl}$	$< 2.8 \times 10^{-14}$	296 ± 2	RR [relative to k (<i>trans</i> -2-butene) $= 3.89 \times 10^{-13}$] ^a	Atkinson <i>et al.</i> ¹¹⁴

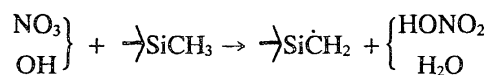
TABLE 11. Rate constants k for the gas-phase reactions of the NO_3 radical with phosphorus-, selenium- and silicon- containing organic compounds - Continued

Organic	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
<i>Organoselenium Compounds</i>				
Dimethyl selenide [(CH_3) ₂ Se]	1.4×10^{-11b}	296 ± 2	RR [relative to $k(2\text{-methyl-2-butene})$ $= 9.37 \times 10^{-12}$ and $k(2,3\text{-dimethyl-2-butene})$ $= 5.72 \times 10^{-11}a$	Atkinson <i>et al.</i> ¹¹⁵
<i>Organosilicon Compounds</i>				
Tetramethylsilane [(CH_3) ₄ Si]	$<6 \times 10^{-17}$	297 ± 2	RR [relative to $k(n\text{-heptane})$ $= 1.37 \times 10^{-16}a$	Atkinson ¹¹⁶
Hexamethyldisiloxane [(CH_3) ₃ SiOSi(CH_3) ₃]	$<6 \times 10^{-17}$	297 ± 2	RR [relative to $k(n\text{-heptane})$ $= 1.37 \times 10^{-16}a$	Atkinson ¹¹⁶
Hexamethylcyclotri- siloxane [-(CH_3) ₂ SiO-] ₃	$<1.4 \times 10^{-16}$	297 ± 2	RR [relative to $k(n\text{-heptane})$ $= 1.37 \times 10^{-16}a$	Atkinson ¹¹⁶
Octamethylcyclotetra- siloxane [-(CH_3) ₂ SiO-] ₄	$<1.4 \times 10^{-16}$	297 ± 2	RR [relative to $k(n\text{-heptane})$ $= 1.37 \times 10^{-16}a$	Atkinson ¹¹⁶
Decamethylcyclopenta- siloxane [-(CH_3) ₂ SiO-] ₅	$<2.1 \times 10^{-16}$	297 ± 2	RR [relative to $k(n\text{-heptane})$ $= 1.37 \times 10^{-16}a$	Atkinson ¹¹⁶

^aFrom present recommendations (see text).

^bExtrapolated to zero NO_2 concentration (see text). $k[(\text{CH}_3)_2\text{Se}] = \{(1.41 \pm 0.11) \times 10^{-11} + (1.74 \pm 0.18) \times 10^{-26} [\text{NO}_2]\} \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, where the NO_2 concentration is in molecule cm^{-3} units and the indicated errors are the two least-squares standard deviations.

observed.¹¹⁶ The upper limits to the rate constants for the NO_3 radical reactions and the corresponding OH radical reaction rate constants¹¹⁶ are consistent with the reaction mechanisms

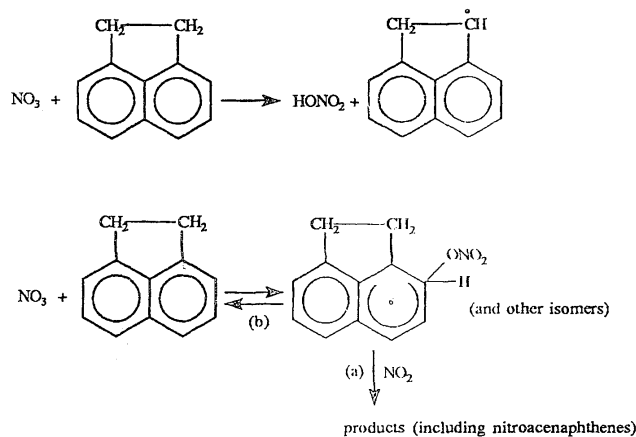


2.12. Aromatic Compounds

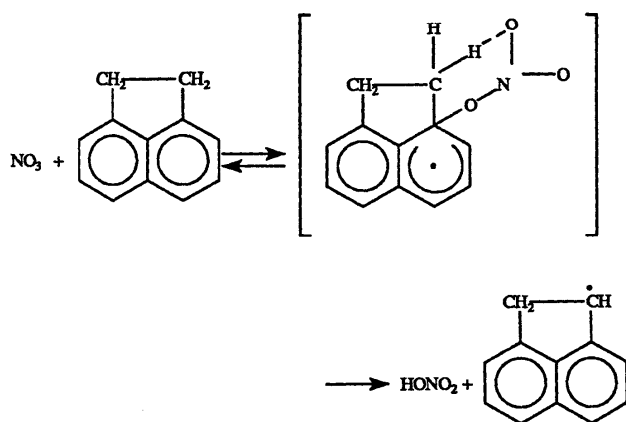
2.12.a. Kinetics and Mechanisms

Numerous experimental studies have been carried out to investigate the kinetics and products of the gas-phase reactions of aromatic compounds, including the polycyclic aromatic hydrocarbons (PAH) and their derivatives, in NO_3 radical - NO_2 - air mixtures.^{38,39,42,63,68,69,73,75-77,104,117-127} As a result of the kinetic and mechanistic data obtained from these studies, especially the kinetic and mechanistic data from the recent kinetic studies of Atkinson and Aschmann⁶⁹ and Atkinson *et al.*,¹⁰⁴ it is recognized that the reactions of the NO_3 radical with aromatic compounds proceed by two reaction channels, one involving overall H-atom abstraction from, or NO_3 radical addition to, the substituent group(s)⁶⁹ and

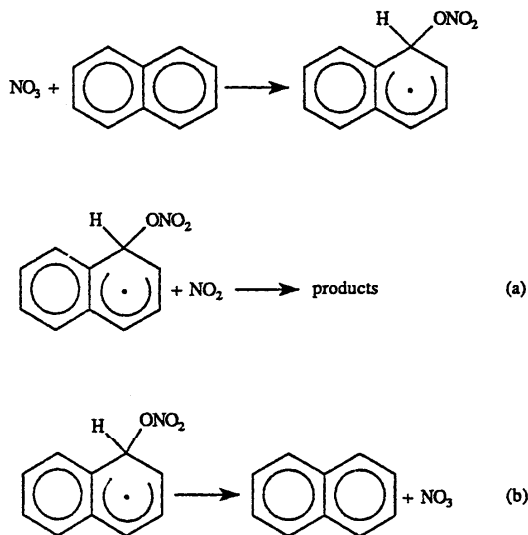
the other involving NO_3 radical addition to the aromatic ring to form a nitratocyclohexadienyl-type radical.¹⁰⁴ The nitratocyclohexadienyl-type radicals either rapidly thermally decompose back to reactants or react exclusively with NO_2 to form products.¹⁰⁴ Thus, taking acenaphthene as an example,^{69,76,104}



where the H-atom abstraction process may take place via the intermediate formation of a nitratocyclohexadienyl addition radical with a six-membered transition state^{42,119}



The NO_3 addition reaction pathway which involves initial addition of the NO_3 radical to the aromatic ring to form a nitratocyclohexadienyl-type radical, which either thermally decomposes back to reactants or reacts with NO_2 , has a reaction rate which is first order in both the NO_3 radical and NO_2 concentrations [i.e., on $([\text{NO}_3][\text{NO}_2])$] and is kinetically equivalent to reaction with N_2O_5 under conditions where NO_3 radicals, NO_2 and N_2O_5 are in equilibrium.^{69,104} For the reaction sequence,



then under conditions where $k_b \gg k_a[\text{NO}_2]$,

$$-d[\text{aromatic compound}]/dt = \frac{k k_a [\text{NO}_3][\text{NO}_2][\text{aromatic compound}]/k_b}{k_{\text{obs}}[\text{NO}_3][\text{NO}_2][\text{aromatic compound}]},$$

where k is the rate constant for the initial NO_3 radical addition to the aromatic ring and k_a and k_b are the rate constants for the reactions (a) and (b), respectively. To date, this reaction pathway has only been observed for polycyclic aromatic compounds containing fused six-membered rings. The measured rate coefficient, k_{obs} , is then given by

$$k_{\text{obs}} = k k_a/k_b.$$

The available rate constant data for the reactions of the NO_3 radical with aromatic compounds which proceed by NO_3 radical reaction with the substituent groups and for which the reaction rates are independent of the NO_2 concentration are given in Table 12, while the rate coefficients k_{obs} for interaction of the NO_3 radical with the aromatic rings are given in Table 13.

2.12.b. NO_3 Radical Reactions with the Aromatic Ring Substituent Groups

(1) Benzene

Only upper limits to the rate constant, obtained from relative rate studies carried out at room temperature, are available (Table 12). Based on the upper limits to the rate constant determined by Japar and Niki³⁸ and Atkinson *et al.*,^{39,63} an upper limit to the rate constant of

$$k(\text{bcnzcnc}) < 3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1} \text{ at } 298 \text{ K}$$

is recommended. This recommendation is consistent with the room temperature rate constant of $2 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$ estimated by Sabljic and Gusten⁸⁸ from the observed correlation of the NO_3 radical reaction rate constants with the vertical ionization energies.

