Rate Constants for Reactions of Inorganic Radicals in Aqueous Solution

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Foreword

The National Standard Reference Data System provides access to the quantitative data of physical science, critically evaluated and compiled for convenience and readily accessible through a variety of distribution channels. The System was established in 1963 by action of the President's Office of Science and Technology and the Federal Council for Science and Technology, and responsibility to administer it was assigned to the National Bureau of Standards.

NSRDS receives advice and planning assistance from a Review Committee of the National Research Council of the National Academy of Sciences-National Academy of Engineering. A number of Advisory Panels, each concerned with a single technical area, meet regularly to examine major portions of the program, assign relative priorities, and identify specific key problems in need of further attention. For selected specific topics, the Advisory Panels sponsor subpanels which make detailed studies of users' needs, the present state of knowledge, and existing data resources as a basis for recommending one or more data compilation activities. This assembly of advisory services contributes greatly to the guidance of NSRDS activities.

The System now includes a complex of data centers and other activities in academic institutions and other laboratories. Components of the NSRDS produce compilations of critically evaluated data, reviews of the state of quantitative knowledge in specialized areas, and computations of useful functions derived from standard reference data. The centers and projects also establish criteria for evaluation and compilation of data and recommend improvements in experimental techniques. They are normally associated with research in the relevant field.

The technical scope of NSRDS is indicated by the categories of projects active or being planned: nuclear properties, atomic and molecular properties, solid state properties, thermodynamic and transport properties, chemical kinetics, and colloid and surface properties.

Reliable data on the properties of matter and materials are a major foundation of scientific and technical progress. Such important activities as basic scientific research, industrial quality control, development of new materials for building and other technologies, measuring and correcting environmental pollution depend on quality reference data. In NSRDS, the Bureau's responsibility to support American science, industry, and commerce is vitally fulfilled.

E. Ambler.

ERNEST AMBLER, *Director*

Preface

This report is one of a series of data publications on radiation chemistry; the aim of the series is to compile, evaluate, and present the numerical results on processes occurring in systems which have been subjected to ionizing radiation. Various kinds of data are important in radiation chemistry. The quantities which were measured first were the observed radiation yields or G values (molecules formed or destroyed per 100 eV). Various indirect methods based on G values have been used to determine yields of transient species and relative rates of reactions. The spectral properties (optical, electron spin resonance) of transients have provided a direct method for their identification, and rates of the very fast reactions of transients which occur in irradiated systems have been measured directly by spectroscopic methods. Conductivity and luminescence methods have also provided a means of measuring properties of transients and their kinetics. Some reactions which occur in irradiated systems have also been studied by other methods, such as photochemistry, electric discharge, ultrasonics, chemical initiation, electron impact, etc. The emphasis in these publications is on the data of radiation chemistry, but where other pertinent data exist, they are included.

The data of radiation chemistry are voluminous; thousands of systems have been investigated. As a result there are certain collections, *e.g.* rate constants of particular types of reactions or certain properties of transients, for which tabulations of the data are considered essential, but for which critical assessment of each value is impossible. On the other hand, certain systems and properties have been studied so extensively that critical examination of these data is desirable and timely. Authors of this series of data publications have been asked to evaluate the extent to which the data can be critically assessed, to describe their criteria for evaluation, and to designate preferred values whenever possible.

Contents

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Rate constants have been compiled for reactions of various transient inorganic radicals produced by radiolysis or photolysis in aqueous solution. Data are included for the carbonate radical, sulfate radical, phosphate radical, nitrate radical and other nitrogen-, sulfur- and selenium-containing radicals, and the halide and pseudohalide radicals Cl_2^-, Br_2^-, I_2^- and $(SCN)_2^-$. The radicals react with other inorganic ions, as well as aliphatic, aromatic and heterocyclic compounds.

Keywords: Aqueous solution; carbonate radical; chemical kinetics; halogen radical anions; nitrate radical; oxyanion radicals; phosphate radical; photolysis; radiolysis; rates; selenium radicals; sulfate radical; thiocyanate radical anion.

Introduction

The radiolysis of water produces short-lived intermediates, hydrated electrons, hydrogen atoms and hydroxyl radicals, which react rapidly with solutes in the water to form other short-lived reaction intermediates (73–0030, 75–0001, 75–0002, 77–0011)[1]. This compilation includes reaction rates for short-lived species derived from a number of inorganic ions, including carbonate, sulfate, sulfite, phosphate, nitrate, thiocyanate, and the halide ions by radiolysis or photolysis. The radicals react by oxidizing a wide variety of solutes in aqueous media, most commonly by electron transfer, but also by hydrogen abstraction, addition, substitution, and disproportionation.

Methods

Carbonate radical. The CO_3^- radical is produced by oxidation of carbonate or bicarbonate ions with OH or SO_4^- radicals,

$$CO_3^{2-} + OH \rightarrow CO_3^- + OH^-$$

$$CO_3^{2-} + SO_4^- \rightarrow CO_3^- + SO_4^{2-}$$

by photoionization of carbonate

$$CO_3^{2-} + h\nu \rightarrow CO_3^- + e_{aq}^-$$

or by photolysis of certain carbonato-metal complexes, e.g.

$$Co(NH_3)_4CO_3^+ + h\nu \rightarrow CO_3^- + Co^{2+} + 4\ NH_3$$

The CO_3^- radical has a broad optical absorption with λ_{max} 600 nm and ϵ_{max} 1880 M^{-1} cm^{-1} (66–0001). The protonation

$$CO_3^- + H^+ \rightleftharpoons CO_3H$$

was suggested to have pK_a 9.6 (73–7109), but it does not result in shifts in the optical (73–7109) or ESR spectra (75–5244).

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[1] Literature references are cited following the tables.

The majority of the rate constants for reactions of CO_3^- or CO_3H were determined by following the decay of these radicals through their optical absorption. The carbonate radical can oxidize certain aromatic and heterocyclic compounds and inorganic ions, probably by direct electron transfer. It can also abstract hydrogen from aliphatic compounds, but this reaction is generally slow. Intermediate or stable products from CO_3^- reactions were identified in only a limited number of cases and the mechanisms are mostly speculative.

Sulfate radical. The SO_4^- radical is produced from peroxodisulfate ions by reaction with e_{aq}^-

$$S_2O_8^{2-} + e_{aq}^- \rightarrow SO_4^- + SO_4^{2-}.$$

Reaction with various other radicals and metal ions can also yield SO_4^-. The other most commonly used method for production of this radical is photolysis of $S_2O_8^{2-}$

$$S_2O_8^{2-} + h\nu \rightarrow 2\ SO_4^-$$

Oxidation of sulfate ions to yield SO_4^- radicals can be also carried out photolytically or radiolytically, but those processes are relatively inefficient and were not used frequently for obtaining rate constants.

The SO_4^- radical has an optical absorption at λ_{max} 450 nm and ϵ_{max} 1100 M^{-1} cm^{-1} (66–0019, 69–0158). This radical may protonate in strongly acidic solutions (67–7274) but no pK_a value has been determined. The rate constants for reactions of SO_4^- were determined in most cases by following the decay of the 450 nm absorption. In some cases, the kinetics of formation of the product radicals was monitored.

This radical is a strong oxidant which can react with many organic and inorganic compounds by direct electron transfer oxidation. The reaction with benzene and most aromatic and heterocyclic compounds involves this mechanism. However, addition to aliphatic double bonds and abstraction from saturated compounds were also shown to take place. The products and mechanism of reaction of this radical were studied in some detail, many of which are summarized under the corresponding reactions in table 2.

Phosphate radical. The PO_4^{2-} radical and its protonated forms are produced from peroxodiphosphate or phosphate ions by the same methods as described for SO_4^-. The acid-base forms and their optical absorption properties can be summarized as follows (78–1075):

	H_2PO_4	HPO_4^-	PO_4^{2-}	
pK_a	5.7	8.9		
λ_{max}	520	510	530	nm
ϵ_{max}	1850	1550	2150	M^{-1} cm^{-1}

The rate constants for reactions of these radicals were determined in most cases by following the decay of their broad absorption in the 500–540 nm region. These radicals can abstract hydrogen from saturated organic compounds, add to olefins, and oxidize many aromatic compounds. H_2PO_4 is somewhat similar to SO_4^- in its reactivity, but HPO_4^- and PO_4^{2-} are less reactive, both in H abstraction reactions and in electron transfer oxidations.

Other sulfur-, nitrogen- and selenium radicals. Various radicals have been produced from sulfite, selenite, nitrite, nitrate, and related anions, by one-electron oxidation or reduction, carried out either radiolytically or photolytically. Some of the details for the production and observation of these radicals are given in tables 3 and 4. Representative examples are:

$$SO_3^{2-} + OH \rightarrow SO_3^- + OH^-$$
$$NO_2^- + OH \rightarrow NO_2 + OH^-$$
$$NO_3^- + e_{aq}^- \rightarrow NO_3^{2-}$$
$$S_2O_6^{2-} + h\nu \rightarrow 2\ SO_3^-$$
$$S_2O_3^{2-} + h\nu \rightarrow S_2O_3^- + e_{aq}^-$$

Only a few rate constants have been reported for these various radicals, most of them are for the radical-radical reaction. The reactions of these radicals with organic and inorganic compounds were studied in only a very limited number of cases so that the rates and mechanisms are largely unknown.

Halide and pseudohalide radicals. Radicals of the type X_2^- can be produced from halides and some pseudohalides. Tables 6 – 9 list the rates for Cl_2^-, Br_2^-, I_2^- and $(SCN)_2^-$, respectively. The radicals are produced by oxidation of the halide ion followed by the complex formation. Oxidation of X^- can be achieved in most cases by reaction with OH

$$X^- + OH \rightarrow X + OH^-$$

although complex and acid-base equilibria are involved, which cause the Cl^- reaction to be efficient only in acid solution (73–1039). Oxidation of Cl^- in neutral and alkaline solutions can be carried out by SO_4^- (e.g. 75–5244).

$$SO_4^- + Cl^- \rightarrow SO_4^{2-} + Cl$$

Photolysis of halides can also result in their oxidation.

The X_2^- radicals are formed in the equilibrium

$$X + X^- \rightleftharpoons X_2^-$$

which is shifted predominantly to the right ($K \cong 10^5\ M^{-1}$) (65–0383, 68–0375, 73–1039). Their reaction kinetics are conveniently studied by observing their intense absorptions near 340 for Cl_2^-, 360 for Br_2^-, 380 for I_2^- and 480 for $(SCN)_2^-$, all of the radicals having ϵ of the order of $10^4\ M^{-1}\ cm^{-1}$.

The reactivities of the X_2 radicals generally decrease in this order: Cl_2^-, Br_2^-, $(SCN)_2^-$, I_2^-. Cl_2^- can abstract hydrogen from aliphatic compounds but the equivalent reactions of the other X_2^- radicals are barely detectible in the pulse experiments. The reaction of Cl_2^- with some unsaturated compounds produces Cl adducts, and presumably the other X_2^- radicals may react in a similar fashion, although little information is available on them. The main reaction of the X_2^- radicals is the one-electron oxidation, which takes place with many aromatic and heterocyclic compounds and with certain inorganic ions. However, X_2^- radicals are weaker oxidants than SO_4^- and H_2PO_4. The latter can oxidize benzene and most of its derivatives, while X_2^- can only oxidize phenols, anilines, and anisoles.

Arrangement of the Tables

Entries in each table have been numbered in order to provide for the assembly of an index. Within the tables reactions of the transient with the same or other transient species are listed first. Next are reactions of inorganic solutes which have been ordered alphabetically by main element; the organic reactants follow in alphabetical order by name. The reaction is given whenever evidence for the nature of the products is available; otherwise, only the reactants are given in column 2.

Rate Constants (k): Most of the second order rate constants are derived from pseudo-first order rates for the decay of the transient or the build-up of a product. The error limits given are those reported in the original papers; lacking such a statement the uncertainty in the rate constant should be assumed to be $\pm 25\%$. Second order rates for reaction of two radicals have usually been derived from measurements of $2k/\epsilon$; the value of ϵ used to calculate $2k$ has been listed in the *Comments* column. Possibilities for error in the determination of ϵ increase the error limits for $2k$, which should be assumed to be $\pm 50\%$, lacking a specific error statement.

In some cases the rates are designated (rel.) and have been calculated with reference to the rate of a competing reaction, given in the *Comments* column. Ratios of rates are listed for a few reactions in the form k/k_x in which k_x is the rate of reaction of the transient with competing solute, X.

Ionic Strength (I): The ionic strength has been quoted from the original paper or calculated from the given solute concentrations, if that information was available. When the reported rate constants were corrected for ionic strength the designation $\rightarrow 0$ is used.

Comments: The source of the transient and method of measurement are included in this column, along with other information on product identification, or related values for equilibrium constants, pK, or isotope effects. Temperature is assumed to be room temperature unless otherwise specified.

References: The references are designated by the serial number of the paper assigned by the Radiation Chemistry Data Center; the first two digits of the number represent the year in which the work was published.

Abbreviations and Symbols

A	frequency factor
abs.	absorption
alk.	alkaline
bipy	2,2′–bipyridine
BuOH	butanol
calcd.	calculated
c.k.	competition kinetics
concn.	concentration
contg.	containing
cor.	corrected
detd.	determined
dien	diethylenetriamine
d.k.	decay kinetics
e–r.	electron radiolysis
ϵ	extinction coefficient (molar absorptivity)
E_a	activation energy
esr	electron spin resonance
estd.	estimated
f.phot.	flash photolysis
formn.	formation
G	radiation yield (molecules per 100 eV)
ΔG°	free energy
γ–r.	gamma radiolysis
gly	glycinato
$\Delta H^\ddagger$	activation enthalpy
ident.	identification
K	equilibrium constant
k_f	specific rate of the forward reaction
k_r	specific rate of the reverse reaction
L	ligand
M	mol dm^{-3}
meas.	measured
MeOH	methanol
obs.	observed
ϕ	quantum yield
p.b.k.	product–buildup kinetics
phot.	photolysis
polymn.	polymerization
p.r.	pulse radiolysis
2–PrOH	2–propanol
rel.	relative
RNO	N,N–dimethyl–p–nitrosoaniline
$\Delta S^\ddagger$	activation entropy
satd.	saturated
soln.	solution
T	temperature
$t_{0.5}$	half–life
therm.	thermal
unpub.	unpublished

TABLE 1. Rates of reaction of CO_3^- in aqueous solution[a]

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
1.1	$CO_3^- + CO_3^- \rightarrow CO_2 + CO_4^{2-}$ See 78–1506 for mechanism	$2k = 1.2_5 \times 10^7$	8.4–13.5	$\rightarrow 0$	p.r.	D.k. at 600 nm in N_2O–satd. soln.; $\epsilon = 1860\ M^{-1}\ cm^{-1}$; $k_{obs} \cong 5 \times 10^7$ at pH 13–13.5	66–0139
		$2k = 4 \times 10^7$	7–9	0.1	f.phot.	D.k. at 600 nm in air–satd. $Co(NH_3)_4CO_3^+$ soln.; $\epsilon = 1830\ M^{-1}\ cm^{-1}$.	73–7109
		$2k = 1.9 \times 10^7$ $2k = 2.9 \times 10^7$	10.2 12.7	–	p.r.	D.k. at 600 nm in N_2O–satd. soln.; $\epsilon = 1830\ M^{-1}\ cm^{-1}$; 0.1 M K_2CO_3.	73–7109
		$2k = 6.9 \times 10^7$	11.8	–	p.r.	D.k. in 0.1 M Na_2CO_3 soln.; See above.	73–7109
1.2	$CO_3^- + O_2^- \rightarrow CO_3^{2-} + O_2$ (or $\rightarrow CO_5^{2-}$ See 70–0247)	1.5×10^9	11.6	0.3	p.r.	D.k. of CO_3^- at 600 nm or O_2^- at 260 nm in O_2–satd. soln.; ϵ(260 nm) for $O_2^- = 1220\ M^{-1}\ cm^{-1}$ assuming ϵ(600 nm) for $CO_3^- = 1800\ M^{-1}\ cm^{-1}$.	66–0001
		$(4 \pm 1) \times 10^8$	~11.8	0.6	f.phot.	D.k. at 260 nm (O_2^-), $\epsilon = 1850\ M^{-1}\ cm^{-1}$ and 600 nm (CO_3^-) in O_2–satd. soln., $\epsilon = 1860\ M^{-1}\ cm^{-1}$; product ($CO_5^{2-}$?) has ϵ(260 nm) = $410\ M^{-1}\ cm^{-1}$.	70–0247
		7.5×10^8	8–13	–	f.phot.	D.k. at 600 nm in air–satd. soln. contg. $NaHCO_3$ and 2,6–anthraquinonesulfonate.	72–7335, 72–7464
1.2a	$CO_3^- + Br^-$	$< 5 \times 10^5$	~11	–	p.r.	No reaction.	78–1506
1.3	$CO_3^- + BrO^- \rightarrow CO_3^{2-} + BrO$	$(4.3 \pm 0.4) \times 10^7$	13	0.4	p.r.	D.k.	68–0153
1.4	$CO_3^- + BrO_2 \rightarrow CO_3^{2-} + BrO_2$	$(1.1 \pm 0.1) \times 10^8$	13	0.4	p.r.	D.k.	68–0153
	Co(II) ions						
1.5	$CO_3^- + Co_{aq}^{2+}$	$(4.4 \pm 0.4) \times 10^6$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7109
		2.8×10^6	6.5	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
1.5a	$CO_3^- + CoL(H_2O)_2^{2+}$	6.9×10^8	4.7	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
	L = 5,7,7,12,14,14–hexamethyl–1,4,8,11–tetraazacyclotetradeca–1,4,8,11–tetraene						
1.5b	$CO_3^- + CoL(H_2O)_2^{2+}$	7.3×10^6	4.7	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
	L = 5,7,7,12,14,14–hexamethyl–1,4,8,11–tetraazacyclotetradeca–4,11–diene						
	Co(III) complexes						
1.6	$CO_3^- + Co(NH_3)_4CO_3^+$	$< 10^6$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7109
1.7	$CO_3^- + Co(NH_3)_4(OH_2)_2^{3+}$	$(1.4 \pm 0.1) \times 10^7$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7109
1.7a	$CO_3^- + Co(NH_3)_6^{3+}$	$< 5 \times 10^4$	6.5	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
1.7b	$CO_3^- + Co(en)_3^{3+}$	$< 1 \times 10^5$	6.5	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
1.7c	$CO_3^- + Co(NH_3)_5OPO_3H^+$	$< 4 \times 10^5$	6.5	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
1.7d	$CO_3^- + Co(NH_3)_5Cl^{2+}$	2.0×10^6	6.5	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501