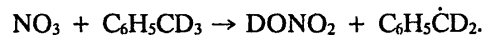
(2) Toluene, Toluene- d_3 ($\text{C}_6\text{H}_5\text{CD}_3$) and Toluene- d_8

The available rate constant data for toluene of Japar and Niki,³⁸ Carter *et al.*,⁴² Atkinson *et al.*^{39,63} and Atkinson and Aschmann,⁶⁹ all obtained from relative rate studies carried out at room temperature, are given in Table 12. The rate constants of Atkinson *et al.*^{39,63} and Atkinson and Aschmann⁶⁹ are in good agreement and are consistent with the upper limits to the rate constants of Carter *et al.*⁴² and, marginally, of Japar and Niki.³⁸ A unit-weighted average of the rate constants of Atkinson *et al.*^{39,63} and Atkinson and Aschmann⁶⁹ yields the recommendation of

$$k(\text{toluene}) = 6.8 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty of a factor of 2.

The room temperature rate constants determined by Atkinson and Aschmann⁶⁹ for the reactions of the NO_3 radical with toluene- d_8 and toluene- d_3 ($\text{C}_6\text{H}_5\text{CD}_3$) are identical within the experimental errors and are a factor of ~ 2 lower than the room temperature rate constant for toluene- h_8 . These kinetic data show that the reactions of the NO_3 radical with toluene and the fully and partially deuterated toluenes proceed by H (or D) atom abstraction from the $-\text{CH}_3$ (or $-\text{CD}_3$) substituent group, with the rate-determining step being H (or D) atom abstraction. For example,



(3) *m*-Xylene

The available rate constants of Atkinson *et al.*^{39,63} are given in Table 12. These room temperature rate constants, determined relative to the equilibrium constant K_5 ³⁹ and to the reactions of the NO_3 radical with ethene³⁹ and *n*-heptane,⁶³ are in good agreement. A unit-weighted average of these rate constants^{39,63} yields the recommendation of

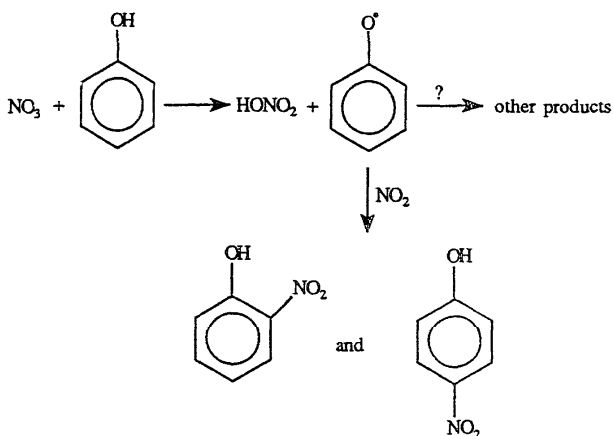
$k(m\text{-xylene}) = 2.33 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, with an estimated overall uncertainty of a factor of 2.

(4) Phenol

The available rate constants of Carter *et al.*⁴² and Atkinson *et al.*⁶³ are given in Table 12. These room temperature rate constants, all obtained from relative rate studies, vary over a range of a factor of 2.3, with the rate constant of Atkinson *et al.*⁶³ determined relative to the equilibrium constant K_5 being significantly higher than the rate constants determined relative to the rate constants for the reactions of the NO_3 radical with *cis*-2-butene⁴² or 2-methyl-2-butene.⁶³ This may indicate the occurrence of secondary reactions in the relative rate method which involved monitoring the enhanced decay rate of N_2O_5 in the presence of excess known concentrations of phenol.⁶³ The rate constant determined by Atkinson *et al.*⁶³ relative to the rate constant for the reaction of the NO_3 radical with 2-methyl-2-butene is used to recommend that

$k(\text{phenol}) = 3.64 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, with an estimated overall uncertainty of a factor of 1.5.

Arey *et al.*¹²⁷ have identified 2-nitrophenol and 4-nitrophenol as products of this reaction, with a 2-nitrophenol formation yield of $\sim 16\%$. The formation of these products suggests that the reaction mechanism is



with the reaction possibly proceeding by initial NO_3 radical addition to the aromatic ring (see Sec. 2.12.a. above). This reaction scheme is consistent with the product data obtained by Niki *et al.*¹²⁸ from a study of the Cl atom-initiated reaction of benzaldehyde in the presence of NO_2 .

(5) *o*-, *m*- and *p*-Cresol

The available rate constants of Carter *et al.*⁴² and Atkinson *et al.*⁶³ obtained from relative rate studies carried out at room temperature, are given in Table 12. The rate constants from these two studies disagree by up to a factor of 2. A unit-weighted average of the rate constants of Carter *et al.*⁴² and Atkinson *et al.*⁶³ for *m*-cresol (not using the semi-quantitative rate constant of Atkinson *et al.*⁶³ derived relative to the equilibrium constant K_5) yields the recommendation of

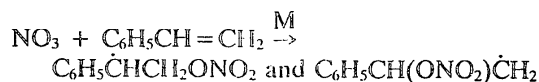
$k(m\text{-cresol}) = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, with an estimated overall uncertainty of a factor of 3.

Since the rate constants of Atkinson *et al.*⁶³ for *o*- and *p*-cresol are relative to the rate constant for the reaction of the NO_3 radical with *m*-cresol, no recommendations for *o*- and *p*-cresol are made, although it is evident from the data of Carter *et al.*⁴² and Atkinson *et al.*⁶³ that the room temperature rate constants for *o*-, *m*- and *p*-cresol are in the order $k(o\text{-cresol}) \sim k(p\text{-cresol}) > k(m\text{-cresol})$.

Grosjean¹¹⁷ and Arey *et al.*¹²⁷ have investigated the products of the NO_3 radical-initiated reaction of *o*-cresol in the presence of one atmosphere of air. 2-Methyl-6-nitrophenol and 2-methyl-4-nitrophenol were observed as products in both studies.^{117,127} The observed nitrocresol yields were 2.5–20% (2-methyl-6-nitrophenol + 2-methyl-4-nitrophenol)¹¹⁷ and $\sim 5\%$ (2-methyl-6-nitrophenol only).¹²⁷ The reaction mechanism then appears to be analogous to that shown above for phenol.

(6) Other Aromatic Compounds

Apart from tetralin (for which the relative rate constants of Atkinson *et al.*¹¹⁹ and Atkinson and Aschmann⁶⁹ are in agreement within the experimental error limits), rate constants for the other aromatic compounds studied are available only from single studies. For styrene and acenaphthylene, the reactions proceed by initial addition of the NO_3 radical to the $-\text{CH}=\text{CH}_2$ group (styrene) or to the unsaturated cyclopenta-fused ring (acenaphthylene).^{69,76} For example, for styrene,



and the subsequent reactions are expected to be analogous to those discussed in Sec. 2.3.b. for the alkenes. For example, for the $\text{C}_6\text{H}_5\text{CH}(\text{ONO}_2)\dot{\text{C}}\text{H}_2$ radical

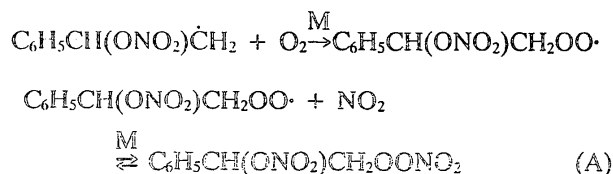


TABLE 12. Rate constants k for the gas-phase reactions of the NO_3 radical with aromatic compounds, which are independent of the NO_2 concentration

Aromatic	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
Benzene	$< 6.2 \times 10^{-17}$	300	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 2.65 \times 10^{-11} \text{ J}^a$	Japar and Niki ³⁸
	$\leq 2.7 \times 10^{-17}$	298 ± 1	RR [relative to $k(\text{ethene})$ $= 2.05 \times 10^{-16} \text{ J}^a$	Atkinson <i>et al.</i> ³⁹
	$< 5.5 \times 10^{-17}$	298 ± 1	RR [relative to $k(n\text{-heptane})$ $= 1.37 \times 10^{-16} \text{ J}^a$	Atkinson <i>et al.</i> ⁶³
Toluene	$< 6.2 \times 10^{-17}$	300	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 2.65 \times 10^{-11} \text{ J}^a$	Japar and Niki ³⁸
	$\leq 3.6 \times 10^{-15}$	300 ± 1	RR [relative to $k(\text{propene})$ $= 9.45 \times 10^{-15} \text{ J}^a$	Carter <i>et al.</i> ⁴²
	$(6.56 \pm 2.46) \times 10^{-17}$	298 ± 1	RR [relative to $k(\text{ethene})$ $= 2.05 \times 10^{-16} \text{ J}^a$	Atkinson <i>et al.</i> ³⁹
	$(6.17 \pm 1.51) \times 10^{-17}$	298 ± 1	RR [relative to $k(n\text{-heptane})$ $= 1.37 \times 10^{-16} \text{ J}^a$	Atkinson <i>et al.</i> ⁶³
	$(7.81 \pm 0.83) \times 10^{-17}$	296 ± 2	RR [relative to $k(n\text{-heptane})$ $= 1.37 \times 10^{-16} \text{ J}^a$	Atkinson and Aschman ¹
Toluene- d_3 [$\text{C}_6\text{H}_5\text{CD}_3$]	$(3.84 \pm 0.69) \times 10^{-17}$	296 ± 2	RR [relative to $k(n\text{-heptane})$ $= 1.37 \times 10^{-16} \text{ J}^a$	Atkinson and Aschman ¹
Toluene- d_8 [$\text{C}_6\text{D}_5\text{CD}_3$]	$(3.43 \pm 1.78) \times 10^{-17}$	296 ± 2	RR [relative to $k(n\text{-heptane})$ $= 1.37 \times 10^{-16} \text{ J}^a$	Atkinson and Aschman ¹
Ethylbenzene	$\leq 5.7 \times 10^{-16}$	298 ± 2	RR [relative to $k(\text{propene})$ $= 9.45 \times 10^{-15} \text{ J}^a$	Atkinson <i>et al.</i> ¹¹⁹
<i>o</i> -Xylene	$(3.77 \pm 0.53) \times 10^{-16}$	298 ± 1	RR [relative to $k(n\text{-heptane})$ $= 1.37 \times 10^{-16} \text{ J}^a$	Atkinson <i>et al.</i> ⁶³
<i>m</i> -Xylene	$(2.10 \pm 0.37) \times 10^{-16}$	298 ± 1	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 3.41 \times 10^{-11} \text{ J}^a$	Atkinson <i>et al.</i> ³⁹
	$(2.54 \pm 0.50) \times 10^{-16}$	298 ± 1	RR [relative to $k(\text{ethene})$ $= 2.05 \times 10^{-16} \text{ J}^a$	Atkinson <i>et al.</i> ³⁹
	$(2.36 \pm 0.43) \times 10^{-16}$	298 ± 1	RR [relative to $k(n\text{-heptane})$ $= 1.37 \times 10^{-16} \text{ J}^a$	Atkinson <i>et al.</i> ⁶³
<i>p</i> -Xylene	$(4.53 \pm 0.33) \times 10^{-16}$	298 ± 1	RR [relative to $k(n\text{-heptane})$ $= 1.37 \times 10^{-16} \text{ J}^a$	Atkinson <i>et al.</i> ⁶³

TABLE 12. Rate constants k for the gas-phase reactions of the NO_3 radical with aromatic compounds, which are independent of the NO_3 concentration — Continued

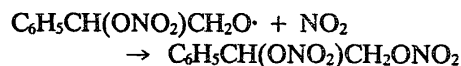
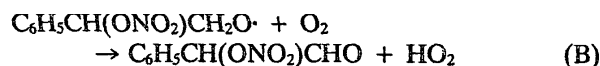
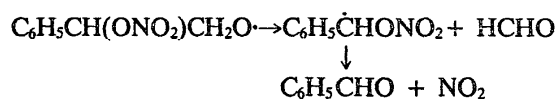
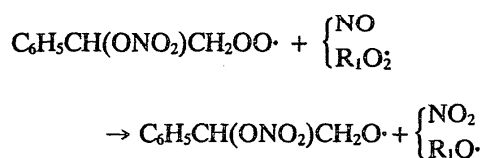
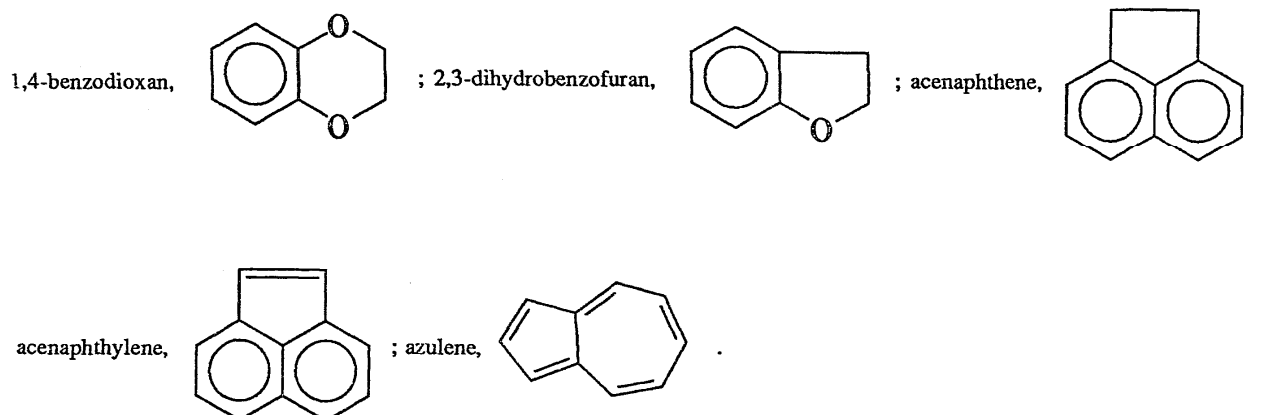
Aromatic	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference
1,3,3-Trimethylbenzene	$(1.86 \pm 0.22) \times 10^{-15}$	294	RR [relative to $k(n\text{-heptane}) = 1.37 \times 10^{-16} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁶³
1,2,4-Trimethylbenzene	$(1.81 \pm 0.21) \times 10^{-15}$	294	RR [relative to $k(n\text{-heptane}) = 1.37 \times 10^{-16} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁶³
1,3,5-Trimethylbenzene	$(8.00 \pm 0.62) \times 10^{-16}$	298 ± 1	RR [relative to $k(n\text{-heptane}) = 1.37 \times 10^{-16} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁶³
1-Methyl-4-isopropylbenzene (<i>p</i> -cymene)	$(1.00 \pm 0.07) \times 10^{-15}$	295 ± 2	RR [relative to $k(2,3\text{-dimethylbutane}) = 4.08 \times 10^{-16} \text{ s}^{-1}$]	Corchnoy and Atkinson ⁷⁷
Benzaldehyde [$\text{C}_6\text{H}_5\text{CHO}$]	$\leq 9.6 \times 10^{-15}$	300 ± 1	RR [relative to $k(\text{propene}) = 9.45 \times 10^{-15} \text{ s}^{-1}$]	Carter <i>et al.</i> ⁴²
	$(2.55 \pm 0.08) \times 10^{-15}$	294	RR [relative to $k(\text{propene}) = 9.45 \times 10^{-15} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁶³
Methoxybenzene [$\text{C}_6\text{H}_5\text{OCH}_3$]	$\leq 4.8 \times 10^{-15}$	300 ± 1	RR [relative to $k(\text{propene}) = 9.45 \times 10^{-15} \text{ s}^{-1}$]	Carter <i>et al.</i> ⁴²
	$(9.45 \pm 4.73) \times 10^{-17}$	294	RR [relative to $k(\text{propene}) = 9.45 \times 10^{-15} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁶³
	$(2.10 \pm 0.18) \times 10^{-16}$	294	RR [relative to $k(n\text{-heptane}) = 1.37 \times 10^{-16} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁶³
Phenol [$\text{C}_6\text{H}_5\text{OH}$]	$(2.59 \pm 0.52) \times 10^{-12}$	300 ± 1	RR [relative to $k(\text{cis-2-butene}) = 3.50 \times 10^{-13} \text{ s}^{-1}$]	Carter <i>et al.</i> ⁴²
	$(3.64 \pm 0.14) \times 10^{-12}$	294	RR [relative to $k(2\text{-methyl-2-butene}) = 9.37 \times 10^{-12} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁶³
	$(5.89 \pm 0.64) \times 10^{-12}$	298 ± 1	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5) = 3.41 \times 10^{-11} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁶³
<i>o</i> -Cresol	$(1.39 \pm 0.24) \times 10^{-11}$	300 ± 1	RR [relative to $k(2\text{-methyl-2-butene}) = 9.37 \times 10^{-12} \text{ s}^{-1}$]	Carter <i>et al.</i> ⁴²
	$(1.56 \pm 0.17) \times 10^{-11}$	298 ± 1	RR [relative to $k(m\text{-cresol}) = 1.20 \times 10^{-11} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁶³
<i>m</i> -Cresol	$(8.10 \pm 1.16) \times 10^{-12}$	300 ± 1	RR [relative to $k(2\text{-methyl-2-butene}) = 9.37 \times 10^{-12} \text{ s}^{-1}$]	Carter <i>et al.</i> ⁴²
	$(1.59 \pm 0.17) \times 10^{-11}$	298 ± 1	RR [relative to $k(\text{phenol}) = 3.64 \times 10^{-12} \text{ s}^{-1}$]	Atkinson <i>et al.</i> ⁶³

TABLE 12. Rate constants k for the gas-phase reactions of the NO_3 radical with aromatic compounds, which are independent of the NO_2 concentration - Continued