TABLE 1. Rates of reaction of CO_3^- in aqueous solution[a]—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
1.7e	$CO_3^- + Co(NH_3)_5Br^{2+}$	5.7×10^6	6.5	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
1.7f	$CO_3^- + Co(NH_3)_5OSO_3^+$	1.5×10^6	6.5	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
1.7g	$CO_3^- + Co(NH_3)_5O_2CC_6H_5^{2+}$	7×10^5	6.5	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
1.7h	$CO_3^- + Co(NH_3)_5O_2CCH_3^{2+}$	1.1×10^6	6.5	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
1.7i	$CO_3^- + Co(NH_3)_5NO_2^{2+}$	1.0×10^8	6.5	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
1.7j	$CO_3^- + Co(NH_3)_5OSO_2^+$	1.1×10^6	6.5	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
1.8	$CO_3^- + Co(NH_3)_5(OH_2)^{3+}$	$(2.9 \pm 0.3) \times 10^6$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7109
		1.7×10^6	>7.6	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
		$\sim 3 \times 10^4$	<5.6	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.; pK_a for complex = 6.6.	78–1501
1.8a	$CO_3^- + Cr(NH_3)_5Cl^{2+}$	$< 1 \times 10^5$	6.5	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
1.8b	$CO_3^- + Cr(NH_3)_5OH_2^{3+}$	7×10^5	>6.3	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
		4×10^5	<4.3	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.; pK_a for complex = 5.3.	78–1501
1.8c	$CO_3^- + Cu_{aq}^{2+}$	$\sim 10^4$	4.5	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
1.9	$CO_3^- + Fe(CN)_6^{4-} \rightarrow CO_3^{2-} + Fe(CN)_6^{3-}$	2.7×10^8	11.6	-	p.r.	D.k. at 600 nm as well as p.b.k. at 420 nm for ferricyanide ion in soln. contg. 0.072 M Na_2CO_3, 1.22×10^{-4} M ferrocyanide, 0.03% oxygen and 0.1 atm. N_2O; at pH 13 $k \cong (3.5–4.0) \times 10^8$.	66–0139
1.9a	$CO_3^- + H_2O_2$	8×10^5	8–9	3	f.phot.	D.k. at 600 nm in N_2–satd. soln.; pH–dependent (9–13).	70–0247
	$CO_3^- + HO_2^-$	5.6×10^7	13–14				
1.10	$CO_3^- + I^- \rightarrow CO_3^{2-} + I$	$(1.3 \pm 0.3) \times 10^8$	~11	$\rightarrow 0$	p.r.	D.k. at 600 nm.	78–1506
1.10a	$CO_3^- + Ir(NH_3)_5Cl^{2+}$	2.4×10^7	6.5	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
1.10b	$CO_3^- + Mn_{aq}^{2+}$	1.5×10^7	6.0	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
1.10c	$CO_3^- + NO_2^- \rightarrow CO_3^{2-} + NO_2$	4.0×10^5	~11	$\rightarrow 0$	p.r.	D.k. at 600 nm.	78–1506
1.10d	$CO_3^- + NO_2 \rightarrow CO_2 + NO_3^-$	1.0×10^9	~11	-	p.r.	Est. from opt. and condy. d.k.	78–1506
1.10e	$CO_3^- + Ni_{aq}^{2+}$	$< 10^4$	5.8	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
1.11	$CO_3^- + cis\text{-}Pt^{II}(gly)_2$	$(4.4 \pm 0.8) \times 10^9$	8.5	0.05	p.r.	D.k. in 0.05 M $NaHCO_3$.	77–1053
1.12	$CO_3^- + trans\text{-}Pt^{II}(gly)_2$	$(3.4 \pm 0.6) \times 10^9$	8.5	0.05	p.r.	D.k. in 0.05 M $NaHCO_3$.	77–1053
1.12a	$CO_3^- + Rh(NH_3)_5Cl^{2+}$	$< 10^4$	6.5	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
1.12b	$CO_3^- + Rh(NH_3)_5OH_2^{3+}$	1×10^5	>6.9	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
		$< 5 \times 10^4$	<4.9	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.; pK_a for complex = 5.9.	78–1501

TABLE 1. Rates of reaction of CO_3^- in aqueous solution[a]—Continued

No.	Reaction	$k(M^{-1} s^{-1})$	pH	I	Method	Comment	Ref.
1.13	$CO_3^- + Ru(bipy)_3^{2+}$	$(4.0 \pm 0.4) \times 10^8$	–	0.02	p.r.	D.k. of the Ru complex in N_2O–satd. soln. contg. 0.005 *M* each of HCO_3^- and CO_3^{2-}.	77–1093
1.13a	$CO_3^- + Ru(NH_3)_6^{3+}$	6.0×10^6	6.5	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
1.13b	$CO_3^- + Ru(NH_3)_5Cl^{2+}$	7.7×10^6	6.5	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
1.13c	$CO_3^- + Ru(NH_3)_5OH_2^{3+}$	1.4×10^9	>5.2	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
		1.8×10^8	<3.2	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.; pK_a for complex = 4.2.	78–1501
1.13d	$CO_3^- + SCN^- \rightarrow CO_3^{2-} + SCN$	$(8 \pm 1.5) \times 10^5$	~11	–	p.r.	D.k. at 600 nm.	78–1506
1.13e	$CO_3^- + SO_3^{2-} \rightarrow CO_3^{2-} + SO_3^-$	1.0×10^7	~11	→ 0	p.r.	D.k. at 600 nm.	78–1506
1.13f	$CO_3^- + SO_3^- \rightarrow CO_2 + SO_4^{2-}$	5.0×10^8	9.6	–	p.r.	D.k. at 260 nm; also condy. study	78–1506
1.14	$CO_3^- + UO_2^{2+}$	$\sim 1.5 \times 10^5$	–	0.16	f.phot.	D.k. at 580 nm; results somewhat irreproducible.	76–7279
1.14a	$CO_3^- + Zn_{aq}^{2+}$	$< 10^4$	4.7	0.04	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	78–1501
1.15	Acetanilide	3.2×10^5	7.0	0.06	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	75–7313
1.16	Acetate ion	6×10^2	12.1–12.7	–	f.phot.	D.k. at 600 nm in air-satd. soln. contg. 0.05 *M* $Na_2S_2O_8$, 0.5 *M* Na_2CO_3; CO_3^- from reaction of $SO_4^- + CO_3^{2-}$.	72–7383
1.17	Acetone	1.6×10^2	12.1–12.7	–	f.phot.	D.k. at 600 nm in air-satd. soln. contg. 0.05 *M* $Na_2S_2O_8$, 0.5 *M* Na_2CO_3; CO_3^- from reaction of $SO_4^- + CO_3^{2-}$.	72–7383
1.18	Acetonitrile	3.2×10^9	12.1–12.7	–	f.phot.	D.k. at 600 nm in air-satd. soln. contg. 0.05 *M* $Na_2S_2O_8$, 0.5 *M* Na_2CO_3; CO_3^- from reaction of $SO_4^- + CO_3^{2-}$.	72–7383
1.19	Acetophenone	1.0×10^7	~12.5	–	f.phot.	D.k. at 550 nm in deoxygenated soln. contg. 0.3 *M* Na_2CO_3.	71–7574
		$(3 \pm 1) \times 10^5$	–	–	p.r.	D.k. at 600 nm; CO_3^- also reacts with acetophenone–OH adduct, $k = (1.5 \pm 0.5) \times 10^9$.	78–1506
1.20	*N*-Acetylcysteine	$(1.8 \pm 0.4) \times 10^8$	12.0	0.003	f.phot.	D.k. at 600 nm; rate pH dependent; value from graph; CO_3^- generated from $Co(NH_3)_4CO_3^+$	75–7110
1.21	*N*-Acetylglycine	$< 10^4$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
1.22	*N*-Acetylglycylglycine	$< 10^4$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
1.23	*N*-Acetyltryptophan	$(4.2 \pm 0.4) \times 10^8$	7	0.1	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7109
		$(6.2 \pm 1.5) \times 10^8$	11.8	0.1	f.phot.		
1.24	Alanine	$< 10^3$	7.0	0.06	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352

TABLE 1. Rates of reaction of CO_3^- in aqueous solution[a]—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
1.25	Aniline	5.4×10^8	7.0	0.06	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	75–7313
		6.0×10^8	–	–	p.r.	D.k. at 600 nm.	78–1506
1.25a	Anisole	2.8×10^5	–	–	p.r.	D.k. at 600 nm; CO_3^- also reacts with anisole–OH adduct, $k \cong 3 \times 10^9$	78–1506
1.26	Anthrasemiquinone–1–sulfonate radical ion $\cdot CO_3^- + AQ^- \rightarrow CO_3^{2-} + AQ$	4.6×10^9	–	–	f.phot.	D.k. at 600 nm in air–satd. soln. contg. 0.05 *M* $Na_2S_2O_8$ and 0.5 *M* Na_2CO_3; CO_3^- from reaction of $SO_4^- + CO_3^{2-}$; semiquinone formed from CO_3^{2-} + triplet AQ.	72–7383
1.27	Anthrasemiquinone–2–sulfonate radical ion	2.2×10^9	–	–	f.phot.	See 1.26.	72–7383
1.28	Anthrasemiquinone–2,6–disulfonate radical ion	$(5.4 \pm 0.6) \times 10^8$	7.5	–	f.phot.	D.k. in Na_2CO_3 soln.	69–7297
		2×10^9	8.0	–	f.phot.	D.k. in O_2–free carbonate soln.	73–7569
		1.2×10^9	6.5	–	f.phot.	D.k. in $NaHCO_3$ soln.	72–7335
		1.4×10^9	8–13	–	f.phot.	D.k. in air–satd. 0.05 *M* $NaHCO_3$ soln.	72–7464
1.29	Anthrasemiquinone–2,7–disulfonate radical ion	1.9×10^9	–	–	f.phot.	See 1.26.	72–7383
1.30	Arginine	$(9 \pm 0.9) \times 10^4$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
1.31	Ascorbate ion $CO_3^- + AH^- \rightarrow \cdot A^- + CO_3^{2-} + H^+$	$(1.1 \pm 0.1) \times 10^9$	11	–	p.r.	D.k. at 600 nm in N_2O–satd. 0.5 *M* carbonate soln.	73–3006
1.32	Aspartate ion	$< 10^4$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
1.33	Benzene	3×10^3	7.0	0.06	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln; uncertainty 50–100%.	75–7313
		$< 5 \times 10^4$	11.7	–	p.r.	Benzene (1.4×10^{-3} M) had no effect on decay of CO_3^-; CO_3^- reacts with benzene–OH adduct, $k = 2 \times 10^9$	78–1506
1.34	Benzophenone	1.5×10^6	–	–	f.phot.	D.k. at 550 nm in O_2–free carbonate soln.	71–7574
1.35	*p*–Bromophenoxide ion	1.8×10^8	12.2	0.3	p.r.	D.k. at 570 nm in N_2O–satd. carbonate soln.	77–1098
	tert–Butanol *See* 2–Methyl–2–propanol.						
1.36	Carbon tetrachloride	–	12.0–13.5	–	p.r.	Decay of CO_3^- faster in CCl_4 than in N_2O soln.	66–0139
1.37	Chloroacetate ion	$\leqslant 2.0 \times 10^3$	12.1–12.7	1.65	f.phot.	D.k. at 600 nm in air–satd. $S_2O_8^{2-}$ soln.; CO_3^- generated by $SO_4^- + CO_3^{2-} \rightarrow SO_4^{2-} + CO_3^-$.	72–7383
1.38	*p*–Chlorophenoxide ion	1.9×10^8	12.2	0.3	p.r.	D.k. at 570 nm in N_2O–satd. carbonate soln.	77–1098
1.39	α–Chymotrypsin	1.0×10^9	11.3	0.12	p.r.	D.k. in N_2O–satd. soln.; mol wt. 20,000; concn. effect.	74–1096
		$(1.2 \pm 0.1) \times 10^9$	7–11	0.03	f.phot.	D.k. at 600 nm; mol. wt. 25,000; HCO_3 or CO_3^- generated from $Co(NH_3)_4CO_3^+$; *k* independent of pH.	73–7352, 75–7110

TABLE 1. Rates of reaction of CO_3^- in aqueous solution[a]—Continued

No.	Reaction	$k(M^{-1} s^{-1})$	pH	I	Method	Comment	Ref.
1.40	Cysteine	$(2.7 \pm 0.3) \times 10^8$	11.2± 0.3	0.3	p.r.	D.k. in N_2O–satd. soln.	72–0036
		$(4.6 \pm 0.5) \times 10^7$	7.0	0.03	f.phot.	D.k. at 600 nm; HCO_3^-	73–7352,
		3.5×10^8	9–10	0.003	f.phot.	or CO_3^- generated from	75–7110
		2.5×10^8	12	0.003	f.phot.	$Co(NH_3)_4CO_3^+$.	
1.41	Cysteine methyl ester	$\sim 1 \times 10^7$	4–10	0.003	f.phot.	D.k. at 600 nm; value from graph; HCO_3^- or CO_3^- generated from $Co(NH_3)_4CO_3^+$.	75–7110
1.42	Cystine dimethyl ester	$(7.2 \pm 0.7) \times 10^6$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
1.43	Diethyl disulfide	4.5×10^7	~8	–	p.r.	D.k. at 600 nm in N_2O–satd. soln.; 0.1–1.0 M HCO_3^- or CO_3^{2-}.	76–1143
		6.6×10^7	~11				
1.44	*N,N*–Dimethylaniline	1.8×10^9	7.0	0.06	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	75–7313
		$(1.4 \pm 0.2) \times 10^9$	–	–	p.r.	D.k. at 600 nm, as well as condy.	78–1506
1.45	Dimethyl disulfide	1.0×10^8	~8	–	p.r.	D.k. at 600 nm in N_2O–satd. soln.; 0.1–1.0 M HCO_3^- or CO_3^{2-}.	76–1143
		8.0×10^7	~11				
1.46	3,3′–Dithiobis(propionate ion)	$(1.3 \pm 0.1) \times 10^7$	6.8	0.1	f.phot.	D.k. at 600 nm; CO_3H and CO_3^- generated from $Co(NH_3)_4CO_3^+$.	73–7109
		$(3.0 \pm 0.3) \times 10^7$	11.5				
		$(1.0 \pm 0.1) \times 10^7$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
		1.3×10^7	7–12	0.003	f.phot.	D.k. at 600 nm; CO_3H and CO_3^- generated from $Co(NH_3)_4CO_3^+$; value from graph.	75–7110
1.47	Dithiothreitol (*threo*–2,3–Dihydroxy–1,4–dithiobutane)	$(4.1 \pm 0.4) \times 10^8$	11	0.3	p.r.	D.k. at 600 nm in N_2O–satd. carbonate soln.	73–1020
1.48	Duroquinone	$< 10^6$	12	–	p.r.	No reaction; previously reported (76–7587) $k = 2 \times 10^9$ suggested to be for different reaction.	78–1506
1.49	Ethanol $CO_3^- + CH_3CH_2OH\ (+OH^-) \rightarrow CO_3^{2-} + CH_3CHOH + H_2O$	$1.5–1.7 \times 10^4$	12.5	–	f.phot.	D.k. in soln. contg. 0.3 M Na_2CO_3 and 2×10^{-4} M acetophenone or benzophenone.	71–7574
		1.5×10^4	12.5	–	f.phot.	D.k. at 600 nm in air–satd. soln. contg. 0.05 M $Na_2S_2O_8$ and 0.5 M Na_2CO_3; CO_3^- generated from $SO_4^- + CO_3^{2-} \rightarrow SO_4^{2-} + CO_3^-$.	72–7383
1.50	Ethoxybenzene	4.1×10^5	7.0	0.06	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	75–7313
1.50a	Ethylenediaminetetraacetate ion	1.1×10^6	–	$\rightarrow 0$	p.r.	D.k. at 600 nm.	78–1506
1.51	Formate ion	$(1.1 \pm 0.1) \times 10^5$	6.4	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7109
		1.6×10^5	–	$\rightarrow 0$	p.r.	D.k. at 600 nm.	78–1506
1.52	Glucose	$(7 \pm 0.7) \times 10^4$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
1.53	Glutathione	$(5.3 \pm 0.5) \times 10^6$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
1.54	Glutathione disulfide	$(1.3 \pm 0.1) \times 10^6$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352

TABLE 1. Rates of reaction of CO_3^- in aqueous solution[a]—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
1.55	Glycine	$< 10^3$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
1.56	Glycylglycine	$(2 \pm 0.2) \times 10^4$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
1.57	Glycylglycylglycine	$(4 \pm 0.4) \times 10^4$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
1.58	Glycylglycyltrypto-phan	$(7 \pm 0.7) \times 10^8$	7.0	0.003	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln; k is pH dependent, $k = 4 \times 10^8$ at pH 10.	74–7296
1.59	Glycylhistidine	$(4.3 \pm 0.4) \times 10^6$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
1.60	Glycyltryptophan	$(7.2 \pm 0.7) \times 10^8$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
		$(7.8 \pm 0.8) \times 10^8$	7	0.003	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$; k is pH dependent, $k = 4.5 \times 10^8$ at pH 10.	74–7296
1.61	Glycyltyrosine	$(3.0 \pm 0.3) \times 10^7$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
1.62	Histidine	$(7 \pm 0.7) \times 10^6$	11.2 ± 0.3	0.3	p.r.	D.k. in N_2O-satd. soln.	72–0036
		$(5.6 \pm 0.6) \times 10^6$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
		8.5×10^6	10	0.003	f.phot.	D.k. at 600 nm; k is pH dependent; $k \sim 1 \times 10^6$ at pH 5 (values from graph); CO_3^- generated from $Co(NH_3)_4CO_3^+$.	75–7110
1.63	*p*-Hydroxybenzoate ion	7.9×10^7	12.2	0.3	p.r.	D.k. at 570 nm in N_2O-satd. carbonate soln.	77–1098
1.64	Imidazole	$(5.5 \pm 0.6) \times 10^5$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
1.65	Indole	3.2×10^8	7.0, 12.0	0.1	f.phot.	D.k. at 600 nm; CO_3H or CO_3^- generated from $Co(NH_3)_4CO_3^+$.	73–7109
		4.1×10^8	5–13	0.003	f.phot.	D.k. at 600 nm; CO_3H or CO_3^- generated from $Co(NH_3)_4CO_3^+$; value from graph.	74–7296
1.66	Indole-3-propionate ion	$(4.1 \pm 0.4) \times 10^8$ $(6.8 \pm 1.7) \times 10^8$	7.0 12.0	0.1 0.1	f.phot.	D.k. at 600 nm; CO_3H and CO_3^- generated from $Co(NH_3)_4CO_3^+$.	73–7109
		4.2×10^8	7–11	0.003	f.phot.	D.k. at 600 nm; CO_3H and CO_3^- generated from $Co(NH_3)_4CO_3^+$; at $\mu = 0.1$ k increases with pH; values from graph.	74–7296
	Isopropanol	*See* 2-Propanol.					
1.67	Lysozyme	$(5.5 \pm 0.6) \times 10^8$	7.0–12	0.03	f.phot.	D.k. at 600 nm; CO_3H and CO_3^- generated from $Co(NH_3)_4CO_3^+$.	73–7352 75–7110
1.68	3-Mercaptopropionate ion	$(2.4 \pm 0.6) \times 10^8$	12.0	0.003	f.phot.	D.k. at 600 nm; CO_3H and CO_3^- generated from $Co(NH_3)_4CO_3^+$; k is dependent on pH, $k \sim 3 \times 10^7$ at pH 7, values from graph.	75–7110

TABLE 1. Rates of reaction of CO_3^- in aqueous solution[a]—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
1.69	Methanol	5×10^3	12.5	–	f.phot.	D.k. at 600 nm in air-satd. soln. contg. 0.5 *M* Na_2CO_3; CO_3^- generated from $SO_4^- + CO_3^{2-} \rightarrow SO_4^{2-} + CO_3^-$.	72–7383
		$\leqslant 2.6 \times 10^3$	6.4	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7109
1.70	Methionine	$(1.2 \pm 0.1) \times 10^8$	11.2± 0.3	0.3	p.r.	D.k. in N_2O–satd. soln.	72–0036
		$(3.6 \pm 0.4) \times 10^7$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
		$(4.8 \pm 0.5) \times 10^7$	11.0	0.003	f.phot.	D.k. at 600 nm; CO_3^- generated from $Co(NH_3)_4CO_3^+$; slight pH effect.	75–7110
1.71	*p*–Methoxyphenoxide ion	5.2×10^8	12.2	0.3	p.r.	D.k. at 570 nm in N_2O–satd. carbonate soln.	77–1098
1.71a	Methyl radical $CO_3^- + CH_3 \rightarrow CH_3OCO_2^-$	$(3 \pm 1) \times 10^9$	–	–	p.r.	D.k. at 600 nm in Na_2CO_3–CH_3Cl soln.	78–1506
1.71b	*N*–Methylaniline	1.8×10^9	–	–	p.r.	D.k. at 600 nm.	78–1506
1.72	*S*–Methylcysteine	$(2.5 \pm 0.2) \times 10^7$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
		$(5 \pm 0.5) \times 10^7$	11.0	0.003	f.phot.	D.k. at 600 nm; CO_3^- generated from $Co(NH_3)_4CO_3^+$; slight pH effect.	75–7110
1.73	*p*–Methylphenoxide ion	4.8×10^8	12.2	0.3	p.r.	D.k. at 570 nm in N_2O–satd. carbonate soln.	77–1098
1.74	2–Methyl–2–propanol (*tert*–Butanol)	$\leqslant 1.6 \times 10^6$	6.4	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7109
1.75	*N*–Methyltryptophan	$(4.3 \pm 0.4) \times 10^8$	7–11	0.003	f.phot.	D.k. at 600 nm; CO_3H and CO_3^- generated from $Co(NH_3)_4CO_3^+$.	74–7296
1.76	Nitromethane	$(1 \pm 0.1) \times 10^6$	7	0.003	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	75–7110
1.77	*aci*–Nitromethane anion $CO_3^- + CH_2{=}NO_2^- \rightarrow {}^-O_2COCH_2NO_2^-$	$(1.5 \pm 0.4) \times 10^7$	12	0.003	f.phot.	D.k. at 600 nm; CO_3^- generated from $Co(NH_3)_4CO_3^+$; product obs. by esr (72–5050).	75–7110
1.78	*p*–Nitrophenoxide ion	4.8×10^7	12.2	0.3	p.r.	D.k. at 570 nm in N_2O–satd. carbonate soln.	77–1098
1.79	Norpseudopelletierine–*N*–oxyl (9–Azabicyclo[3,3,1]nonan–3–one–9–oxyl)	$(1.1 \pm 0.1) \times 10^9$	–	0.015	p.r.	D.k. at 600 nm in N_2O–satd. carbonate soln.	71–0061
1.80	Penicillamine (3–Mercaptovaline)	2×10^7 2.4×10^8 1.2×10^8	4 10 12	0.003	f.phot.	D.k. at 600 nm; CO_3H or CO_3^- generated from $Co(NH_3)_4CO_3^+$; values from graph.	75–7110
1.81	Phenol	$(2.2 \pm 0.2) \times 10^7$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
		4.9×10^6	7.0	0.06	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.; *k* increases with pH to 5×10^7 at pH 12.	75–7313
1.82	Phenoxide ion	2.4×10^8	12.2	0.3	p.r.	D.k. at 570 nm in N_2O–satd. carbonate soln.	77–1098
		3.3×10^8	–	–	p.r.	D.k. at 600 nm.	78–1506

TABLE 1. Rates of reaction of CO_3^- in aqueous solution[a]—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
1.83	Phenylalanine	$< 1 \times 10^6$	11.2± 0.3	0.3	p.r.	D.k. in N_2O–satd. soln.	72–0036
		$(5 \pm 0.5) \times 10^4$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
1.84	Phenylalanylglycine	$(4.0 \pm 0.4) \times 10^5$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
1.85	1–Propanol	1.9×10^4	12.1–12.7	–	f.phot.	D.k. at 600 nm in air–satd. soln. contg. 0.05 *M* $Na_2S_2O_8$ and 0.5 *M* Na_2CO_3; CO_3^- generated from $SO_4^- + CO_3^{2-}$.	72–7383
1.86	2–Propanol $CO_3^- + (CH_3)_2CHOH \rightarrow HCO_3^- + (CH_3)_2COH$	3.9×10^4	12.1–12.7	–	f.phot.	D.k. at 600 nm in air–satd. soln. contg. 0.05 *M* $Na_2S_2O_8$ and 0.5 *M* Na_2CO_3; CO_3^- generated from $SO_4^- + CO_3^{2-}$.	72–7383
		$\leqslant 4 \times 10^4$	6.4	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7109
		5×10^4	–	–	p.r.	D.k. at 600 nm.	78–1506
1.87	Ribonuclease A	$(5.0 \pm 0.5) \times 10^7$	7.0	0.03	f.phot.	D.k. at 600 nm; CO_3H	73–7352,
		1.4×10^8	11.0	0.03	f.phot.	or CO_3^- generated from $Co(NH_3)_4CO_3^+$; *k* is pH dependent; value from graph; mol. wt. 13,700.	75–7110
1.88	2,2,6,6–Tetra–methyl–4–oxo–1–piperidinyloxyl (TAN)	$(4.8 \pm 0.5) \times 10^8$	–	0.015	p.r.	D.k. at 600 nm in N_2O–satd. carbonate soln.	71–0061
		4.6×10^8	10–11	–	p.r.	D.k. at 600 nm in air–satd. soln.	71–0618
1.89	Thymine	$< 10^4$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73–7352
1.90	Toluene	4.3×10^4	7.0	0.06	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	75–7313
1.91	Trichloroacetate ion	$\leqslant 1.5 \times 10^2$	12.1–12.7	–	f.phot.	D.k. in air–satd. soln. contg. 0.5 *M* Na_2CO_3 and 0.05 *M* $Na_2S_2O_8$; CO_3^- generated from $SO_4^- + CO_3^{2-}$.	72–7383
1.92	Trypsin	$(6.8 \pm 0.7) \times 10^8$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$; mol. wt. 23,800.	73–7352
1.93	Tryptamine	$(1.25 \pm 0.1) \times 10^9$	8	0.003	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$; *k* is pH dependent, $k \cong 9 \times 10^8$ at pH 12; values from graph.	74–7296
1.94	Tryptophan	$(4.4 \pm 0.4) \times 10^8$	11.2± 0.3	0.3	p.r.	D.k. in N_2O–satd. soln.	72–0036
		4.3×10^8	12	0.003	f.phot.	D.k. at 600 nm; CO_3H	74–7296
						or CO_3^- generated from $Co(NH_3)_4CO_3^+$; *k* is pH dependent, $k \cong 6.2 \times 10^8$ at pH 9 and 7×10^8 at pH 7; values from graph.	73–7352
1.95	Tryptophan methyl ester	$(9.5 \pm 1) \times 10^8$	7	0.003	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.; *k* pH–dependent.	74–7296
1.96	Tryptophanamide	$(1.3 \pm 0.1) \times 10^9$	7	0.003	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.; *k* pH–dependent.	74–7296

TABLE 1. Rates of reaction of CO_3^- in aqueous solution[a]—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
1.97	Tryptophanylglycine	$(7 \pm 0.7) \times 10^8$	6	0.003	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.; k pH-dependent.	74-7296
1.98	Tyrosine	$(2.9 \pm 0.3) \times 10^8$	11.2± 0.3	0.3	p.r.	D.k. in N_2O-satd. soln.	72-0036
		$(4.5 \pm 0.4) \times 10^7$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73-7352
		$(1.4 \pm 0.1) \times 10^8$	11	0.03	f.phot.	D.k. at 600 nm; CO_3^- generated from $Co(NH_3)_4CO_3^+$; k pH dependent.	75-7110
1.99	Uracil	$< 10^4$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73-7352
1.100	Urea	$< 10^3$	7.0	0.03	f.phot.	D.k. at 600 nm in $Co(NH_3)_4CO_3^+$ soln.	73-7352

[a]The transient is represented in the anionic form; pK_a has been reported to be 9.6.

TABLE 2. Rates of reactions of SO_4^- in aqueous solution

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
2.1	$SO_4^- + SO_4^- \rightarrow S_2O_8^{2-}$	$2k = 1.0 \times 10^9$	5.5	0.06	f.phot.	D.k. at 455 nm in aerated sulfate soln.; recalcd. for $\epsilon_{455} = 1100\ M^{-1}\ cm^{-1}$.	67–7012
		$2k = (8.8 \pm 0.8) \times 10^8$	0.1	1	f.phot.	D.k. at 455 nm in aerated $S_2O_8^{2-}$ soln.; recalcd. for $\epsilon_{455} = 1100\ M^{-1}\ cm^{-1}$.	67–7058
		$(7.5 \pm 0.25) \times 10^8$	1.0	0.13			
		$(9.5 \pm 1) \times 10^8$	4.8	0.03			
		$2k = (1.6 \pm 0.3) \times 10^9$	–	1 *M* H_2SO_4	f.phot.	D.k. in aerated 2.5×10^{-4} *M* ceric sulfate; recalcd. for $\epsilon_{455} = 1100\ M^{-1}\ cm^{-1}$.	67–7274
		$2k = 3.6 \times 10^9$	–	4 *M* H_2SO_4	p.r.	D.k.; used $\epsilon_{450} \cong 1000\ M^{-1}\ cm^{-1}$ (66–0019).	73–1030
2.2	$SO_4^- + AsO_2^- \rightarrow SO_4^{2-} + \cdot AsO_2$	8.0×10^8 (rel.)	7–8	–	phot.	C.k. with fumarate ion in $S_2O_8^{2-}$ soln.; effect of solute on fumarate–SO_4^- adduct obs. by esr; rel. to $k(SO_4^- + OH^-) = 7.3 \times 10^7$.	73–5403
2.3	$SO_4^- + Br^- \rightarrow SO_4^{2-} + Br$	$(3.5 \pm 0.4) \times 10^9$	7	0.03	p.r.	D.k. at 450 nm in air-satd. $S_2O_8^{2-}$ soln. contg. 0.05 *M tert*–BuOH.	75–1069
		1.6×10^9 (rel.)	7–8	–	phot.	C.k. with fumarate ion in $S_2O_8^{2-}$ soln.; effect of solute on fumarate–SO_4^- adduct obs. by esr; rel. to $k(SO_4^- + OH^-) = 7.3 \times 10^7$.	73–5403
2.4	$SO_4^- + HCO_3^- \rightarrow SO_4^{2-} + CO_3^- + H^+$	$(9.1 \pm 0.4) \times 10^6$	7.5–8.5	0.03	f.phot.	D.k. at 330 nm (SO_4^-) as well as p.b.k. at 600 nm (CO_3^-) in aerated 10^{-2} *M* $S_2O_8^{2-}$ soln.	67–7058
		9.3×10^6 (rel.)	7–8	–	phot.	C.k. with fumarate in $S_2O_8^{2-}$ soln.; effect of solute on fumarate–SO_4^- adduct obs. by esr; rel. to $k(SO_4^- + OH^-) = 7.3 \times 10^7$.	73–5403
2.5	$SO_4^- + CN^-$	8.0×10^7 (rel.)	7–8	–	phot.	C.k. with fumarate in $S_2O_8^{2-}$ soln.; effect of solute on fumarate–SO_4^- adduct obs. by esr; rel. to $k(SO_4^- + OH^-) = 7.3 \times 10^7$.	73–5403
2.6	$SO_4^- + OCN^-$	5.0×10^8 (rel.)	7–8	–	phot.	C.k. with fumarate in $S_2O_8^{2-}$ soln.; effect of solute on fumarate–SO_4^- adduct obs. by esr; rel. to $k(SO_4^- + OH^-) = 7.3 \times 10^7$.	73–5403
2.7	$SO_4^- + SCN^- \rightarrow SO_4^{2-} + SCN$	$(5.2 \pm 0.5) \times 10^9$	7	0.03	p.r.	D.k. at 450 nm in air-satd. $S_2O_8^{2-}$ soln. contg. 0.05 *M tert*–BuOH.	75–1069