Aromatic	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
	$\sim 1.6 \times 10^{-11}$	298 ± 1	RR [relative to $K_3(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 3.41 \times 10^{-11}]^a$	Atkinson <i>et al.</i> ⁶³
<i>p</i> -Cresol	$(1.50 \pm 0.24) \times 10^{-11}$	300 ± 1	RR [relative to k (2-methyl-2-butene) $= 9.37 \times 10^{-12}]^a$	Carter <i>et al.</i> ⁴²
	$(1.66 \pm 0.18) \times 10^{-11}$	298 ± 1	RR [relative to k (<i>m</i> -cresol) $= 1.20 \times 10^{-11}]^a$	Atkinson <i>et al.</i> ⁶³
Styrene [$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$]	$(1.51 \pm 0.04) \times 10^{-13}$	296 ± 2	RR [relative to k (<i>trans</i> -2-butene) $= 3.89 \times 10^{-13}]^a$	Atkinson and Aschmann ⁶
Benzyl chloride [$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$]	$< 5.7 \times 10^{-16}$	298 ± 2	RR [relative to k (propene) $= 9.45 \times 10^{-15}]^a$	Atkinson <i>et al.</i> ¹¹⁹
<i>p</i> -Dichlorobenzene	$< 3.4 \times 10^{-17}$	298 ± 2	RR [relative to k (cyclohexane) $= 1.35 \times 10^{-16}]^a$	Atkinson <i>et al.</i> ¹²⁵
Tetralin (1,2,3,4-tetrahydro- naphthalene)	$(1.11 \pm 0.23) \times 10^{-14}$	298 ± 2	RR [relative to k (propene) $= 9.45 \times 10^{-15}]^a$	Atkinson <i>et al.</i> ¹¹⁹
	$(8.64 \pm 0.59) \times 10^{-15}$	296 ± 2	RR [relative to k (propene) $= 9.45 \times 10^{-15}]^a$	Atkinson and Aschmann ⁶
1,4-Naphthoquinone	$< 9.5 \times 10^{-16}$	298 ± 2	RR [relative to k (propene) $= 9.45 \times 10^{-15}]^a$	Atkinson <i>et al.</i> ¹²³
1,4-Benzodioxan ^c	$(6.0 \pm 3.0) \times 10^{-16}$	298 ± 2	RR [relative to k (propene) $= 9.45 \times 10^{-15}]^a$	Atkinson <i>et al.</i> ¹¹⁹
2,3-Dihydrobenzofuran ^c	$(1.15 \pm 0.25) \times 10^{-13}$	298 ± 2	RR [relative to k (<i>trans</i> -2-butene) $= 3.90 \times 10^{-13}]^a$	Atkinson <i>et al.</i> ¹¹⁹
Azulene ^c	$(3.89 \pm 0.27) \times 10^{-10}$	298 ± 2	RR [relative to k (2,3-dimethyl-2-butene) $= 5.72 \times 10^{-11}]^a$	Atkinson <i>et al.</i> ¹²⁶
Acenaphthene ^c	$(4.59 \pm 2.45) \times 10^{-13}$	296 ± 2	RR [relative to k (<i>trans</i> -2-butene) $= 3.89 \times 10^{-13}]^a$	Atkinson and Aschmann ⁶
Acenaphthylene ^c	$(5.45 \pm 0.47) \times 10^{-12}$	296 ± 2	RR [relative to k (<i>trans</i> -2-butene) $= 3.89 \times 10^{-13}]^a$	Atkinson and Aschmann ⁶
1-Nitronaphthalene	$\leq 7.2 \times 10^{-15}$	298 ± 2	RR [relative to k (propene) $= 9.45 \times 10^{-15}]^a$	Atkinson <i>et al.</i> ¹²³
2-Nitronaphthalene	$\leq 7.3 \times 10^{-15}$	298 ± 2	RR [relative to k (propene) $= 9.45 \times 10^{-15}]^a$	Atkinson <i>et al.</i> ¹²³

TABLE 12. Rate constants k for the gas-phase reactions of the NO_3 radical with aromatic compounds, which are independent of the NO_2 concentration — Continued

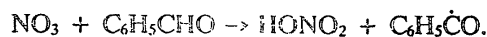
Aromatic	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference
2-Methyl-1-nitro-naphthalene	$(1.13 \pm 0.57) \times 10^{-14}$	298 ± 2	RR [relative to $k(\text{propene}) = 9.45 \times 10^{-15}$] ^a	Arey <i>et al.</i> ¹²⁴

^a From present recommendations (see text).^b From Table 1.^c Structures:

and similarly for the $\text{C}_6\text{H}_5\dot{\text{C}}\text{HCH}_2\text{ONO}_2$ radical. From a product study of this reaction utilizing FT-IR absorption spectroscopy, Atkinson *et al.*¹²⁵ observed that formaldehyde and benzaldehyde were formed in small yield (~10–12% each). Three major products were observed,¹²⁵ one being a thermally labile species with $-\text{ONO}_2$ and $-\text{OONO}_2$ groups [product (A) or its isomer] and two more stable products having $-\text{ONO}_2$ and $>\text{C}=\text{O}$ groups [product (B) and its isomer]. Similarly, the reaction of the NO_3 radical with azulene, which has a room temperature rate constant approaching the gas-kinetic collision frequency,¹²⁶ must proceed by addition.

For the monocyclic aromatic compounds with substituent groups not containing a $>\text{C}=\text{C}<$ bond, such as

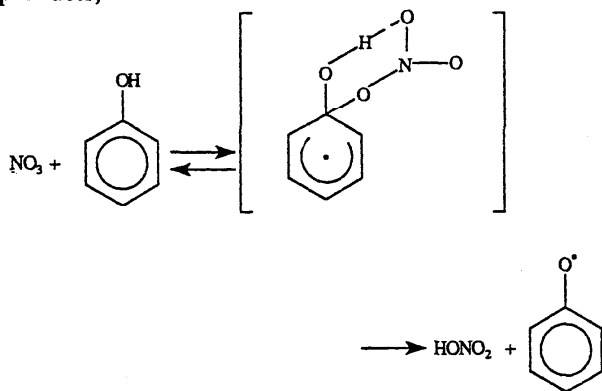
toluene, the xylenes, the trimethylbenzenes, *p*-cymene, benzaldehyde, methoxybenzene, phenol, the cresols, tetralin, 1,4-benzodioxan and 2,3-dihydrobenzofuran (and acenaphthene), the kinetic data indicate that the NO_3 radical reactions proceed by H-atom abstraction. Thus, the kinetic data of Atkinson and Aschmann⁶⁹ for the reactions of the NO_3 radical with toluene-*h*₈, toluene-*d*₃ ($\text{C}_6\text{H}_5\text{CD}_3$) and toluene-*d*₈ show that the rate-determining step involves H (or D) atom abstraction from the $-\text{CH}_3$ (or $-\text{CD}_3$) substituent group. Also, analogous to the reactions of the OH radical with acetaldehyde and benzaldehyde (which proceed by H-atom abstraction from the $-\text{CHO}$ group),⁸⁷ the NO_3 radical reaction rate constant for benzaldehyde is essentially identical to that for acetaldehyde, strongly suggesting that the reaction of the NO_3 radical with benzaldehyde proceeds by H-atom abstraction from the $-\text{CHO}$ group



Furthermore, the rate constants for the reactions of the NO_3 radical with the xylene, trimethylbenzene and cresol isomers do not exhibit the substituent pattern expected for electrophilic addition to the aromatic ring and observed for the corresponding OH radical reactions,⁸⁷ in which the 1,3- and 1,3,5- substituent distributions have significantly higher rate constants than do the 1,2-, 1,4-, 1,2,3- and 1,2,4- substituent distributions.⁸⁷ Rather, for the NO_3 radical reactions the inverse is observed (Table 12), with the 1,3- and 1,3,5- substituent group distributions having the lowest rate constants.