TABLE 2. Rates of reactions of SO_4^- in aqueous solution—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
2.8	$SO_4^- + Ce^{III} \rightarrow SO_4^{2-} + Ce^{IV}$	$(1.43 \pm 0.3) \times 10^8$	–	1 *M* H_2SO_4	f.phot.	D.k. at 455 nm; Ce^{III} produced from ceric sulfate.	67–7274
		1.3×10^8 (rel.)	–	4 *M* H_2SO_4	γ–r.	Air–satd. soln. contains Ce^{IV}, Ce^{III} and formic acid; ratios calcd. from assumed mechanism: $k(SO_4^- + Ce^{III})/k(SO_4^- + HCOOH) \cong 160$; $k(SO_4^- + Ce^{III})/k(SO_4^- + 2\text{-PrOH}) = 1.6$; rel. to $k(SO_4^- + 2\text{-PrOH}) = 8 \times 10^7$.	72–0094
2.9	$SO_4^- + Cl^- \rightarrow SO_4^{2-} + Cl$	1.9×10^8 (rel.)	7–8	–	phot.	C.k. with fumarate ion in $S_2O_8^{2-}$ soln.; effect of solute on fumarate–SO_4^- adduct obs. by esr; rel. to $k(SO_4^- + OH^-) = 7.3 \times 10^7$.	73–5403
		3.1×10^8	6.8	–	p.r.	D.k. at 480 nm; soln. contains $S_2O_8^{2-}$, *tert*–BuOH and phosphate buffer.	75–5244
		1.3×10^8	–	–	p.r.	P.b.k. (Cl_2^-) in 0.002 *M* $S_2O_8^{2-}$; $k = 4.1 \times 10^8$ in 2 *M* SO_4^{2-} soln.	76–1141
2.10	$SO_4^- + Cr^{2+}$	$> 10^9$	1.0	–	therm.	Estimated.	68–9084
2.11	$SO_4^- + Fe^{2+} \rightarrow SO_4^{2-} + Fe^{3+}$	9.9×10^8	–	1	p.r.	D.k. at 450 nm.	66–0019
2.12	$SO_4^- + NH_2OH$	8.5×10^8	8.2	–	p.r.	–	78–1075
2.13	$SO_4^- + NH_3OH^+$	1.5×10^7	4.1	–	p.r.	–	78–1075
2.14	$SO_4^- + N_2H_4$	8.1×10^8	9.5	–	p.r.	–	78–1075
2.15	$SO_4^- + N_2H_5^+$	2.1×10^8	4	–	p.r.	–	78–1075
2.16	$SO_4^- + N_3^- \rightarrow SO_4^{2-} + \cdot N_3$	7.4×10^8 (rel.)	7–8	–	phot.	C.k. with fumarate in $S_2O_8^{2-}$ soln.; effect of solute on fumarate–SO_4^- adduct obs. by esr; rel. to $k(SO_4^- + OH^-) = 7.3 \times 10^7$.	73–5403
		$\sim 3 \times 10^9$	7	–	p.r.	–	78–1075
2.17	$SO_4^- + NO_2^- \rightarrow SO_4^{2-} + NO_2$	8.8×10^8	7	–	p.r.	–	78–1075
2.18	$SO_4^- + NO_3^-$	1.4×10^6 (rel.)	9	–	phot.	C.k. with RNO in air–satd. $S_2O_8^{2-}$ soln.; rel. to $k(SO_4^- + EtOH) = 6.2 \times 10^7$.	70–7234
		2.1×10^6 (rel.)	7–8	–	phot.	C.k. with fumarate in $S_2O_8^-$ soln.; effect of solute on fumarate–SO_4^- adduct obs. by esr; rel. to $k(SO_4^- + OH^-) = 7.3 \times 10^7$.	73–5403
2.19	$SO_4^- + OH^- \rightarrow SO_4^{2-} + OH$	4.6×10^7	>11	–	p.r.	D.k. at 460 nm; soln. contains $S_2O_8^{2-}$.	69–0158
		$(6.5 \pm 1.0) \times 10^7$	alk.	–	p.r.	D.k. *vs.* OH^- concn. in O_2–free $S_2O_8^{2-}$ soln.	72–7008
		$(8.3 \pm 0.8) \times 10^7$ (rel.)	>11	0.06–0.08	p.r.	C.k. with tyrosine; effect of pH on formn. of tyrosine transient at 410 nm; rel. to $k(SO_4^- + tyr) = 3.2 \times 10^9$ at pH 7.	75–1069
		7.3×10^7	–	–	p.r.	D.k. at 450 nm; soln. contains $S_2O_8^{2-}$ and *tert*–BuOH.	75–5244

TABLE 2. Rates of reactions of SO_4^- in aqueous solution—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
2.20	$SO_4^- + H_2O \rightarrow HSO_4^- + OH$	10^3–$10^4\ s^{-1}$	–	–	therm.	Estimated.	68–9084
		$< 3 \times 10^3\ s^{-1}$	7	–	p.r.	Extrapolated from d.k. *vs.* OH^- concn. (see 2.19).	72–7008
2.21	$SO_4^- + H_2O_2$	1.2×10^7	7	–	p.r.	–	78–1075
2.22	$SO_4^- + H_2PO_2^- \rightarrow SO_4^{2-} + H^+ + HPO_2^-$	3.6×10^8 (rel.)	7–8	–	phot.	C.k. with fumarate ion in $S_2O_8^{2-}$ soln.; effect of solute on fumarate–SO_4^- adduct obs. by esr; rel. to $k(SO_4^- + OH^-) = 7.3 \times 10^7$.	73–5403
		1.8×10^8	7	–	p.r.	–	78–1075
2.23	$SO_4^- + HPO_3^{2-} \rightarrow SO_4^{2-} + H^+ + PO_3^{2-}$	4.3×10^7 (rel.)	7–8	–	phot.	C.k. with fumarate ion in $S_2O_8^{2-}$ soln.; effect of solute on fumarate–SO_4^- adduct obs. by esr; rel. to $k(SO_4^- + OH^-) = 7.3 \times 10^7$.	73–5403
		6.2×10^7	8.3	–	p.r.	–	78–1075
2.24	$SO_4^- + H_2PO_3^-$	1.6×10^7	4	–	p.r.	–	78–1075
2.25	$SO_4^- + H_2PO_4^-$	$\leqslant 7 \times 10^4$	7	–	p.r.	–	78–1075
2.26	$SO_4^- + HPO_4^{2-}$	$(1.2 \pm 0.3) \times 10^6$	9	–	p.r.	–	78–1075
2.27	$SO_4^- + SO_3^{2-} \rightarrow SO_4^{2-} + SO_3^-$	$\geqslant 5.3 \times 10^8$	–	–	p.r.	Rate with HSO_3^- higher by at least a factor of 2.5.	72–7008
		2.6×10^8 (rel.)	7–8	–	phot.	C.k. with fumarate ion in $S_2O_8^{2-}$ soln.; effect of solute on fumarate–SO_4^- adduct obs. by esr; rel. to $k(SO_4^- + OH^-) = 7.3 \times 10^7$.	73–5403
2.28	$SO_4^- + HSO_5^- \rightarrow HSO_4^- + SO_5^-$	$< 10^5$	–	–	p.r.	D.k. at 450 nm.	77–1047
2.29	$SO_4^- + SiO_3^{2-} \rightarrow SO_4^{2-} + SiO_3^-$	2×10^7	–	–	f. phot.	–	70–7262
2.30	$SO_4^- + Tl^+$	$(1.70 \pm 0.2) \times 10^9$	–	1 *M* H_2SO_4	f.phot.	D.k. at 455 nm; soln. contains ceric sulfate–H_2SO_4.	67–7274
2.31	Acetanilide $SO_4^- + C_6H_5NHCOCH_3 \rightarrow SO_4^{2-} + C_6H_5{}^+NHCOCH_3$	3.6×10^9	7	–	p.r.	D.k. at 450 nm; soln. contains 0.01–0.05 *M* $S_2O_8^{2-}$.	77–1001
2.32	Acetate ion $SO_4^- + CH_3COO^- \rightarrow SO_4^{2-} + \cdot CH_3 + CO_2$ (1) $SO_4^- + CH_3COO^- \rightarrow HSO_4^- + \cdot CH_2COO^-$ (2)	5.0×10^6	6.8	–	p.r.	D.k. at 450 nm; soln. contains $S_2O_8^{2-}$, *tert*–BuOH, and phosphate buffer; predominantly (1); CO_2 yield meas. by γ–r. (78–1505).	75–5244
		8.7×10^6 (rel.)	7–8	–	phot.	C.k. with fumarate ion in $S_2O_8^{2-}$ soln.; effect of solute on fumarate–SO_4^- adduct obs. by esr; rel. to $k(SO_4^- + OH^-) = 7.3 \times 10^7$; product ident. by esr.	73–5403
2.33	Acetic acid	$(8.8 \pm 0.2) \times 10^4$	–	1 *M* H_2SO_4	p.r.	D.k. at 455 nm; soln. contains ceric sulfate–H_2SO_4.	67–7274
2.34	Acetophenone $SO_4^- + C_6H_5COCH_3 \rightarrow SO_4^{2-} + C_6H_5{}^+COCH_3$	3.1×10^8	7	0.03	p.r.	D.k. at 450 nm in $\sim 10^{-2}$ *M* $S_2O_8^{2-}$ soln.	77–1001
2.35	*p*–Acetylbenzoate ion $SO_4^- + CH_3COC_6H_4COO^- \rightarrow SO_4^{2-} + CH_3COC_6H_4{}^+COO^-$	2.0×10^8	7	0.03	p.r.	D.k. at 450 nm in $\sim 10^{-2}$ *M* $S_2O_8^{2-}$ soln.	77–1001

No.	Reaction	$k(M^{-1}\,s^{-1})$	pH	I	Method	Comment	Ref.
2.36	Acrylamide $SO_4^- + CH_2 = CHCONH_2$	1.6×10^8	7.3	–	p.r.	–	77–1503
2.37	Acrylate ion $SO_4^- + CH_2 = CHCOO^-$	1.1×10^8	6.5	–	p.r.	–	77–1503
2.38	Acrylonitrile $SO_4^- + CH_2 = CHCN(+H_2O) \rightarrow CH_2OHCHCN + HSO_4^-$	1.7×10^8	~7	–	p.r.	Soln. contains $S_2O_8^{2-}$; product obs. by absorption spectrum.	69–0158
		8.1×10^7	7.4	–	p.r.	–	77–1503
2.39	Alanine $SO_4^- + CH_3CHNH_3^+ COO^-$	$(1.0 \pm 0.1) \times 10^7$	7	0.03	p.r.	D.k.	75–1069
2.40	Allyl alcohol $SO_4^- + CH_2 = CHCH_2OH$	1.5×10^9	6.8	–	p.r.	–	77–1503
2.41	Allyl cyanide $SO_4^- + CH_2 = CHCH_2CN$	1.1×10^9	7	–	p.r.	–	77–1503
2.42	Anisole $SO_4^- + C_6H_5OCH_3 \rightarrow \cdot C_6H_5^+ OCH_3 + SO_4^{2-}$	$(4.9 \pm 0.5) \times 10^9$	–	–	p.r.	P.b.k.; product ident. by esr.	75–1171
2.43	Benzamide $SO_4^- + C_6H_5CONH_2 \rightarrow SO_4^{2-} + \cdot C_6H_5^+ CONH_2$	1.9×10^8	7	0.03	p.r.	D.k. at 450 nm in $\sim 10^{-2}\,M$ $S_2O_8^{2-}$ soln.	77–1001
2.44	Benzene $SO_4^- + C_6H_6 \rightarrow \cdot C_6H_6^+ + SO_4^{2-}$	8.0×10^8	~7	–	p.r.	Soln. contains $S_2O_8^{2-}$; final product ident. by absorption spectrum.	69–0158
	$\cdot C_6H_6^+ (+H_2O) \rightarrow \cdot C_6H_6OH + H^+$	6.7×10^8 (rel.)	9	–	phot.	C.k. with RNO in air-satd. $S_2O_8^{2-}$ soln.; rel. to $k(SO_4^- + EtOH) = 6.2 \times 10^7$.	70–7234
		$\sim 3 \times 10^9$	7	0.03	p.r.	D.k. at 450 nm in $S_2O_8^{2-}$ soln. contg. 0.1 *M* *tert*–BuOH; also p.b.k. at 315 nm (76–1187).	77–1001
	1,3,5–Benzenetricarboxylate ion	*See* Trimesate ion.					
	1,2,4,5–Benzenetetracarboxylate ion	*See* Pyromellitate ion.					
2.45	Benzoate ion $SO_4^- + C_6H_5COO^- \rightarrow SO_4^{2-} + C_6H_5^+ COO^-$ $C_6H_5^+COO^- (+H_2O) \rightarrow HOC_6H_5COO^- + H^+$(1) $C_6H_5^+COO^- \rightarrow \cdot C_6H_5 + CO_2$(2)	1.2×10^9	7	0.03	p.r.	D.k. at 450 nm in $\sim 10^{-2}\,M$ $S_2O_8^{2-}$ soln.; CO_2 yield in γ-r. suggests reaction (2) contributes 56% (78–1505). Absorption of OH adduct in p.r. suggests reaction (1) contributes 20% (78–1504).	77–1001
2.46	Benzonitrile $SO_4^- + C_6H_5CN \rightarrow SO_4^{2-} + \cdot C_6H_5^+ CN$	1.2×10^8	7	0.03	p.r.	D.k. at 450 nm in $\sim 10^{-2}\,M$ $S_2O_8^{2-}$ soln.	77–1001
2.47	Benzyl methyl ether $SO_4^- + C_6H_5CH_2OCH_3$	$k/k_{2\text{-PrOH}} = 18$	1.8	–	therm.	$T = 75°C$; c.k. in $S_2O_8^{2-}$–alcohol soln.; obs. C_6H_5CHO yield.	74–9006
2.48	o–Bromobenzoate ion $SO_4^- + BrC_6H_4COO^- \rightarrow SO_4^{2-} + BrC_6H_4^+ COO^-$ $BrC_6H_4^+ COO^- (+H_2O) \rightarrow \cdot OC_6H_4COO^- + 2H^+ + Br^-$ (1) $BrC_6H_4^+ COO^- (+H_2O) \rightarrow BrC_6H_4(OH)COO^- + H^+$ (2) $BrC_6H_4^+ COO^- \rightarrow \cdot C_6H_4Br + CO_2$(3)	8.7×10^8	7	0.03	p.r.	D.k at 450 nm in $\sim 10^{-2}\,M$ $S_2O_8^{2-}$ soln.; Br^- and CO_2 yields meas. on γ-r. indicate reaction (1) contributes ~16% and reaction (3) ~10% (78–1505).	77–1001

TABLE 2. Rates of reactions of SO_4^- in aqueous solution—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
2.49	*p*–Bromobenzoate ion	1.0×10^9	7	0.03	p.r.	D.k. at 450 nm in ~ 10^{-2} *M* $S_2O_8^{2-}$ soln.; Br^- and CO_2 yields meas. on γ–r. indicate ~ 30% debromination and ~ 40% decarboxylation; see reactions under *o*–bromobenzoate (78–1505).	77–1001
	tert–Butanol *See* 2–Methyl–2–propanol.						
2.50	*p*–Chlorobenzoate ion	3.6×10^8	7	0.03	p.r.	D.k. at 450 nm in ~ 10^{-2} *M* $S_2O_8^{2-}$ soln.; CO_2 yield meas. on γ–r. indicates ~ 40% decarboxylation (78–1505).	77–1001
2.51	Crotonic acid	7.7×10^8	4.8	–	p.r.	–	77–1503
	Crotononitrile *See* Allyl cyanide						
2.52	*p*–Cyanobenzoate ion	3.3×10^7	4.8	0.03	p.r.	D.k. at 450 nm in ~ 10^{-2} *M* $S_2O_8^{2-}$ soln.; CO_2 yield meas. on γ–r. indicates ~ 30% decarboxylation (78–1505).	77–1001
2.53	Cycloheptanol	$k/k_{2\text{-}PrOH} = 2.4$	1.8	–	therm.	$T = 75°C$; c.k. in $S_2O_8^{2-}$–alcohol soln.; obs. ketone formn.; for 1–*d*–cycloheptanol ratio = 1.5.	74–9006
2.54	Cyclohexene $SO_4^- + C_6H_{10}\ (+H_2O) \rightarrow C_6H_{10}OH + HSO_4^-$	4.1×10^8	~ 7	–	p.r.	Soln. contains $S_2O_8^{2-}$; product obs. by absorption spectrum.	69–0158
2.55	Diethyl disulfide $SO_4^- + RSSR \rightarrow SO_4^{2-} + (RSSR)^{\cdot+}$	2.6×10^8	~ 4.5	0.3	p.r.	D.k. at 300 nm in Ar–satd. 0.1 *M* $S_2O_8^{2-}$ soln.	76–1143
2.56	1,2–Dimethoxy–benzene $SO_4^- + DMB \rightarrow SO_4^{2-} + (DMB)^{\cdot+}$	$(5.0 \pm 0.5) \times 10^9$	–	0.003	p.r.	P.b.k.; product ident. by esr and absorption spectra.	75–1171
2.57	1,3–Dimethoxy–benzene $SO_4^- + DMB \rightarrow SO_4^{2-} + (DMB)^{\cdot+}$	$(7.0 \pm 0.7) \times 10^9$	–	0.003	p.r.	P.b.k.; product ident. by esr and absorption spectra.	75–1171
2.58	1,4–Dimethoxy–benzene $SO_4^- + DMB \rightarrow SO_4^{2-} + (DMB)^{\cdot+}$	$(7.2 \pm 0.7) \times 10^9$	–	0.003	p.r.	P.b.k.; product ident. by esr and absorption spectra.	75–1171
2.59	2,3–Dimethoxy–benzoate ion	8.5×10^9	> 3	0.03	p.r.	P.b.k. in Ar–satd. $S_2O_8^{2-}$ soln.	77–1006
2.60	2,4–Dimethoxy–benzoate ion	3.8×10^9	> 3	0.03	p.r.	P.b.k. in Ar–satd. $S_2O_8^{2-}$ soln.	77–1006
2.61	3,4–Dimethoxy–benzoate ion	4.5×10^9	> 3	0.03	p.r.	P.b.k. in Ar–satd. $S_2O_8^{2-}$ soln.	77–1006
2.62	2,6–Dimethoxy–benzoate ion	2.5×10^9	> 3	0.03	p.r.	P.b.k. in Ar–satd. $S_2O_8^{2-}$ soln.	77–1006
2.63	3,5–Dimethoxy–benzoate ion	4.4×10^9	> 3	0.03	p.r.	P.b.k. in Ar–satd. $S_2O_8^{2-}$ soln.	77–1006
2.64	Dimethyl disulfide $SO_4^- + RSSR \rightarrow SO_4^{2-} + (RSSR)^{\cdot+}$	3.8×10^8	~ 4.5	0.3	p.r.	D.k. at 300 nm in Ar–satd. 0.1 *M* $S_2O_8^{2-}$ soln.	76–1143

TABLE 2. Rates of reactions of SO_4^- in aqueous solution—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
2.64a	Dioxane $SO_4^- + C_4H_8O_2 \rightarrow HSO_4^- + C_4H_7O_2$	1.6×10^7	7–8	0.003	p.r.	C.k.; rel. to $k(SO_4^- + TMB) = 2.4 \times 10^9$; obs. buildup of TMB^+ (see 2.108); $k_H/k_D = 1.7$.	78–1076
2.65	Ethanol $SO_4^- + CH_3CH_2OH \rightarrow HSO_4^- + CH_3CHOH$	3×10^7	–	1	p.r.	D.k. at 450 nm; HSO_4 soln.	66–0019
		$(7.7 \pm 2.2) \times 10^7$	4.8	0.03	f.phot.	D.k. in aerated 10^{-2} M $K_2S_2O_8$ soln.	67–7058
		$(6.2 \pm 1.4) \times 10^7$	1.0	1			
		$(3.4 \pm 0.3) \times 10^7$	–	1 M H_2SO_4	f.phot.	D.k. at 455 nm in ceric sulfate–H_2SO_4 soln.	67–7274
		1.6×10^7	7–8	0.003	p.r.	C.k., rel. to $k(SO_4^- + TMB) = 2.4 \times 10^9$; obs. buildup of TMB^+ (see 2.108); $k_H/k_D = 2.4$.	78–1076
2.66	1-(*p*-Ethylphenyl)ethanol	$k/k_{2\text{-PrOH}} = 26$	1.8	–	therm.	$T = 75°C$; c.k. in $S_2O_8^{2-}$ alcohol soln.; obs. ketone formation.	74–9006
2.67	Formate ion $SO_4^- + HCOO^- \rightarrow SO_4^{2-} + CO_2^-$	$(1.7 \pm 0.2) \times 10^8$	7	0.03	p.r.	D.k.; $S_2O_8^{2-}$ soln.	75–1069
		2.7×10^8	7–8	–	phot.	C.k. with fumarate ion in $S_2O_8^{2-}$ soln.; effect of solute on fumarate–SO_4^- adduct obs. by esr; rel. to $k(SO_4^- + OH^-) = 7.3 \times 10^7$.	73–5403
2.68	Formic acid	$(1.35 \pm 0.2) \times 10^6$	–	1 M H_2SO_4	f.phot.	D.k. at 455 nm in ceric sulfate–H_2SO_4 soln.	67–7274
2.69	Fumarate ion $SO_4^- + {}^-OOCCH{=}CHCOO^- \rightarrow {}^-OOCCHCH(OSO_3^-)COO^-$ (1) $SO_4^- + {}^-OOCCH{=}CHCOO^- \rightarrow SO_4^{2-} + {}^-OOCCH{=}CH\cdot + CO_2$ (2)	1.6×10^7	7	–	p.r.	D.k. at 450 nm; $k_1/k_2 \cong 1$ from $G(CO_2)$ by γ-r. (78–1505); adduct obs. by esr (75–5244).	77–1106
2.70	Glycine	$(9 \pm 0.9) \times 10^6$	7	–	p.r.	D.k. in $S_2O_8^{2-}$ soln.	75–1069
2.71	Histidine	$\sim 2.5 \times 10^9$	7	0.03	p.r.	D.k. in $S_2O_8^{2-}$ soln.	75–1069
2.72	Homophthalate ion $SO_4^- + ArCH_2COO^- \rightarrow SO_4^{2-} + ArCH_2 + CO_2$	$(1.1 \pm 0.2) \times 10^9$	7	–	p.r.	D.k. at 450 nm as well as p.b.k. at 328 nm ($ArCH_2\cdot$) in $S_2O_8^{2-}$ soln.; CO_2 yield meas. by γ-r. (78–1505) and absorption of $ArCH_2$ radical by p.r. (78–1504) indicate predominant decarboxylation from side chain.	76–1187
2.73	*p*-Hydroxybenzoate ion $SO_4^- + HOC_6H_4COO^- \rightarrow SO_4^{2-} + \cdot OC_6H_4COO^- + H^+$	2.5×10^9	7	–	p.r.	D.k. in $S_2O_8^{2-}$ soln.	77–1001
2.74	Lysozyme	1.8×10^{10}	7	0.03	p.r.	D.k. in $S_2O_8^{2-}$–*tert*-BuOH soln.	75–1069
2.75	Malonate ion $SO_4^- + {}^-OOCCH_2COO^- \rightarrow SO_4^{2-} + {}^-OOCCH_2 + CO_2$	5.5×10^6	7	–	p.r.	D.k. at 450 nm; radical obs. by esr; CO_2 yield meas. by γ-r. (78–1505).	77–1106
2.76	Methacrylic acid	1.1×10^9	2.9	–	p.r.	–	77–1503
		7×10^8	6.9	–	p.r.		
2.77	Methacrylonitrile	3.8×10^8	7	–	p.r.	–	77–1503

TABLE 2. Rates of reactions of SO_4^- in aqueous solution—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
2.78	Methanol	2×10^7	–	1	p.r.	D.k. at 450 nm.	66-0019
	$SO_4^- + CH_3OH \rightarrow$	$(2.5 \pm 0.4) \times 10^7$	4.8	0.03	f.phot.	D.k. in aerated 10^{-2} *M*	67-7058
	$HSO_4^- + CH_2OH$	$(2.5 \pm 0.6) \times 10^7$	1.0	–		$K_2S_2O_8$ soln.	
		$(1.1 \pm 0.2) \times 10^7$	–	1 *M* H_2SO_4	f.phot.	D.k. at 455 nm in ceric sulfate–H_2SO_4 soln.	67-7274
		7.6×10^6 (rel.)	9	–	phot.	C.k. with RNO in air-satd. $S_2O_8^{2-}$ soln.; rel. to $k(SO_4^- + EtOH) = 6.2 \times 10^7$.	70-7234
		1.3×10^7 (rel.)	7–8	–	phot.	C.k. with fumarate in $S_2O_8^{2-}$ soln.; effect of solute on fumarate–SO_4^- adduct obs. by esr; rel. to $k(SO_4^- + OH^-) = 7.3 \times 10^7$.	73-5403
		$(1.1 \pm 0.1) \times 10^7$	7	0.03	p.r.	D.k. in $S_2O_8^{2-}$ soln.	75-1069
		3.2×10^6	7–8	0.003	p.r.	C.k.; rel. to $k(SO_4^- + TMB) = 2.4 \times 10^9$; obs. buildup of TMB^+ (see 2.108); $k_H/k_D = 2.7$.	78-1076
2.79	Methionine	1.1×10^9	7	0.03	p.r.	D.k. in $S_2O_8^{2-}$ soln.	75-1069
	Methoxybenzene *See* Anisole						
2.80	2-Methoxybenzoate ion	7.0×10^9	> 3	0.03	p.r.	P.b.k. in Ar-satd. $S_2O_8^{2-}$ soln.	77-1006
2.81	3-Methoxybenzoate ion	7.6×10^9	> 3	0.03	p.r.	P.b.k. in Ar-satd. $S_2O_8^{2-}$ soln.	77-1006
2.82	4-Methoxybenzoate ion	3.5×10^9	7	–	p.r.	P.b.k. at 560 nm (cation radical) in $S_2O_8^{2-}$ soln.	77-1001
	$SO_4^- + CH_3OC_6H_4COO^- \rightarrow$ $SO_4^{2-} + CH_3OC_6H_4{}^+COO^-$						
		7.6×10^9	> 3	0.03	p.r.	P.b.k. in Ar-satd. $S_2O_8^{2-}$ soln.	77-1006
2.83	1-Methoxy-2-methyl-1-phenylpropane	$k/k_{2\text{-PrOH}} = 14$	1.8	–	therm.	$T = 75°C$; c.k. in $S_2O_8^{2-}$–alcohol soln.; obs. benzaldehyde and isopropyl phenyl ketone formn.	74-9006
	$SO_4^- + C_6H_5CH(OCH_3)CH(CH_3)_2$						
2.84	Methyl methacrylate	1.0×10^9	7.3	–	p.r.	–	77-1503
	$SO_4^- + CH_2{=}C(CH_3)COOCH_3$						
2.85	2-Methyl-2-propanol	$(9.1 \pm 1.0) \times 10^5$	–	–	p.r.	D.k. in $S_2O_8^{2-}$ soln.	72-7008
	$SO_4^- + (CH_3)_3COH \rightarrow$ $HSO_4 + CH_2C(CH_3)_2OH$	$k/k_{2\text{-PrOH}} = 0.05$	1.8	–	therm.	$T = 75°$ C; c.k. in $S_2O_8^{2-}$–alcohol soln.; obs. acetone formn.	74-9006
		$(8.0 \pm 0.8) \times 10^5$	7	0.03	p.r.	D.k. in $S_2O_8^{2-}$ soln.	75-1069
		4.0×10^5	7–8	0.003	p.r.	C.k.; rel. to $k(SO_4^- + TMB) = 2.4 \times 10^9$; obs. buildup of TMB^+ (see 2.108).	78-1076
2.86	*p*-Nitroso-*N*,*N*-dimethylaniline	2.3×10^9 (rel.)	7	–	phot.	Air-satd. $S_2O_8^{2-}$ soln.; rel. to $k(SO_4^- + EtOH) = 6.2 \times 10^7$.	70-7234
	$SO_4^- + NOC_6H_4N(CH_3)_2$						
2.87	3-Pentanol	$k/k_{2\text{-PrOH}} = 1.3$	1.8	–	therm.	$T = 75°C$; c.k. in $S_2O_8^{2-}$–alcohol soln.; obs. ketone formn.	74-9006
	$SO_4^- + (C_2H_5)_2CHOH$						
2.88	1-Phenyl-3-butanol	$k/k_{2\text{-PrOH}} = 25$	1.8	–	therm.	$T = 75°C$; c.k. in $S_2O_8^{2-}$–alcohol soln.; obs. ketone and acetaldehyde formn.	74-9006
	$SO_4^- + C_6H_5CH_2CH_2CHOHCH_3$						

TABLE 2. Rates of reactions of SO_4^- in aqueous solution—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
2.89	1-Phenylethanol $SO_4^- + C_6H_5CHOHCH_3$	$k/k_{2\text{-PrOH}} = 22$	1.8	–	therm.	$T = 75°C$; c.k. in $S_2O_8^{2-}$–alcohol soln.; obs. ketone formn.	74–9006
2.90	1-Phenyl-2-propanol $SO_4^- + C_6H_5CH_2CHOHCH_3$	$k/k_{2\text{-PrOH}} = 42$	1.8	–	therm.	$T = 75°C$; c.k. in $S_2O_8^{2-}$–alcohol soln.; obs. acetaldehyde formn.	74–9006
2.91	2-Phenyl-2-propanol $SO_4^- + C_6H_5COH(CH_3)_2$	$k/k_{2\text{-PrOH}} = 8.4$	1.8	–	therm.	$T = 75°C$; c.k. in $S_2O_8^{2-}$–alcohol soln.; *obs. ketone formn.*	74–9006
2.92	1-Propanol	4.8×10^7 (rel.)	9	–	phot.	C.k. with RNO in air-satd. $S_2O_8^{2-}$ soln.; rel. to $k(SO_4^- + EtOH) = 6.2 \times 10^7$.	70–7234
		5.8×10^7	7–8	–	phot.	C.k. with fumarate in $S_2O_8^{2-}$ soln.; effect of solute on fumarate-SO_4^- adduct obs. by esr; rel. to $k(SO_4^- + OH^-) = 7.3 \times 10^7$.	73–5403
2.93	2-Propanol	$(8.5 \pm 3.0) \times 10^7$	4.4	–	f.phot.	D.k. in aerated 10^{-2} *M* $K_2S_2O_8$ soln.	67–7058
		$(9.1 \pm 2.8) \times 10^7$	1.0	–			
		$(4.6 \pm 0.2) \times 10^7$	–	1 *M* H_2SO_4	f.phot.	D.k. at 455 nm in ceric sulfate-H_2SO_4 soln.	67–7274
		8.5×10^7 (rel.)	9	–	phot.	C.k. with RNO in air-satd. $S_2O_8^{2-}$ soln.; rel. to $k(SO_4^- + EtOH) = 6.2 \times 10^7$.	70–7234
		4.0×10^7	7–8	–	phot.	C.k. with fumarate in $S_2O_8^{2-}$ soln.; effect of solute on fumarate-SO_4^- adduct obs. by esr; rel. to $k(SO_4^- + OH^-) = 7.3 \times 10^7$.	73–5403
		8.0×10^7	7	0.03	p.r.	D.k. at 450 nm; $S_2O_8^{2-}$–*tert*-BuOH soln.	75–1069
		3.2×10^7	7–8	0.003	p.r.	C.k.; rel. to $k(SO_4^- + TMB) = 2.4 \times 10^9$; obs. buildup of TMB^+ (see 2.108); $k_H/k_D = 2.7$.	78–1076
2.94	Propionate ion $SO_4^- + CH_3CH_2COO^- \rightarrow SO_4^{2-} + CH_3CH_2 + CO_2$	4.6×10^6	7	–	p.r.	D.k. at 450 nm; CO_2 yield obs. by γ-r. (78–1505).	77–1106
2.95	Pyridine $SO_4^- + C_5H_5N$	$(2.2 \pm 0.2) \times 10^8$	7	–	p.r.	D.k. at 450 nm; $S_2O_8^{2-}$ soln.	76–1187
2.96	Pyridinium ion $SO_4^- + C_5H_5NH^+$	$(2.0 \pm 0.4) \times 10^7$	3.9	–	p.r.	D.k. at 450 nm; $S_2O_8^{2-}$ soln.	76–1187
2.97	Pyromellitate ion (1,2,4,5-Benzene-tetracarboxylate ion)	$(1.7 \pm 0.2) \times 10^7$	9	–	p.r.	D.k. at 450 nm; $S_2O_8^{2-}$ soln.	76–1187
2.98	Ribonuclease	1.2×10^{10}	7	0.03	p.r.	D.k. at 450 nm; $S_2O_8^{2-}$–*tert*-BuOH soln.	75–1069
2.99	Serine $SO_4^- + HOCH_2CHNH_3^+COO^-$	2.3×10^7	7	0.03	p.r.	D.k. at 450 nm; $S_2O_8^{2-}$–*tert*-BuOH soln.	75–1069
2.100	Succinate ion $SO_4^- + {}^-OOCCH_2CH_2COO^- \rightarrow SO_4^{2-} + {}^-OOCCH_2CH_2 + CO_2$	7.1×10^6	7	–	p.r.	D.k. at 450 nm; CO_2 yield obs. by γ-r. (78–1505).	77–1106