The conclusion that these NO_3 radical reactions proceed by overall H-atom abstraction from the substituent group(s) is supported by the observations of Sabljic and Gsten⁸⁸ that benzaldehyde, phenol and the cresols do not obey the same correlation between the room temperature NO_3 radical reaction rate constants and the vertical ionization energies as do the other aromatic compounds, but rather fall on a separate correlation together with alkanes, alkenes, haloalkenes, aldehydes, ethers, thiols and thioethers.⁸⁸

However, comparison of the room temperature rate constants for H-atom abstraction from the methyl-substituted benzenes, phenol, the cresols and methoxybenzene by the OH radical⁸⁷ with the corresponding NO_3 radical reaction rate constants (Table 12) shows that the NO_3 radical reaction rate constants are significantly higher than expected from the correlation shown in Fig. 2. Thus, for example, based on the H-atom abstraction rate constants for the OH radical reactions with the methyl-substituted benzenes and phenol,⁸⁷ the H-atom abstraction rate constants for the reactions of the NO_3 radical with toluene, the xylenes and the trimethylbenzenes are predicted to be $\sim 7 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ per $-\text{CH}_3$ group at 298 K, and that for phenol $\sim 1.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, much lower than observed. In particular, the room temperature rate constants for the NO_3 radical reactions with phenol and the cresols are 4–5 orders of magnitude higher than expected on the basis of a direct H-atom abstraction reaction,^{42,119} suggesting that these reactions proceed by initial addition of the NO_3 radical to the aromatic ring, followed by rapid decomposition back to reactants or to the H-atom abstraction products,



with the addition adduct possibly involving a six-membered transition state.^{42,119}

Further evidence for this reaction scheme arises from a comparison of the rate constants for the reactions of phenol and methoxybenzene with OH and NO_3 radicals. Thus, for the OH radical reactions with phenol and methoxybenzene, the room temperature rate constants for OH radical addition to the aromatic ring are similar, as are the rate constants at $\sim 400 \text{ K}$ for H-atom abstraction from the $-\text{OH}$ or $-\text{OCH}_3$ substituent groups.⁸⁷ The OH radical addition reaction rate data indicate that the $-\text{OH}$ and $-\text{OCH}_3$ groups have equivalent activating effects on the aromatic ring, as expected from their similar

electrophilic substituent constants,¹²⁹ while the H-atom abstraction rate data⁸⁷ indicate that the X—H bond dissociation energies in the $-\text{OH}$ and $-\text{OCH}_3$ groups are also similar. Hence it may be expected that the NO_3 radical reaction rate constants for phenol and methoxybenzene should be reasonably similar. However, this is not the case, with the room temperature rate constant for the reaction of the NO_3 radical with phenol being 4 orders of magnitude higher than that for reaction with methoxybenzene.

The conclusion that a six-membered transition state greatly facilitates the overall H-atom abstraction process during these NO_3 radical reactions then explains the lower room temperature rate constants observed for methoxybenzene and, to a lesser extent, 1,4-benzodioxan.^{42,119}

2.12.c. NO_3 Radical Reaction with the Aromatic Rings (Kinetically Equivalent to Reaction with N_2O_5)

The available rate coefficient data are given in Table 13. The majority of these data concern naphthalene and the methyl-substituted naphthalenes.

(1) Naphthalene and Naphthalene-*d*₈

The available rate coefficient data of Pitts *et al.*,⁷³ Atkinson *et al.*,^{68,77,104} and Atkinson and Aschmann⁶⁹ are given in Table 13 and those of Atkinson *et al.*,^{68,104} and Atkinson and Aschmann⁶⁹ for naphthalene are plotted in Arrhenius form in Fig. 13. In the most recent temperature-dependent study of Atkinson *et al.*,¹⁰⁴ rate coefficients k_{obs} for naphthalene were obtained relative to the rate constant for the reaction of the NO_3 radical with thiophene and also relative to the equilibrium constant K_5 . The rate coefficients k_{obs} were determined relative to K_5 from the measured naphthalene and N_2O_5 time-concentration profiles, with

$$-\frac{d \ln[\text{naphthalene}]}{dt} = k_{\text{obs}}[\text{N}_2\text{O}_5]/K_5$$

As seen from Table 13, the rate coefficients determined relative to the equilibrium constant K_5 and to the rate constant for the reaction of the NO_3 radical with thiophene are in excellent agreement. However, since the determination of rate coefficients relative to the equilibrium constant K_5 assumed that NO_3 radicals, NO_2 and N_2O_5 were in equilibrium under the experimental conditions employed (which was not the original intent of these experiments¹⁰⁴), the rate coefficients determined relative to the rate constant for the reaction of the NO_3 radical with thiophene are preferred, and only these rate coefficients from the study of Atkinson *et al.*¹⁰⁴ are plotted in Fig. 13.

Atkinson *et al.*¹⁰⁴ carried out further experiments at 272 K and at total pressures of ~ 65 and 740 Torr (the lifetime of N_2O_5 due to thermal decomposition being 10–17 mins under these conditions²²) in which 2,3-dimethyl-2-butene was added to scavenge NO_3 radicals. Despite

TABLE 13. Rate constants $k_{\text{obs}} = k k_a/k_b$ for the gas-phase reactions of the NO_3 radical with the aromatic rings of aromatic compounds (kinetically equivalent to reaction with N_2O_5)

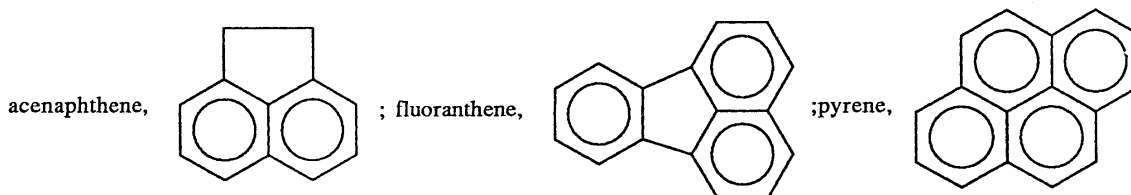
Aromatic	$k_{\text{obs}} = k k_a/k_b$ ($\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference
Biphenyl	$< 5 \times 10^{-30}$	298 ± 2	RR [relative to $k_{\text{obs}}(\text{naphthalene}) = 3.6 \times 10^{-28}]^a$	Atkinson <i>et al.</i> ⁶⁸
Naphthalene	$\sim (7-10) \times 10^{-28}$	298 ± 2	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5) = 3.41 \times 10^{-11}]^a$	Pitts <i>et al.</i> ⁷³
	$(4.77 \pm 0.69) \times 10^{-28}$	298 ± 2	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5) = 3.41 \times 10^{-11}]^a$	Atkinson <i>et al.</i> ⁶⁸
	3.31×10^{-28}	296 ± 2	RR [relative to $k(\text{propene}) = 9.45 \times 10^{-15}]^a$	Atkinson and Aschmann ⁶⁹
	$(1.28 \pm 0.20) \times 10^{-27}$	272.0 ± 0.6	RR [relative to $k(\text{thiophene}) = 3.93 \times 10^{-14}]^a$	Atkinson <i>et al.</i> ¹⁰⁴
	$(1.10 \pm 0.27) \times 10^{-27}$	275.2 ± 0.6		
	$(1.32 \pm 0.25) \times 10^{-27}$	275.2 ± 0.6		
	$(6.96 \pm 1.73) \times 10^{-28}$	281.9 ± 0.6		
	$(5.31 \pm 1.18) \times 10^{-28}$	289.1 ± 0.6		
	$(3.64 \pm 1.11) \times 10^{-28}$	296.3 ± 0.6		
	$(3.66 \pm 1.26) \times 10^{-28}$	296.9 ± 0.6		
	$(1.38 \pm 0.04) \times 10^{-27}$	272.0 ± 0.6	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5) = 1.26 \times 10^{-27} e^{11275/T}]^a$	Atkinson <i>et al.</i> ¹⁰⁴
	$(1.26 \pm 0.04) \times 10^{-27}$	275.2 ± 0.6		
	$(8.84 \pm 0.32) \times 10^{-28}$	275.2 ± 0.6		
	$(8.95 \pm 0.39) \times 10^{-28}$	281.9 ± 0.6		
	$(7.13 \pm 0.21) \times 10^{-28}$	289.1 ± 0.6		
	$(4.18 \pm 0.17) \times 10^{-28}$	296.3 ± 0.6		
	$(4.23 \pm 0.12) \times 10^{-28}$	296.9 ± 0.6		
Naphthalene- d_8	$(4.76 \pm 0.39) \times 10^{-28}$	296 ± 2	RR [relative to $k_{\text{obs}}(\text{naphthalene}) = 3.9 \times 10^{-28}]^a$	Atkinson <i>et al.</i> ⁷⁷
1-Methylnaphthalene	$(8.39 \pm 1.01) \times 10^{-28}$	298 ± 2	RR [relative to $k_{\text{obs}}(\text{naphthalene}) = 3.6 \times 10^{-28}]^a$	Atkinson and Aschmann ¹²⁰
	7.00×10^{-28}	296 ± 2	RR [relative to $k(\text{trans-2-butene}) = 3.89 \times 10^{-13}]^a$	Atkinson and Aschmann ⁶⁹
2-Methylnaphthalene	$(1.07 \pm 0.16) \times 10^{-27}$	298 ± 2	RR [relative to $k_{\text{obs}}(\text{naphthalene}) = 3.6 \times 10^{-28}]^a$	Atkinson and Aschmann ¹²⁰
	1.09×10^{-27}	296 ± 2	RR [relative to $k(\text{propene}) = 9.45 \times 10^{-15}]^a$	Atkinson and Aschmann ⁶⁹
2,3-Dimethylnaphthalene	$(1.48 \pm 0.44) \times 10^{-27}$	298 ± 2	RR [relative to $k_{\text{obs}}(\text{naphthalene}) = 3.6 \times 10^{-28}]^a$	Atkinson and Aschmann ¹²⁰
	1.61×10^{-27}	296 ± 2	RR [relative to $k(\text{propene}) = 9.45 \times 10^{-15}]^a$	Atkinson and Aschmann ⁶⁹