TABLE 2. Rates of reactions of SO_4^- in aqueous solution—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
2.101	Terephthalate ion $SO_4^- + C_6H_4(COO^-)_2 \rightarrow$ $SO_4^{2-} + C_6H_4COO^- + CO_2$ (1) $SO_4^- + C_6H_4(COO^-)_2(+OH^-) \rightarrow$ $SO_4^{2-} + HOC_6H_4(COO^-)_2$ (2)	1.7×10^8	9	–	p.r.	D.k. at 450 nm; ~ 60% (1) and ~ 40% (2) based on CO_2 yields by γ-r. (78–1505).	77–1001
2.101a	Tetrahydrofuran $SO_4^- + C_4H_8O \rightarrow$ $HSO_4^- + C_4H_7O$	1.0×10^8	7–8	0.003	p.r.	C.k.; rel. to $k(SO_4^- + TMB) = 2.4 \times 10^9$; obs. buildup of TMB^+ (see 2.108); $k_H/k_D = 2.0$.	78–1076
2.102	*o*–Toluate ion $SO_4^- + CH_3C_6H_4COO^- \rightarrow$ $HSO_4^- + \cdot CH_2C_6H_4COO^-$	1.4×10^9	7	–	p.r.	D.k. at 450 nm; product ident. by abs. spectrum by p.r. (78–1504); CO_2 yield by γ-r. < 10% (78–1505).	77–1001
2.103	*m*–Toluate ion	2.0×10^9	7	–	p.r.	D.k. at 450 nm.; abs. spectrum by p.r. indicates predominant formation of OH adducts (78–1504).	77–1001
2.104	*p*–Toluate ion $SO_4^- + CH_3C_6H_4COO^- \rightarrow$ $SO_4^{2-} + CH_3C_6H_4 + CO_2$ (1) $SO_4^- + CH_3C_6H_4COO^- \rightarrow$ $SO_4^{2-} + CH_3C_6H_4COO^-$ (2) $SO_4^- + CH_3C_6H_4COO^- (+OH^-) \rightarrow$ $SO_4^{2-} + CH_3C_6H_4(OH)COO^-$ (3)	1.8×10^9	7	–	p.r.	D.k. at 450 nm; ~ 30% (1), 30% (2) and 40% (3) based on CO_2 yields by γ-r. (78–1505) and abs. spectra by p.r. (78–1504).	77–1001
2.105	Trimesate ion (1,3,5–Benzenetri–carboxylate ion)	$(8.3 \pm 0.8) \times 10^7$	9	–	p.r.	D.k. at 450 nm.	76–1187
2.106	1,2,3–Trimethoxy–benzene	~ (6 to 8) $\times 10^9$	–	0.003	p.r.	P.b.k.; product ident. by optical absorption and esr spectra.	75–1171
2.107	1,2,4–Trimethoxy–benzene	$(7.8 \pm 0.8) \times 10^8$	–	0.003	p.r.	P.b.k.; product ident. by optical absorption and esr spectra (see 2.108).	75–1171
2.108	1,3,5–Trimethoxy–benzene (TMB) $SO_4^- + TMB \rightarrow$ $SO_4^{2-} + (TMB)^{\cdot +}$	$(1.8 \pm 0.2) \times 10^9$ $(2.4 \pm 0.5) \times 10^9$	– 7–8	0.003 0.003	p.r. p.r.	P.b.k.; product ident. by optical absorption and esr spectra. P.b.k. at 580 nm.	75–1171 78–1076
2.109	2,3,4–Trimethoxy–benzoate ion	2.5×10^9	> 3	0.03	p.r.	P.b.k. in Ar–satd. $S_2O_8^{2-}$ soln.	77–1006
2.110	3,4,5–Trimethoxy–benzoate ion	5.0×10^9	> 3	0.03	p.r.	P.b.k. in Ar–satd. $S_2O_8^{2-}$ soln.	77–1006
2.111	2,4,5–Trimethoxy–benzoate ion	4.4×10^9	> 3	0.03	p.r.	P.b.k. in Ar–satd. $S_2O_8^{2-}$ soln.	77–1006
2.112	2,4,6–Trimethoxy–benzoate ion	2.6×10^9	> 3	0.03	p.r.	P.b.k. in Ar–satd. $S_2O_8^{2-}$ soln.	77–1006
2.113	Trimethylanilinium ion $SO_4^- + C_6H_5N(CH_3)_3^- \rightarrow$ $SO_4^{2-} + \cdot C_6H_5^+N(CH_3)_3^+$	1.5×10^8	7	–	p.r.	D.k. at 450 nm; $S_2O_8^{2-}$ soln.	77–1001
2.114	Tryptophan	~ 2.3×10^9	7	0.03	p.r.	D.k. at 450 nm; $S_2O_8^{2-}$–*tert*–BuOH soln.	75–1069
2.115	Tyrosine $SO_4^- + ArOH \rightarrow$ $SO_4^{2-} + ArOH^+$ $ArOH^+ \rightarrow ArO\cdot + H^+$	3.2×10^9 $(3.0 \pm 0.2) \times 10^9$	7 6.8	0.03 –	p.r. p.r.	D.k. at 450 nm; $S_2O_8^{2-}$–*tert*–BuOH soln. D.k. at 450 nm as well as p.b.k. at 407 nm (aryloxy radical).	75–1069 76–1112
2.116	Vinyl acetate $SO_4^- + AcOCHCH_2 (+H_2O) \rightarrow$ $AcOCHCH_2OH + HSO_4^-$	1.1×10^9	~ 7	–	p.r.	Soln. contains $S_2O_8^{2-}$; product obs. by absorption spectrum.	69–0158

TABLE 3. Rates of reaction of SO_2^-, SO_3^-, $S_2O_3^-$, $S_2O_2^-$, SO_5^-, SeO_2^- and SeO_3^- in aqueous solution

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
3.1	$2SO_2^- \rightarrow S_2O_4^{2-}$	$2k = (1.0 \pm 0.1) \times 10^{10}$	~4	→0	f.phot.	D.k. at 370 nm, as well as p.b.k. at 330 nm in 0.06 *M* HSO_3^- soln.; assumed $\epsilon(330\ nm) = 5700\ M^{-1}\ cm^{-1}$; $2k \leqslant 1.3 \times 10^{10}$ based on $2k/\epsilon(370) \cong 2.5 \times 10^7$.	72–7008
		$2k = (1.3 \pm 0.4) \times 10^9$	acid	–	p.r.	D.k. at 360 nm ($\epsilon = 600\ M^{-1}\ cm^{-1}$) as well as p.b.k. at 320 nm in $SO_2 + HSO_3^-$ soln.	74–1033
		$2k = (2.2 \pm 0.3) \times 10^9$	3.1	~1	p.r.	P.b.k. at 320 nm in 10^{-3} *M* HSO_3^-/SO_2 soln. contg. 1 *M* $HCOO^-$/HCOOH; $\epsilon(320) \cong 8500\ M^{-1}\ cm^{-1}$.	75–1118
3.2	$2SO_3^- \rightarrow SO_3 + SO_3^{2-}$ $2SO_3^- \rightarrow S_2O_6^{2-}$	–	–	0.03	f.phot.	D.k. at 270–290 nm in N_2 or air–satd. SO_3^{2-} soln.; $2k/\epsilon = 1.3$ to 1.9×10^6.	68–7072
		–	–	0.03	f.phot.	D.k. at 275 nm in air-free 0.1 *M* $Na_2S_2O_6$ soln.; $2k/\epsilon = (3.5 \pm 2.0) \times 10^6$.	68–7281
		$2k = 1.9 \times 10^9$ (rel.)	11.8	0.03	*e*–r.	Obs. steady-state SO_3^- concn. by esr in N_2O–satd. SO_3^{2-} soln.; rel. to $2k(\cdot CH_2CO_2^- + \cdot CH_2CO_2^-) = 1.0 \times 10^9$.	72–5049
		$2k = (1.1 \pm 0.2) \times 10^9$	3.7–9.8	→0	f.phot.	D.k. at 255–320 nm in SO_3^{2-}/HSO_3^- soln.; $2k/\epsilon = 8.3 \times 10^5 - 3.6 \times 10^6$; same in $S_2O_6^{2-}$ soln.	72–7008
		$2k = 8.5 \times 10^8$	5.4, 10.2	→0	p.r.	D.k. in SO_3^{2-}/HSO_3^- soln.	72–7008
		$2k = 5.4 \times 10^8$ (rel.)	–	–	phot.	C.k. in soln. contg. 1.6×10^{-3} *M* SO_3^{2-}, 0.68 *M* acetone and 10^{-3} *M* $Na_4B_2O_7$; rel. to $2k = 1.4 \times 10^9$ for second-order decay of $(CH_3)_2COH$.	73–5022
		$2k = (1.4 \pm 0.2) \times 10^9$ $2k = (0.85 \pm 0.2) \times 10^9$	10 5	–	p.r.	D.k. at 255 nm ($\epsilon = 1200 \pm 50\ M^{-1}\ cm^{-1}$) in SO_2/HSO_3^- soln., $k = 1.4 \times 10^9$ by pulse conductivity at pH 9.5; sulfate is formed by hydrolysis of SO_3; rel. amounts of sulfate and dithionate formed depend on pH.	74–1033
3.3	$SO_3^- + N_2O \rightarrow SO_3 + O^- + N_2$	$(3.5 \pm 1.0) \times 10^7$	13	1	p.r.	D.k. at 260 nm in N_2O–satd. soln. contg. 0.002 *M* SO_3^{2-}; best fit with $k(O^- + SO_3^{2-}) = 2.5 \times 10^8$ and $\epsilon(260\ nm)$ for $SO_3^- = 1300\ M^{-1}\ cm^{-1}$.	71–0461
3.4	$SO_3^- + O_2 \rightarrow SO_5^-$	$< 10^9$	–	–	f.phot.	Estd.	72–7008
3.5	$SO_3^- + CH_3CH_2OH$	$\leqslant 2 \times 10^3$	–	0.1	f.phot.	D.k. at 270 nm in N_2–satd. 0.1 *M* $S_2O_6^{2-}$ soln.	72–7008
3.6	$SO_3^- + (CH_3)_2CHOH$	$\leqslant 10^3$	–	0.1	f.phot.	D.k. in N_2–satd. 0.1 *M* $S_2O_6^{2-}$ soln.	72–7008

TABLE 3. Rates of reaction of SO_2^-, SO_3^-, $S_2O_3^-$, $S_2O_2^-$, SO_5^-, SeO_2^- and SeO_3^- in aqueous solution—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
3.7	$S_2O_3^- + S_2O_3^-$	$2k = (7.1 \pm 1.8) \times 10^9$	7	0.003	f.phot.	D.k. at 380 nm in N_2–satd. $S_2O_3^{2-}$ soln.; $2k/\epsilon = 4.1 \times 10^6$; same at pH 10.9; addn. of ethanol, carbonate ion or allyl alcohol did not affect the decay rate.	68–7072
3.8	$S_2O_3^- + S_2O_3^{2-} \rightarrow S_4O_6^{3-}$	8×10^8	4.5, 9.6	<0.002	p.r.	P.b.k. at 370 nm or d.k. at 320 nm in $S_2O_3^{2-}$ soln.; $k = 1.8 \times 10^9$ at I = 0.1.	73–1027
3.9	$S_2O_2^- + S_2O_2^-$	$2k/\epsilon \cong 5 \times 10^4$	7, 10.9	0.003	f.phot.	D.k. at 270 nm in $S_2O_3^{2-}$ soln.; addn. of O_2, methanol, ethanol or allyl alcohol did not affect the decay rate.	68–7072
3.10	$SO_5^- + SO_5^-$	$2k \cong 4 \times 10^8$	–	1	p.r.	D.k. in N_2O–satd. HSO_5^- soln.; $\epsilon(265\ nm) > 560\ M^{-1}\ cm^{-1}$; not simple order.	72–7008
3.11	$SO_5^- + CH_3CH_2OH$	$< 10^3$	9	–	f.phot.	D.k. in air–contg. $S_2O_6^{2-}$ soln.	72–7008
3.12	$2\ SeO_2^- \rightarrow Se_2O_4^{2-}$	$2k/\epsilon = 8.8 \times 10^5$ $2k/\epsilon = 9.2 \times 10^5$	6.2 4.5–7.5	–	p.r.	D.k. in soln. of SeO_2 contg. 2–methyl–2–propanol; $\lambda_{max} = 330$ nm; $\epsilon_{max} = 1450\ M^{-1}\ cm^{-1}$.	77–1173
3.13	$2\ SeO_3^- \rightarrow Se_2O_6^{2-}$ or $\rightarrow SeO_3 + SeO_3^{2-}$	$2k/\epsilon = 4.0 \times 10^5$	9–11	–	p.r.	D.k. in soln. of SeO_2 contg. N_2O; $\lambda_{max} = 430$ nm; $\epsilon_{max} = 1350\ M^{-1}\ cm^{-1}$.	77–1173
3.14	$2\ HSeO_3 \rightarrow$ products	$2k/\epsilon = 7.5 \times 10^5$	5–6	–	p.r.	D.k. in soln. of SeO_2 contg. N_2O; $\lambda_{max} = 430$ nm; $\epsilon_{max} = 600\ M^{-1}\ cm^{-1}$.	77–1173
3.15	$2\ H_2SeO_3^+ \rightarrow$ products	$2k/\epsilon = 2.1 \times 10^6$	1	–	p.r.	D.k. in soln. of SeO_2 contg. $HClO_4$; $\lambda_{max} = 430$ nm; $\epsilon = 930\ M^{-1}\ cm^{-1}$.	77–1173
3.16	$SeO_3^- +$ tryptophan	$(3.4 \pm 0.4) \times 10^9$	7.4	0.006	p.r.	D.k. in N_2O–satd. SeO_3^{2-} soln.	76–1151

TABLE 4. Rates of reaction of NO_3, NO_2, N_2O_4, NO_3^{2-}, N_2O_3, NO_2^{2-} in aqueous solution

Reaction	$k(M^{-1} s^{-1})$	pH	I	Method	Comment	Ref.
$NO_3 \rightarrow$ first order decay	$(7.59 \pm 0.21) \times 10^3\ s^{-1}$	acid	–	p.r.	D.k. at 635 nm in 0.1–4 *M* HNO_3.	67–0002
	$9.5 \times 10^2\ s^{-1}$	acid	–	f.phot.	D.k. in 0.1–6 *M* HNO_3 contg. $K_2Ce(NO_3)_6$.	67–7274
	$9.7 \times 10^3\ s^{-1}$	2.8	–	p.r.	D.k. at 670 nm in 4 *M* $NaNO_3$; *k* varies with dose, concn. and pH, $k \sim 3 \times 10^4\ s^{-1}$ at pH 7.	69–0417
	$8 \times 10^3\ s^{-1}$	acid	–	p.r.	D.k. at 600 nm in 0.2–15 *M* HNO_3; 1st and 2nd order rates detd. by graphical method; dependent on dose and concn.	74–1140
	$(1.6 \pm 0.2) \times 10^5\ s^{-1}$	nat	–	p.r.	D.k. at 635 nm in 5.0 and 7.35 *M* $NaNO_3$ soln.; discrepancy in *k* values attributed to dose rate effects.	76–1171
$NO_3 + NO_3 \rightarrow N_2O_6$	$2k = 8.4 \times 10^8$	acid	–	p.r.	D.k. at 670 nm in 1–4.0 *M* $NaNO_3$, ≥ 0.12 *M* HNO_3 soln.; $2k/\epsilon = 2.8 \times 10^6$.	69–0417
	$2k = (0.79 \pm 0.04) \times 10^6$	acid	–	f.phot.	D.k. at 635 nm in 3.5–15 *M* HNO_3 and 10^{-3} *M* $(NH_4)_2Ce(NO_3)_6$; ϵ(635 nm) $= 250 \pm 90\ M^{-1} cm^{-1}$.	70–7728
	$2k = 3.7 \times 10^8$	acid	–	p.r.	D.k. at 600 nm in 0.2–15 *M* HNO_3; ϵ(600 nm) $= 285\ M^{-1} cm^{-1}$; $2k/\epsilon = 1.3 \times 10^6$ (±20%).	74–1140
$NO_3 + Ce^{III} \rightarrow Ce^{IV} + NO_3$	$(1.70 \pm 0.04) \times 10^6$	acid	–	f.phot.	D.k. at 635 nm in 6 *M* HNO_3 contg. 10^{-3} *M* $(NH_4)_2Ce(NO_3)_6$; $E_a = 1.0 \pm 0.2$ kcal mol^{-1} (4.2 ± 0.8 kJ mol^{-1}) based on 6 runs at 50°C; *k* in 1–15 *M* HNO_3 varied from 0.64×10^6 to 4.1×10^6 indicating presence of several Ce^{III} complexes.	64–7009 70–7727
	$(3.70 \pm 0.1) \times 10^5$	nat	–	f.phot.	D.k. at 600 nm in 0.1 *M* $K_2Ce(NO_3)_6$ contg. $Ce(NO_3)_3$.	67–7274
	$(1.3 \pm 0.3) \times 10^6$	acid	–	p.r.	D.k. at 600 nm in 2 *M* HNO_3 contg. 10^{-2} *M* Ce^{III}; cor. for $NO_3 + NO_3$.	74–1140
$NO_3 + Cl^-$	1.0×10^8	–	–	p.r.	P.b.k. at 345 nm (Cl_2^-) in 2 *M* NO_3^- soln.	76–1141
$NO_3 + Fe^{2+}$	$(8.0 \pm 1.6) \times 10^6$	acid	–	p.r.	D.k. at 600 nm in 2 *M* HNO_3 contg. 10^{-3} *M* Fe^{2+}; cor. for $NO_3 + NO_3$.	74–1140
$NO_3 + NO_2^-$	1.2×10^9	7	–	p.r.	D.k.	69–0417
$NO_3 + Tl^I$	$(3.46 \pm 0.1) \times 10^7$	–	–	f.phot.	D.k. at 600 nm.	67–7274
Acetic acid $NO_3 + CH_3COOH$	$(4.6 \pm 0.4) \times 10^4$	–	–	f.phot.	D.k. at 600 nm.	67–7274
2,6–Disulfoanthraquinone radical ion (A^-) $NO_3 + A \rightarrow NO_3^- + A$	1.0×10^{11}	8.0	–	f.phot.	D.k.	73–7569
Ethanol $NO_3 + CH_3CH_2OH$	$(3.9 \pm 0.4) \times 10^6$	2	–	f.phot.	D.k. at 600 nm.	67–7274
	$(2.2 \pm 0.4) \times 10^6$	acid	–	p.r.	D.k. at 600 nm in 5 *M* HNO_3; cor. for $NO_3 + NO_3$.	74–1140

TABLE 4. Rates of reaction of NO_3, NO_2, N_2O_4, NO_3^{2-}, N_2O_3, NO_2^{2-} in aqueous solution—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment
4.11	Ethylene glycol $NO_3 + CH_2OHCH_2OH$	$(1.6 \pm 0.3) \times 10^6$	acid	–	p.r.	D.k. at 600 nm in 5 *M* HNO_3; cor. for $NO_3 + NO_3$.
4.12	Formic acid $NO_3 + HCOOH$	$(2.06 \pm 0.1) \times 10^5$	–	–	f.phot.	D.k. at 600 nm.
4.13	Glycerol $NO_3 + CH_2OHCHOHCH_2OH$	$(1.8 \pm 0.4) \times 10^6$	acid	–	p.r.	D.k. at 600 nm in 5 *M* HNO_3; cor. for $NO_3 + NO_3$.
4.14	Methanol $NO_3 + CH_3OH$	$(1.0 \pm 0.1) \times 10^6$	–	–	f.phot.	D.k. at 600 nm.
		$(1.2 \pm 0.2) \times 10^6$	acid		p.r.	D.k. at 600 nm in 5 *M* HNO_3; cor. for $NO_3 + NO_3$.
4.15	2–Propanol $NO_3 + (CH_3)_2CHOH$	$(3.6 \pm 0.2) \times 10^6$	–	–	f.phot.	D.k. at 600 nm.
		$(2.3 \pm 0.5) \times 10^6$	acid	–	p.r.	D.k. at 600 nm in 5 *M* HNO_3; cor. for $NO_3 + NO_3$.
4.16	$NO_2 + NO_2 \rightarrow N_2O_4$	$2k = (7.6 \pm 2.7) \times 10^7$	–	–	f.phot.	C.k. with ferrocyanide ion in NO_3^- soln.; obs. effect of intensity on buildup of ferricyanide at 420 nm; assumed $\epsilon_{Fe}/\epsilon_{NO2} \cong 10$ and $k(NO_2 + Fe(CN_6)^{4-}) = 4.3 \times 10^6$.
		$2k = 3 \times 10^7$	7	–	p.r.	D.k. at 400 nm in $NaNO_3$ (>0.5 *M*) soln.; $2k/\epsilon = 1.44 \times 10^5$; assumed $\epsilon_{400} \cong 208\ M^{-1}\ cm^{-1}$.
		$2k = (9.0 \pm 2.0) \times 10^8$	–	–	p.r.	D.k. at 400 nm in NO_2^- soln. saturated with N_2O; $K = 1.53 \times 10^{-5}\ M$ for $N_2O_4 \rightleftharpoons 2NO_2$.
		$2k = (9.2 \pm 3.0) \times 10^8$	–	–	p.r.	D.k. at 410 nm in NO_2^- soln. saturated with N_2O.
4.17	$NO_2 + Fe(CN)_6^{4-} \rightarrow NO_2^- + Fe(CN)_6^{3-}$	$(4.3 \pm 1.0) \times 10^6$	7	–	f.phot.	P.b.k. at 420 nm in NO_3^- soln.
4.18	$NO_2 + NO \rightarrow N_2O_3$	1.1×10^9	7	–	p.r.	D.k. at 400 nm in NO–N_2O soln.; $k_r = 8.0 \times 10^4\ s^{-1}$.
4.19	N_2O_4 (+ H_2O) $\rightarrow$	$(1.0 \pm 0.1) \times 10^5\ s^{-1}$	7	–	p.r.	–
	$NO_2^- + NO_3^- + 2H^+$	$(6.0 \pm 1.0) \times 10^4\ s^{-1}$	–	–	p.r.	D.k. at 350 nm.
4.20	$NO_3^{2-} + H_2O \rightarrow NO_2 + 2OH^-$	1.0×10^3	alk.	–	p.r.	D.k. at 290 nm; also condy. change; 400 nm absorption obs. (NO_3); $pK = 7.8, 4.8$ for $(H^+ +)$ $NO_3^{2-} \rightleftharpoons HNO_3^- (+ H^+) \rightleftharpoons H_2NO_3$.
		1.3×10^3	–	–	p.r.	Conductivity change in NO_3^- soln. contg. 0.2 *M* MeOH.
		1.6×10^3	–	–	p.r.	D.k. at 260 nm.
4.21	$HNO_3^- \rightarrow NO_2 + OH^-$	–	–	–	p.r.	$t_{0.5} = 3\mu s$.
4.22	$NO_3^{2-} + O_2 \rightarrow NO_3^- + O_2^-$	2×10^8 (rel.)	12	–	γ–r.	Evaluated $k/k(NO_3^{2-} + H_2O) = 2 \times 10^5$ from dependence of $G(NO_3^-)$ on $[O_2]$; assume $k(NO_3^{2-} + H_2O) = 1 \times 10^3$.
4.23	$NO_3^{2-} + H_2PO_4^- \rightarrow HNO_3^- + HPO_4^{2-}$	5×10^8	7	–	p.r.	D.k. at 290 nm.

TABLE 4. Rates of reaction of NO_3, NO_2, N_2O_4, NO_3^{2-}, N_2O_3, NO_2^{2-} in aqueous solution—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
4.24	$N_2O_3 (+ H_2O) \rightarrow 2NO_2^- + 2H^+$	$5.3 \times 10^2\ s^{-1}$	5	–	p.r.	D.k. at 260 nm as well as condy. change in NO_2^-–NO–N_2O soln.; $K(N_2O_3 \rightleftharpoons NO + NO_2) = 7.3 \times 10^{-5}\ M$. (See also 70–7264).	70–0228
4.25	$NO_2^{2-} + H_2O \rightarrow NO + 2OH^-$	1.0×10^3	9.0	–	p.r.	D.k. at 270 nm; soln. contains 0.25 *M tert*–BuOH; $pK = 7.7, 5.7$ for $(H^+ +)$ $NO_2^{2-} \rightleftharpoons HNO_2^- (+ H^+) \rightleftharpoons H_2NO_2$. (See also 70–7264).	69–0439
		$(7.7 \pm 1.7) \times 10^2$	–	–	p.r.	D.k. at 270 nm.	76–1181

TABLE 5. Rates of reaction of PO_4^{2-} in aqueous solution

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
5.1	$H_2PO_4 + H_2PO_4 \rightarrow H_4P_2O_8$	$2k \cong 1 \times 10^9$	3.5, 4.1	~1	p.r.	D.k. at 500 nm in 1 *M* $H_2PO_4^-$ contg. N_2O; $2k/\epsilon = 2.5 \times 10^6$; $\epsilon \cong 400\ M^{-1}\ cm^{-1}$.	70-0302
		$2k = (2.5 \pm 0.5) \times 10^8$	3.8	-	p.r.	D.k. at 500 nm in 1-3 *M* phosphate satd. with N_2O; interpreted from $2k/\epsilon = (11 \pm 1) \times 10^3$ cm s^{-1} and $\epsilon = 230\ M^{-1}\ cm^{-1}$.	73-1050
5.2	$HPO_4^- + HPO_4^- \rightarrow H_2P_2O_8^{2-}$	$2k = 4.7 \times 10^8$	6.6-8.2	~3	p.r.	D.k. at 500 nm in 1 *M* HPO_4^{2-} contg. N_2O; $2k/\epsilon = 5.5 \times 10^5 - 6.1 \times 10^5$; $\epsilon \cong 800\ M^{-1}\ cm^{-1}$.	70-0302
		$2k \cong 1.4 \times 10^8$	~9	→0	p.r.	D.k. at 500 nm in N_2O-satd. 0.3 *M* phosphate; interpreted from $2k/\epsilon \cong 3\text{-}7 \times 10^3$ cm s^{-1} and $\epsilon = 720\ M^{-1}\ cm^{-1}$.	73-1050
5.3	$PO_4^{2-} + PO_4^{2-} \rightarrow P_2O_8^{4-}$	$2k \cong 1 \times 10^9$	11.2-11.7	~6	p.r.	D.k. at 500 nm in 1 *M* PO_4^{3-} contg. N_2O; $2k/\epsilon = 1.9 \times 10^5 - 2.4 \times 10^5$; $\epsilon = 4800\ M^{-1}\ cm^{-1}$.	70-0302
		$2k = (1.0 \pm 0.2) \times 10^8$	~12	→0	p.r.	D.k. at 500 nm in N_2O-satd. 0.3 *M* phosphate; interpreted from $2k/\epsilon \cong 10^3$ cm s^{-1} and $\epsilon = 2700\ M^{-1}\ cm^{-1}$.	73-1050
5.4	$HPO_4^- + Br^- \rightarrow HPO_4^{2-} + Br$	6.5×10^6	9	~0.2	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78-1075
5.5	$H_2PO_4 + Br^-$	8×10^8	4	~0.06	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78-1075
5.6	$HPO_4^- + Cl^-$	$\leqslant 10^4$	7	~0.12	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78-1075
5.7	$H_2PO_4 + Cl^- \rightarrow H_2PO_4^- + Cl$	2.2×10^6	4	~0.06	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78-1075
5.8	$PO_4^{2-} + I^- \rightarrow PO_4^{3-} + I$	3×10^8	12	~0.2	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78-1075
5.9	$HPO_4^- + N_2H_4$	4.9×10^8	9.4	~0.2	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78-1075
5.10	$HPO_4^- + N_2H_5^+$	1.4×10^8	7	~0.12	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78-1075
5.11	$H_2PO_4 + N_2H_5^+$	1.9×10^8	4	~0.06	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78-1075
5.12	$HPO_4^- + N_3^-$	1.1×10^9	7	~0.12	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78-1075
5.13	$HPO_4^- + NH_2OH$	4.9×10^8	9	~0.2	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78-1075
5.14	$H_2PO_4 + NH_3OH^+$	1.2×10^7	4	~0.06	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78-1075
5.15	$HPO_4^- + NO_2^- \rightarrow HPO_4^{2-} + NO_2$	1.4×10^7	7	~0.12	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78-1075
5.16	$PO_4^{2-} + OH^- \rightarrow PO_4^{3-} + OH$	$(2.0 \pm 0.2) \times 10^5$	>12	~1	p.r.	D.k. at 500 nm in 0.3 *M* HPO_4^{2-} soln.; first order decay rate 9.15×10^3 at pH 12.65.	73-1050
		5×10^5	>12	~0.2	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78-1075
5.17	$HPO_4^- + H_2O_2 \rightarrow HPO_4^{2-} + 2H^+ + O_2^-$	$(2.7 \pm 1.0) \times 10^7$	9.0	0.1	f.phot.	D.k. at 500 nm in 0.03 *M* Na_2HPO_4 soln.	70-0326
5.18	$H_2PO_4 + H_2O_2$	$(5.5 \pm 1.0) \times 10^7$	4.5	0.1	f.phot.	D.k. at 500 nm in 0.1 *M* NaH_2PO_4 soln.	70-0326

TABLE 5. Rates of reaction of PO_4^{2-} in aqueous solution — Continued

No.	Reaction	$k(M^{-1} s^{-1})$	pH	I	Method	Comment	Ref.
5.19	$PO_4^{2-} + HPO_3^{2-} \rightarrow PO_4^{3-} + H^+ + PO_3^{2-}$	5.5×10^5	12	~0.2	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78–1075
5.20	$HPO_4^- + HPO_3^{2-}$	5.9×10^6	9	~0.2	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78–1075
5.21	$H_2PO_4 + H_2PO_3^-$	4×10^7	4	~0.06	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78–1075
5.22	$PO_4^{2-} + H_2PO_2^- \rightarrow PO_4^{3-} + H^+ + HPO_2^-$	7.9×10^7	12	~0.2	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78–1075
5.23	$HPO_4^- + H_2PO_2^-$	5.9×10^7	7	~0.12	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78–1075
5.24	$H_2PO_4 + H_2PO_2^-$	3.9×10^8	4	~0.06	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78–1075
5.25	$HPO_4^- + HPO_5^{2-} \rightarrow H_2PO_4^- + PO_5^{2-}$	$< 10^5$	–	–	p.r.	D.k. at 520 nm.	77–1047
5.26	$PO_4^{2-} + SO_3^{2-} \rightarrow PO_4^{3-} + SO_3^-$	4.1×10^7	12	~0.2	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78–1075
5.27	$HPO_4^- + SO_3^{2-}$	2.7×10^7	9	~0.2	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78–1075
5.28	$H_2PO_4 + HSO_3^-$	2.7×10^8	4	~0.06	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78–1075
5.29	$HPO_4^- + S_2O_3^{2-}$	1.0×10^8	7	~0.12	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78–1075
5.30	$HPO_4^- + S_2O_5^{2-}$	1.9×10^8	7	~0.12	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	78–1075
5.31	Acetate ion $HPO_4^- + CH_3COO^- \rightarrow H_2PO_4^- + CH_2COO^-$	8.5×10^4	7.1	~0.12	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
5.32	Acetic acid $H_2PO_4 + CH_3COOH \rightarrow H_3PO_4 + CH_2COOH$ (1) $H_2PO_4 + CH_3COOH \rightarrow H_3PO_4 + CO_2 + CH_3$ (2)	3.4×10^5	3.6	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.; $k_1/k_2 \cong 0.5$ detd. *from* CO_2 *yields by* γ*–r.* (78–1505).	77–1106
5.33	Acetone $H_2PO_4 + CH_3COCH_3 \rightarrow H_3PO_4 + CH_2COCH_3$	3.3×10^5	3.2–4.6	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
5.34	Acrylamide	$\leqslant 10^6$	7.4	~0.12	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	77–1503
		2.2×10^8	4	~0.06	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	77–1503
5.35	Acrylic acid $HPO_4^- + CH_2{=}CHCOO^- \rightarrow {}^-HO_3POCH_2CHOO^-$	6.2×10^6	7.5	~0.12	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.; product radical obs. by esr (77–5209).	77–1503
	$H_2PO_4 + CH_2{=}CHCOOH \rightarrow H_2O_3POCH_2CHCOOH$	1.6×10^8	4	~0.06	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	77–1503
5.36	Acrylonitrile	4.4×10^7	7.3	~0.12	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	77–1503
		6×10^7	3.8	~0.06	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	77–1503
5.37	Alanine $PO_4^{2-} + CH_3CH(NH_2)COO^-$	1.6×10^7	12	~0.2	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
5.38	Allyl alcohol	2.1×10^8	7	~0.12	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	77–1503
		1.4×10^9	4	~0.06	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	77–1503
5.39	Allyl cyanide	3.4×10^7	7.2	~0.12	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	77–1503
		8.8×10^8	4	~0.06	p.r.	D.k. at 520 nm in 0.02 *M* $Li_4P_2O_8$ soln.	77–1503