TABLE 13. Rate constants $k_{\text{obs}} = k k_a/k_b$ for the gas-phase reactions of the NO_3 radical with the aromatic rings of aromatic compounds (kinetic equivalent to reaction with N_2O_5) — Continued

Aromatic	$k_{\text{obs}} = k k_a/k_b$ ($\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$)	at T (K)	Technique	Reference
Acenaphthene ^b	$(1.65 \pm 0.38) \times 10^{-27}$	296 ± 2	RR [relative to $k(\text{trans-2-butene}) = 3.89 \times 10^{-13}]^a$	Atkinson and Aschmann
1-Nitronaphthalene	$(3.02 \pm 1.42) \times 10^{-29}$	298 ± 2	RR [relative to $k(\text{propene}) = 9.45 \times 10^{-15}]^a$	Atkinson <i>et al.</i> ¹²³
2-Nitronaphthalene	$(2.74 \pm 1.14) \times 10^{-29}$	298 ± 2	RR [relative to $k(\text{propene}) = 9.45 \times 10^{-15}]^a$	Atkinson <i>et al.</i> ¹²³
1,4-Naphthoquinone	$< 8.5 \times 10^{-30}$	298 ± 2	RR [relative to $k(\text{propene}) = 9.45 \times 10^{-15}]^a$	Atkinson <i>et al.</i> ¹²³
2-Methyl-1-nitronaphthalene	$(2.74 \pm 1.80) \times 10^{-29}$	298 ± 2	RR [relative to $k(\text{propene}) = 9.45 \times 10^{-15}]^a$	Arey <i>et al.</i> ¹²⁴
Fluoranthene ^b	$(5.1^{+5.1}_{-2.6}) \times 10^{-28}$	296 ± 2	RR [relative to $k_{\text{obs}}(\text{naphthalene}) = 3.9 \times 10^{-28}]^a$	Atkinson <i>et al.</i> ⁷⁷
Pyrene ^b	$(1.6^{+1.6}_{-0.8}) \times 10^{-27}$	296 ± 2	RR [relative to $k_{\text{obs}}(\text{naphthalene}) = 3.9 \times 10^{-28}]^a$	Atkinson <i>et al.</i> ⁷⁷

^a From present recommendations (see text).

^b Structures:



the observed (and expected) presence of N_2O_5 in these experiments, no reaction of naphthalene (or of the thiophene reference organic) was observed, showing conclusively that the reaction of naphthalene in N_2O_5 - NO_3 - NO_2 - air mixtures is with the NO_3 radical and not with N_2O_5 .¹⁰⁴

The approximate rate coefficient derived by Pitts *et al.*⁷³ from a fit of the naphthalene and N_2O_5 time-concentration data from a single experiment to the predictions of a six-step reaction scheme is a factor of 2–3 higher than the more recent and accurate rate coefficient data,^{68,69,104} and is not used in the evaluation. The room temperature rate coefficients of Atkinson *et al.*^{68,104} and Atkinson and Aschmann⁶⁹ are in good agreement, and a unit-weighted least-squares analysis of these rate coefficients of Atkinson *et al.*^{68,104} and Atkinson and

Aschmann,⁶⁹ using the Arrhenius expression, yields a recommendation of

$$k_{\text{obs}}(\text{naphthalene}) = (3.9^{+69.9}_{-3.7}) \times 10^{-34} e^{(4090 \pm 840)/T} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

over the temperature range 272–298 K, where the indicated errors are the two least-squares standard deviations, and

$$k_{\text{obs}}(\text{naphthalene}) = 3.6 \times 10^{-28} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty of a factor of 1.5 at 298 K. The kinetic data of Atkinson *et al.*⁷⁷ yield a rate coefficient k_{obs} for naphthalene- d_8 20 ± 1 higher than that for naphthalene- h_8 , showing that

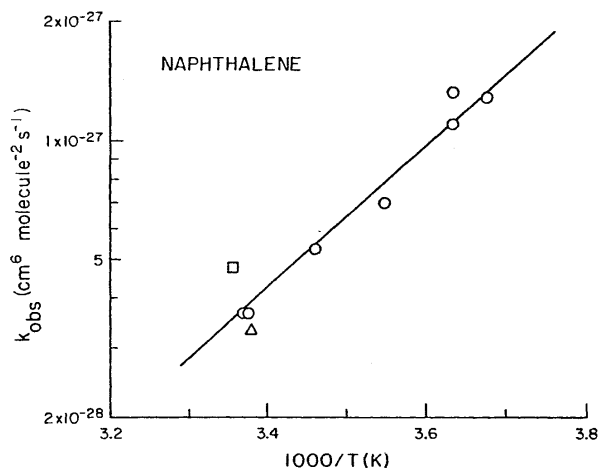


FIG 13. Arrhenius plot of rate coefficients k_{obs} for the gas-phase reaction of naphthalene in $\text{NO}_3\text{-NO}_2\text{-air}$ mixtures. (\square) Atkinson *et al.*;⁶⁸ (\triangle) Atkinson and Aschmann;⁶⁹ (\circ) Atkinson *et al.*,¹⁰⁴ relative to rate constant for reaction of the NO_3 radical with thiophene; (—) recommendation, see text.

deuterium isotope effect is small, consistent with an addition reaction being the rate-determining step.

(2) 1-Methylnaphthalene, 2-Methylnaphthalene and 2,3-Dimethylnaphthalene

The available rate coefficients of Atkinson and Aschmann,^{69,120} determined relative to the rate constant for the reaction of the NO_3 radical with propene or *trans*-2-butene⁶⁹ and to the rate coefficient k_{obs} for naphthalene,¹²⁰ are given in Table 13. These rate coefficients are in good agreement for all three methyl-substituted naphthalenes, and unit-weighted averages of these data^{69,120} lead to the recommendations of

$$k_{\text{obs}}(\text{1-methylnaphthalene}) = 7.7 \times 10^{-28} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1},$$

$$k_{\text{obs}}(\text{2-methylnaphthalene}) = 1.08 \times 10^{-27} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1},$$

and

$$k_{\text{obs}}(\text{2,3-dimethylnaphthalene}) = 1.55 \times 10^{-27} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1},$$

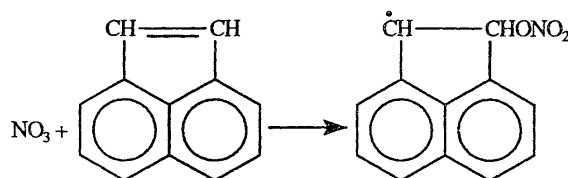
all at 298 K and with estimated overall uncertainties of a factor of 2.

(3) Other Aromatic Compounds

For the remaining aromatic compounds for which data are available (Table 13), only single experimental studies have been carried out, and hence no recommendations are made. It is of interest to note, however, that the room temperature rate coefficient for acenaphthene is similar to that for 2,3-dimethylnaphthalene, suggesting that the cyclopenta-fused ring in acenaphthene acts like two

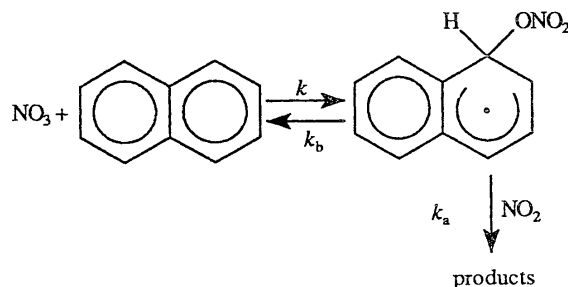
methyl-substituent groups. As discussed above, acenaphthene reacts in $\text{NO}_3\text{-NO}_2\text{-N}_2\text{O}_5\text{-air}$ mixtures by two reaction pathways, involving H-atom abstraction from the two $\text{-CH}_2\text{-}$ groups of the cyclopenta-fused ring together with NO_3 radical addition to the two fused six-member aromatic rings.^{69,76}

In the case of acenaphthylene, the reaction pathway involving NO_3 radical addition to the $>\text{C}=\text{C}<$ bond of the cyclopenta-fused ring



totally dominated over that involving NO_3 radical addition to the fused six-member aromatic rings under the experimental conditions employed in the kinetic and product studies of Atkinson and Aschmann⁶⁹ and Arey *et al.*⁷⁶

The rate coefficients k_{obs} given in Table 13 and evaluated above are the combination of three elementary rate constants. For example, for naphthalene,



with $k_{\text{obs}} = k k_a/k_b$.

As discussed by Atkinson *et al.*,¹⁰⁴ the reasonableness of the temperature-dependent expression for k_{obs} recommended above for naphthalene can be assessed by deriving the rate constant k_b from the above expression and comparing it with the rate constant estimated from thermochemical considerations⁹⁸ and the known decomposition rates of the analogous OH-aromatic adducts.⁸⁷

The rate constant k_b can be derived from the above expression for $k_{\text{obs}}(\text{naphthalene})$ of

$$k_{\text{obs}}(\text{naphthalene}) = k k_a/k_b = 3.9 \times 10^{-34} e^{10900/T} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

if the rate constants k and k_a can be estimated. Assuming that the rate constants k and k_a are similar to those for the addition of the OH radical to naphthalene ($2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K⁸⁷) and for reaction of the hydroxycyclohexadienyl radical with NO_2 ($\sim 2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K^{130,131}), respectively, the recommended expression for k_{obs} yields

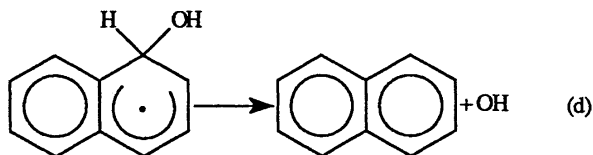
$$k_b \sim 1 \times 10^6 \text{ s}^{-1} \text{ at } 298 \text{ K},$$

and, assuming that k and k_a are independent of temperature,

$$k_b \sim 1 \times 10^{12} e^{-4090/T} \text{ s}^{-1},$$

with the pre-exponential factor being uncertain by ~ 2 orders of magnitude.

The rate constant k_b can also be estimated from the rate constant k_d for the analogous decomposition of the OH-naphthalene adduct



and the thermochemistries of reactions (b) and (d). Assuming that the resonance stabilization energies of the NO_3 -aromatic adducts are identical to those for the OH-aromatic adducts, then the NO_3 -aromatic adducts are $10.9 \text{ kcal mol}^{-1}$ less stable towards thermal decomposition than are the OH-aromatic adducts.⁹⁸ Based upon the thermal decomposition data of Wahner and Zetzsch¹³² and Witte *et al.*¹³³ for the hydroxycyclohexadienyl radical, Atkinson⁸⁷ recommended a thermal decomposition rate expression of

$$k_d(\text{hydroxycyclohexadienyl}) = 9.4 \times 10^{12} e^{-8540/T} \text{ s}^{-1}.$$

Since Lorenz and Zellner¹³⁴ observed that the OH-naphthalene adduct is thermally more stable than the hydroxycyclohexadienyl radical by $3.8 \text{ kcal mol}^{-1}$ (assuming an identical pre-exponential factor), then the decomposition rate of the OH-naphthalene adduct becomes

$$k_d = 9.4 \times 10^{12} e^{-10500/T} \text{ s}^{-1}.$$

The rate constant for thermal decomposition of the NO_3 -naphthalene adduct is then

$$k_b = 9.4 \times 10^{12} e^{-5000/T} \text{ s}^{-1}$$

and

$$k_b = 5 \times 10^5 \text{ s}^{-1} \text{ at } 298 \text{ K}.$$

The value of $k_b = 5 \times 10^5 \text{ s}^{-1}$ at 298 K calculated in this manner is in good agreement with that of $k_b \sim 1 \times 10^6 \text{ s}^{-1}$ derived from the recommended expression for k_{obs} (naphthalene), and the differences in the preexponential factors and the activation energies are well within the estimation uncertainties. The decomposition rate constant for the NO_3 -naphthalene adduct of

$$k_b \sim 3 \times 10^{12} e^{-4550/T} \text{ s}^{-1},$$

with

$$k_b \sim 7 \times 10^5 \text{ s}^{-1} \text{ at } 298 \text{ K},$$

is in accord with the requirements that reactions k and k_b

are in equilibrium¹⁰⁴ and that $k_b \gg k_a[\text{NO}_2]$ at 298 K for NO_2 concentrations $\leq 1.2 \times 10^{15} \text{ molecule cm}^{-3}$.⁶⁹

The observation of Lorenz and Zellner¹³⁴ that the OH-naphthalene adduct is more stable towards thermal decomposition than the OH-benzene adduct by $3.8 \text{ kcal mol}^{-1}$ suggests that the NO_3 -naphthalene adduct may also be correspondingly more stable towards thermal decomposition than the NO_3 -benzene adduct. If so, the rate constant for thermal decomposition of the NO_3 -benzene adduct is $\sim 3 \times 10^{12} e^{-2600/T} \text{ s}^{-1}$ ($\sim 5 \times 10^8 \text{ s}^{-1}$ at 298 K). This 10^3 faster thermal decomposition rate for the NO_3 -monocyclic aromatic hydrocarbon adducts compared to those for the NO_3 -fused-ring polycyclic aromatic hydrocarbon adducts is consistent with the observed lack of reaction of benzene or biphenyl in N_2O_5 - NO_3 - NO_2 -air mixtures^{38,39,63,68,135} (see also Tables 12 and 13).

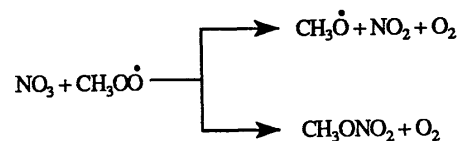
Finally, in order to fit the observed kinetic data, the NO_3 -naphthalene adduct must react exclusively with NO_2 .¹⁰⁴ Significantly, this conclusion that the NO_3 -naphthalene adduct reacts exclusively with NO_2 , and does not react at a significant rate with O_2 ,¹⁰⁴ is consistent with recent product data^{68,136} which show that the OH-benzene, OH-toluene, OH-biphenyl and OH-naphthalene adducts react with NO_2 , and not with O_2 , under conditions where the NO_2 concentrations are $\geq 1.5 \times 10^{13} \text{ molecule cm}^{-3}$.

At present, the reaction mechanisms subsequent to the initial addition of the NO_3 radical to the fused six-membered aromatic rings are not known, apart from the necessity that the nitratocyclohexadienyl-type radicals formed must react exclusively with NO_2 under the experimental conditions employed to date. It is, however, known that nitro-products are formed from these NO_3 radical-initiated reactions,^{68,73,75-77,118,122,123} and the available product data are given in Table 14. Clearly, the nitroarene products observed and quantified account for only a small fraction of the overall reaction products of these NO_3 radical-initiated reactions which proceed by initial addition of the NO_3 radical to the fused six-membered aromatic rings.

2.13. Organic Radicals

2.13.a. Kinetics and Mechanisms

The only rate data available for the reactions of the NO_3 radical with organic radicals concern the methylperoxy ($\text{CH}_3\text{OO}\cdot$) radical, and the rate constant determined by Crowley *et al.*¹³⁷ is given in Table 15. The products of this reaction are not known, although the pathways



are among those possible.¹³⁷

2.14. ADDENDUM

Since the revision of this paper in mid-1990 and the end of 1990, further kinetic and product data have become available¹³⁹⁻¹⁴². These data are briefly discussed by the same compound classes as in the text. The individual references should be consulted for details.

2.14.a. Alkanes

Rate constants for the reactions of the NO₃ radical with ethane, *n*-butane, 2-methylpropane and 2-methylbutane have been determined by Bagley *et al.*¹³⁹ as a function of temperature using a discharge flow system with optical absorption detection of the NO₃ radical. The 298 K rate constants (in units of 10⁻¹⁶ cm³ molecule⁻¹s⁻¹) were: *n*-butane, 0.45 ± 0.06; 2-methylpropane, 1.1 ±

0.2; and 2-methylbutane, 1.6 ± 0.2. This rate constant for 2-methylpropane is in excellent agreement with that determined by Atkinson *et al.*⁶². For *n*-butane, the absolute rate constant of Bagley *et al.*¹³⁹ is 30% lower than (but in agreement within the cited error limits with) that of Atkinson *et al.*⁶², but is a factor of 2 higher than the upper limit to the rate constant determined by Wallington *et al.*⁵¹. For ethane, data were obtained over the temperature range 453–553 K, with

$$k(\text{ethane}) = (5.7 \pm 4.0) \times 10^{-12} e^{-(4426 \pm 337)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

For *n*-butane, 2-methylpropane and 2-methylbutane, rate data were obtained over the temperature range 298–523 K, and the group rate constants k^{prim} , k^{sec} and k^{tert} (in cm³ molecule⁻¹ s⁻¹ units) were derived: $k^{\text{prim}} = 2.85 \times$

TABLE 14. Nitroarene product data for the gas-phase NO₃ radical-initiated reactions of polycyclic aromatic hydrocarbons

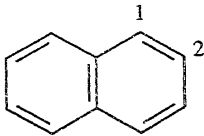
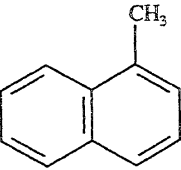
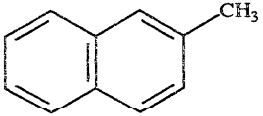
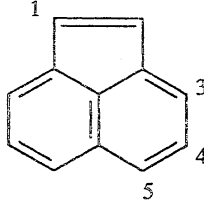
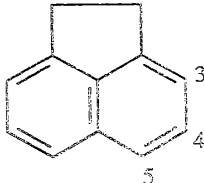
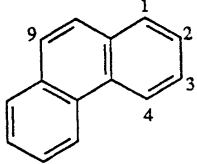
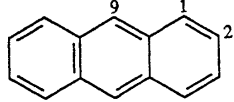
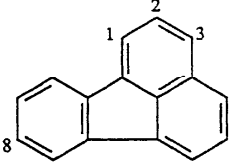
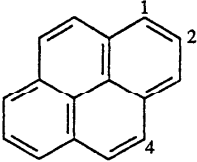
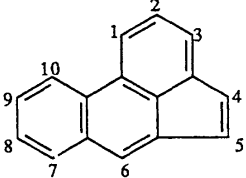
PAH	Structure	Nitroarene Formed (Yield)	References
Naphthalene		1-Nitronaphthalene (17%) 2-Nitronaphthalene (7%)	68,73
1-Methylnaphthalene ^a		1-Methyl-3-nitronaphthalene 1-Methyl-5-nitronaphthalene 1-Methyl-4-nitronaphthalene 1-Methyl-8-nitronaphthalene 1-Methyl-6-nitronaphthalene 1-Methyl-7-nitronaphthalene 1-Methyl-2-nitronaphthalene Total Yield ~30%	122
2-Methylnaphthalene ^a		2-Methyl-4-nitronaphthalene 2-Methyl-1-nitronaphthalene 2-Methyl-5-nitronaphthalene 2-Methyl-8-nitronaphthalene 2-Methyl-3-nitronaphthalene 2-Methyl-7-nitronaphthalene 2-Methyl-6-nitronaphthalene Total Yield ~30%	122
Acenaphthylene		None observed ^b	76
Acenaphthene ^{a,c}		4-Nitroacenaphthene (40%) 3-Nitroacenaphthene (~2%) 5-Nitroacenaphthene (~2%)	76

TABLE 14. Nitroarene product data for the gas-phase NO₃ radical-initiated reactions of polycyclic aromatic hydrocarbons — Continued

PAH	Structure	Nitroarene Formed (Yield)	References
Phenanthrene		Four isomers (including 9-nitrophenanthrene) Total Yield <1%	76
Anthracene ^d		1-Nitroanthracene 2-Nitroanthracene Total Yield <2%	76
Fluoranthene		2-Nitrofluoranthene (24%)	75,77
Pyrene ^e		4-Nitropyrene (0.06%)	77
Acephenanthrylene		None observed ^f	121

^a Nitro-isomers listed in approximate order of decreasing yield.

^b Reacts with the NO₃ radical by NO₃ radical addition to the >C=C< bond in the cyclopenta-fused ring.⁶⁹

^c Yields of reaction pathway proceeding by NO₃ radical addition to the fused six-member aromatic rings. Under atmospheric conditions the pathway involving H-atom abstraction from the -CH₂- groups of the cyclopenta-fused ring will dominate and nitroarenes will not be formed in significant yield.⁷⁶

^d 9-Nitroanthracene also observed but attributed to artifact formation during sample collection.⁷⁶

^e 2-Nitropyrene observed with a yield linearly dependent on the NO₂ concentration.⁷⁷ Under atmospheric conditions the 2-nitropyrene yield will be negligible.⁷⁷

^f Expected to react with the NO₃ radical by NO₃ radical addition to the >C=C< bond in the cyclopenta-fused ring.¹²¹

$10^{-12} e^{-4426/T}$, $k_{\text{sec}} = 1.26 \times 10^{-12} e^{-3248/T}$, and $k_{\text{tert}} = 2.3 \times 10^{-12} e^{-2959/T}$, with values at 298 K of 1.0×10^{-18} , 1.3×10^{-17} , and 1.1×10^{-16} , respectively. These group rate constants at 298 K are in good agreement with those discussed in Sec. 2.1.a. (4).

2.14.b. Alkenes

Using a relative rate method, Shorees *et al.*¹⁴⁰ have determined a rate constant at 297 ± 2 K for the reaction of the NO₃ radical with β -phellandrene of $(7.96 \pm 0.44) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Hjorth *et al.*¹⁴¹ have carried out a product study at 295 ± 2 K and 740 \pm 5 Torr total pressure of air for the reactions of the NO₃ radical with a series of alkenes. The following molar carbonyl yields were reported: from propene, HCHO and CH₃CHO, 0.10 \pm

0.05 each; from 2-methylpropene, HCHO and CH₃COCH₃, 0.24 \pm 0.08 each; from *cis*- and *trans*-2-butene, CH₃CHO, 0.34 \pm 0.12; from 2-methyl-2-butene, CH₃CHO and CH₃COCH₃, 0.22 \pm 0.06 each; and from 2,3-dimethyl-2-butene, CH₃COCH₃, 1.04 \pm 0.26. 3-Nitro-2-butanone and 3-nitro-2-butanol were also observed from the 2-butenes, with molar yields of 0.41 \pm 0.13 and 0.15 \pm 0.05, respectively. While the carbonyl product yields for propene¹⁴¹ are in good agreement with previous studies^{66,74}, the carbonyl product yields from 2-methylpropene and *trans*-2-butene are significantly lower than reported by Barnes *et al.*⁶⁶

2.14.c. Haloalkenes

Using a discharge flow system with optical absorption of the NO₃ radical and a relative rate method, Wängberg

TABLE 15. Rate constants k for the gas-phase reactions of the NO_3 radical with organic radicals

Organic Radical	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
$\text{CH}_3\text{O}\dot{\text{O}}$	2.3 ± 0.7	298	MP-A	Crowley <i>et al.</i> ¹³⁷

*et al.*¹⁴² obtained rate constants for the reaction of the NO_3 radical with $\text{CH}_3\text{CH}_2\text{CCl}=\text{CH}_2$ of $(1.73 \pm 0.31) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 299 K and $(2.2 \pm 0.6) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 ± 1 K, respectively (the latter reevaluated using the presently recommended value of K_5). A product study at room temperature and atmospheric pressure of air of the NO_3 radical reactions with $\text{CH}_3\text{CH}_2\text{CCl}=\text{CH}_2$, $\text{CH}_3\text{CHClCH}=\text{CH}_2$, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Cl}$ and $\text{CH}_3\text{CH}=\text{CClCH}_3$ was also carried out¹⁴².

3. Conclusions and Atmospheric Implications

A substantial data base concerning the rate constants for the gas-phase reactions of the NO_3 radical with organic compounds is now available, with rate constants having been determined using both absolute and relative rate methods. To date, the majority of these kinetic data have been obtained at room temperature using relative rate techniques utilizing both the reactions of the NO_3 radical with other organic compounds and the equilibrium constant K_5 for the $\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5$ reactions as the reference reaction. However, despite significant uncertainties in the equilibrium constant K_5 , the available data base exhibits generally good agreement and self-consistency. Clearly, further absolute rate data are needed, preferably as a function of temperature, before the NO_3 radical reactions can be viewed as being on as firm a base as are the corresponding OH radical reactions.⁸⁷ As for the reactions of the OH radical with organic compounds,^{85,87} there is a general lack of mechanistic and product data available for the reactions of the NO_3 radical with organic compounds.

From the ambient tropospheric NO_3 radical concentration data presented by Atkinson *et al.*,³² the geometric mean maximum NO_3 radical mixing ratio over continental areas is ~ 35 ppt (with a two standard deviations spread of an order of magnitude). Since for a given 12-hr nighttime period the average NO_3 radical concentration is less (sometimes significantly less^{15,14,16,17}) than the maximum, a 12-hr average nighttime NO_3 radical concentration in the tropospheric boundary layer over continental areas of $\sim 5 \times 10^6 \text{ molecule cm}^{-3}$ (20 ppt) appears reasonable. This 12-hr average nighttime NO_3 radical concentration is ~ 300 higher than the global tropospheric 12-hr average OH radical concentration of $1.5 \times 10^6 \text{ molecule cm}^{-3}$ derived from the atmospheric concentration and emissions data for 1,1,1-trichloroethane (CH_3CCl_3).¹³⁸ Thus, since reaction with the OH radical is a major, if not dominant, daytime chemical loss process for organic compounds in the troposphere,⁸⁰ the rate constants for the NO_3 and OH radical reactions must be in

the ratio $k_{\text{NO}_3}/k_{\text{OH}} > 10^{-3}$ for the NO_3 radical reaction with a given organic compound to be significant as a tropospheric loss process.

The NO_3 radical reactions are then potentially significant as a tropospheric loss process for the thiols and alkyl sulfides, the alkenes other than ethene and the 1-alkenes (hence including the monoterpenes and compounds such as acenaphthylene and acephenanthrylene), the hydroxy-substituted aromatic hydrocarbons, and certain other specific compounds such as styrene, acenaphthene, azulene and dimethyl selenide. In particular, since the daytime NO_3 radical concentrations may approach the daytime OH radical concentrations under certain NO_x concentration conditions (see Sec. 1), those organic compounds for which the NO_3 radical reaction rate constants are comparable to, or exceed, the OH radical reaction rate constants (for example, 2,3-dimethyl-2-butene, α -phellandrene, α -terpinene, terpinolene, pyrrole, azulene, dimethyl selenide, and *o*-, *m*- and *p*-cresol) may undergo significant reaction during daytime hours with the NO_3 radical in addition to reaction with the OH radical and/or O_3 .

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