TABLE 5. Rates of reaction of PO_4^{2-} in aqueous solution — Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
5.40	*p*–Aminobenzoic acid $H_2PO_4 + NH_2C_6H_4COOH$	1.5×10^9	3.3	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
5.41	Benzoate ion $HPO_4^- + C_6H_5COO^-$	$\leqslant 10^7$	7.1	~0.12	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
5.42	Benzoic acid $H_2PO_4 + C_6H_5COOH \rightarrow (C_6H_5COOH)^+ + H_2PO_4^-$ $(C_6H_5COOH)^+ \rightarrow C_6H_5 + CO_2 + H^+$ (1) $(C_6H_5COOH)^+ + H_2O \rightarrow HOC_6H_5COOH$ (2)	2.4×10^8	3.2	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.; $k_1/k_2 \cong 1$ detd. from CO_2 yield by γ-r. (78–1505).	77–1106
5.43	*p*–Chlorobenzoate ion $H_2PO_4 + ClC_6H_4COO^-$	4.8×10^7	5.0	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
5.44	*p*–Chlorobenzoic acid $H_2PO_4 + ClC_6H_4COOH$	1.0×10^8	3.3	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
5.45	Crotonate ion $HPO_4^- + CH_3CH{=}CHCOO^-$	3.5×10^6	7.4	~0.12	p.r.	–	77–1503
5.46	Crotonic acid $H_2PO_4 + CH_3CH{=}CHCOOH$	4.5×10^8	4	~0.06	p.r.	–	77–1503
5.47	*p*–Cyanobenzoate ion $H_2PO_4 + CNC_6H_4COO^-$	1.0×10^7	4.6	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
5.47a	*p*–Cyanophenoxide ion	1.9×10^8	11.2	~0.2	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1503
5.48	Deoxyribose $HPO_4^- + C_5H_9O_5 \rightarrow H_2PO_4^- + C_5H_8O_5$	$(7.5 \pm 1.2) \times 10^7$	9.0	–	f.phot.	D.k. at 500 nm in 0.03 *M* HPO_4^{2-}.	70–0326
5.49	Dihydrouracil	$\leqslant (2.9 \pm 0.6) \times 10^7$	9.0	–	f.phot.	D.k. at 500 nm in 0.03 *M* HPO_4^{2-}.	70–0326
5.50	Ethanol						
	$PO_4^{2-} + CH_3CH_2OH \rightarrow HPO_4^{2-} + CH_3CHOH$	1.9×10^7	12.0	~0.2	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
	$HPO_4^- + CH_3CH_2OH \rightarrow H_2PO_4^- + CH_3CHOH$	$(4.0 \pm 0.6) \times 10^7$	9.0	–	f.phot.	D.k. at 500 nm in 0.03 *M* HPO_4^{2-}.	70–0326
		2.0×10^7	7	~0.12	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
	$H_2PO_4 + CH_3CH_2OH \rightarrow H_3PO_4 + CH_3CHOH$	7.7×10^7	4	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
5.51	Formate ion						
	$PO_4^{2-} + HCOO^- \rightarrow HPO_4^{2-} + COO^-$	2.2×10^7	12	~0.2	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
	$HPO_4^- + HCOO^- \rightarrow H_2PO_4^- + COO^-$	$(2.9 \pm 0.7) \times 10^7$	9.0	–	f.phot.	D.k. at 500 nm in 0.03 *M* HPO_4^- soln.	70–0326
		2.5×10^7	7	~0.12	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
	$H_2PO_4 + HCOO^- \rightarrow H_3PO_4 + COO^-$	1.5×10^8	4.5	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
5.52	Fumaric acid $H_2PO_4 + HOOCCH{=}CHCOOH \rightarrow HOOCCHCH(COOH)OPO_3H_2$	1.5×10^7	3.2–4.6	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.; product radical obs. by esr (77–5209).	77–1106
5.53	D–Glucose						
	$HPO_4^- + C_6H_{12}O_6 \rightarrow H_2PO_4^- + C_6H_{11}O_6$	$(8.0 \pm 0.2) \times 10^7$	9.0	–	f.phot.	D.k. at 500 nm in 0.03 *M* HPO_4^{2-} soln.	70–0326
	$H_2PO_4 + C_6H_{12}O_6 \rightarrow H_3PO_4 + C_6H_{11}O_6$	$(1.1 \pm 0.3) \times 10^8$	4.5	–	f.phot.	D.k. at 500 nm in 0.1 *M* $H_2PO_4^-$ soln.	70–0326
5.54	Glycine						
	$PO_4^{2-} + NH_2CH_2COO^- \rightarrow HPO_4^{2-} + NH_2CHCOO^-$	2.6×10^7	12	~0.2	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
	$H_2PO_4 + NH_3^+CH_2COO^- \rightarrow H_3PO_4 + NH_3^+CHCOO^-$	$\leqslant 10^5$	4.5	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106

TABLE 5. Rates of reaction of PO_4^{2-} in aqueous solution — Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
5.55	*p*-Hydroxybenzoate ion						
	$HPO_4^- + OHC_6H_4COO^- \rightarrow H_2PO_4^- + OC_6H_4COO^-$	1.7×10^8	7.2	~0.12	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
	$PO_4^{2-} + OHC_6H_4COO^- \rightarrow HPO_4^- + OC_6H_4COO^-$	5×10^7	11.4	~0.2	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1503
5.56	*p*-Hydroxybenzoic acid						
	$H_2PO_4 + OHC_6H_4COOH$	1.3×10^9	3.3	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
5.57	Maleic acid						
	$H_2PO_4 + HOOCCH{=}CHCOOH \rightarrow HOOCCHCH(COOH)OPO_3H_2$	3.1×10^7	3.2–4.6	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln. Product radical obs. by esr (77–5209).	77–1106
5.58	Malonic acid						
	$H_2PO_4 + CH_2(COOH)_2 \rightarrow H_3PO_4 + CH(COOH)_2$ (1)	1.8×10^5	3.2–4.6	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln. Product radical obs. by esr (77–5209); $k_1/k_2 \cong 1$ detd. from CO_2 yield by γ-r. (78–1505).	77–1106
	$H_2PO_4 + CH_2(COOH)_2 \rightarrow H_3PO_4 + CH_2COOH + CO_2$ (2)						
5.59	Methacrylate ion						
	$HPO_4^- + CH_2{=}C(CH_3)COO^-$	2.3×10^7	7.3	~0.12	p.r.	–	77–1503
5.60	Methacrylic acid						
	$H_2PO_4 + CH_2{=}C(CH_3)COOH$	7.3×10^8	4	~0.06	p.r.	–	77–1503
5.61	Methacrylonitrile						
	$HPO_4^- + CH_2{=}C(CH_3)CN$	2.8×10^7	7.4	~0.12	p.r.	–	77–1503
	$H_2PO_4 + CH_2{=}C(CH_3)CN$	3.9×10^8	3.9	~0.06	p.r.	–	77–1503
5.62	Methanol						
	$PO_4^{2-} + CH_3OH \rightarrow HPO_4^{2-} + CH_2OH$	1.0×10^7	12	~0.2	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
	$HPO_4^- + CH_3OH \rightarrow H_2PO_4^- + CH_2OH$	1.0×10^7	7	~0.12	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
	$H_2PO_4 + CH_3OH \rightarrow H_3PO_4 + CH_2OH$	4.1×10^7	4	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
5.62a	*p*-Methoxyphenoxide ion	8.2×10^8	11.3	~0.2	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1503
5.63	Methyl methacrylate						
	$HPO_4^- + CH_2{=}C(CH_3)COOCH_3$	3.9×10^7	7.3	~0.12	p.r.	–	77–1503
	$H_2PO_4 + CH_2{=}C(CH_3)COOCH_3$	6.2×10^8	4	~0.06	p.r.	–	77–1503
5.64	2-Methyl-2-propanol						
	$PO_4^{2-} + (CH_3)_3COH \rightarrow HPO_4^{2-} + CH_2C(CH_3)_2OH$	4.2×10^5	12	~0.2	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
	$HPO_4^- + (CH_3)_3COH \rightarrow H_2PO_4^- + CH_2C(CH_3)_2OH$	4.5×10^5	7	~0.12	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
	$H_2PO_4 + (CH_3)_3COH \rightarrow H_3PO_4 + CH_2C(CH_3)_2OH$	3.9×10^6	4	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
5.64a	Phenoxide ion	5.9×10^8	11.6	~0.2	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1503
5.65	2-Propanol						
	$PO_4^{2-} + (CH_3)_2CHOH \rightarrow HPO_4^{2-} + (CH_3)_2COH$	1.8×10^7	12	~0.2	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
	$HPO_4^- + (CH_3)_2CHOH \rightarrow H_2PO_4^- + (CH_3)_2COH$	$(4.0 \pm 1.0) \times 10^7$	9.0	–	f.phot.	D.k. at 500 nm in 0.03 *M* HPO_4^{2-} soln.	70–0326
		2.5×10^7	7	~0.12	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
	$H_2PO_4 + (CH_3)_2CHOH \rightarrow H_3PO_4 + (CH_3)_2COH$	$(1.6 \pm 0.3) \times 10^8$	4.5	–	f.phot.	D.k. at 500 nm in 0.1 *M* $H_2PO_4^-$ soln.	70–0326
		1.4×10^8	4	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106

TABLE 5. Rates of reaction of PO_4^{2-} in aqueous solution — Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
5.66	Propionic acid $H_2PO_4 + CH_3CH_2COOH \rightarrow$ $H_3PO_4 + CH_3CHCOOH$ (1) $H_2PO_4 + CH_3CH_2COOH \rightarrow$ $H_3PO_4 + CH_3CH_2 + CO_2$ (2)	4.2×10^6	3.2–4.6	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.; $k_1/k_2 \cong 4$ detd. from CO_2 yield by γ-r. (78–1505).	77–1106
5.67	Ribose $HPO_4^- + C_5H_{10}O_5 \rightarrow$ $H_2PO_4^- + C_5H_9O_5$	$(9.0 \pm 2.0) \times 10^7$	9.0	–	f.phot.	D.k. at 500 nm in 0.03 *M* HPO_4^{2-} soln.	70–0326
5.68	Succinic acid $H_2PO_4 + (CH_2COOH)_2 \rightarrow$ $H_3PO_4 + HOOCCH_2CHCOOH$	1.6×10^6	3.2–4.6	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
5.69	Terephthalate ion $H_2PO_4 + HOOCC_6H_4COO^-$	3.5×10^7	5.2	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
5.70	Terephthalic acid $H_2PO_4 + HOOCC_6H_4COOH$	$\sim 6 \times 10^7$	3.4	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
5.71	Thymine	$(9.6 \pm 1.0) \times 10^7$	9.0	~0.2	f.phot.	D.k. at 500 nm in 0.03 *M* HPO_4^{2-} soln.	70–0326
5.72	Toluic acid $H_2PO_4 + CH_3C_6H_4COOH$	5.4×10^8	3.3	~0.06	p.r.	D.k. at 520 nm in $Li_4P_2O_8$ soln.	77–1106
5.73	Uracil	$(9.7 \pm 2.0) \times 10^7$	9.0	–	f.phot.	D.k. at 500 nm in 0.03 *M* HPO_4^{2-} soln.	70–0326
		$(6.0 \pm 2.0) \times 10^8$	4.5	–	f.phot.	D.k. at 500 nm in 0.1 *M* $H_2PO_4^-$ soln.	70–0326

TABLE 6. Rates of reaction of Cl_2^- in aqueous solution

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
6.1	$Cl_2^- + Cl_2^- \rightarrow Cl_3^- + Cl^-$	$2k = (1.4 \pm 0.2) \times 10^{10}$	1.1, 6	0.5	f.phot.	D.k. in NaCl–$HClO_4$ soln.; assumed $\epsilon(350\ nm) = 1.25 \times 10^4\ M^{-1}\ cm^{-1}$.	67–7171
		$2k = (1.4 \pm 0.3) \times 10^{10}$	3.1	–	p.r.	D.k. in N_2O–satd. Cl^- soln. assuming $\epsilon(360\ nm) = 10^4\ M^{-1}\ cm^{-1}$; independent of pH 0.9 – 3.2.	68–0313
		$2k - (1.2 \pm 0.3) \times 10^{10}$	1.9	0.1	p.r.	D.k.	72–3107
		$2k = 5.2 \times 10^9$	1	0.2	f.phot.	D.k. in $FeCl^{2+}$ soln. ($10^{-3}\ M\ Fe^{3+}$, 0.1 $M\ H^+$, 0.1 $M\ Cl^-$); $\epsilon(366\ nm) = 1.0 \times 10^4\ M^{-1}\ cm^{-1}$.	73–7159
		$2k = (1.8 \pm 0.5) \times 10^{10}$	–	~1	p.r.	D.k. in NaCl or HCl soln. assuming $\epsilon = 1.25 \times 10^4\ M^{-1}\ cm^{-1}$.	74–1087
		$2k - (4\ to\ 14) \times 10^9$	–	<10	p.r.	D.k. in LiCl soln.; values from graph; k increased as concn. decreased.	74–1149
		$2k = (2.7 \pm 0.5) \times 10^9$	7.0	<14	p.r.	D.k. in 1.5–14 M LiCl soln. at 340 nm; calcd. from obs. $2k/\epsilon = (5\ to\ 8) \times 10^5$.	75–1154
		$2k = (1.3 \pm 0.5) \times 10^{10}$	–	–	p.r.	D.k. in Cl^- soln.; $\epsilon(340\ nm) = (1.24 \pm 0.08) \times 10^4\ M^{-1}\ cm^{-1}$.	76–1048
		$2k = 1.7 \times 10^{10}$	7	0.2	p.r.	D.k. in Cl^- soln.; $\epsilon(340\ nm) = 1.25 \times 10^4\ M^{-1}\ cm^{-1}$; obs. change in $[Cl_2^-]$ with dose.	77–1097
6.1a	$Cl_2^- \rightleftharpoons Cl + Cl^-$	$k_f = (1.1 \pm 0.4) \times 10^5\ s^{-1}$	2	0.02	p.r.	Abs. at 340 nm depends on $[Cl^-]$; $k_r = 2.1 \times 10^{10}\ M^{-1}\ s^{-1}$.	73–1039
6.2	$Cl_2^- + O_2^- \rightarrow 2Cl^- + O_2$	$\leqslant 2 \times 10^9$	–	–	p.r.	D.k. in O_2–satd. 1.3 and 5 M LiCl soln. compared with deaerated soln.	74–1149
6.2a	$Cl_2^- + HO_2 \rightarrow 2Cl^- + H^+ + O_2$	$(4.5 \pm 0.5) \times 10^9$	0.4 M H_2SO_4	0.5	p.r.	Calcd. from effect of Cl^- on $G(Fe^{3+})$ in air–satd. Fe^{2+} soln.	77–1170
6.3	$Cl_2^- + SCN^- \rightarrow 2Cl^- + SCN$	$(2.9 \pm 0.3) \times 10^9$	2.6	–	p.r.	D.k. in N_2O–satd. 6×10^{-3} M Cl^- soln.; addn. of 0.1 M $NaClO_4$ gave $k = 3.7 \times 10^9$; product is $(SCN)_2^-$ detd. by absorption spectrum; $K(ClSCN^- + SCN^- \rightleftharpoons Cl^- + (SCN)_2^-) = 3.0 \times 10^4$.	69–0565
6.4	$Cl_2^- + Ce^{3+} \rightarrow Ce^{4+} + 2Cl^-$	$(0.8\ or\ 4.0) \times 10^4$	–	–	γ-r.	Calcd. from $G(Ce^{3+})$ in Ce^{4+} soln. contg. 10 M LiCl assuming $k(Cl_2^- + Cl_2^-) = 2 \times 10^9$.	75–0440
6.5	$Cl_2^- + OClO$	$(1.0 \pm 0.1) \times 10^9$	5	–	f.phot.	D.k. in ClO_2–Cl^- soln.	73–7043

TABLE 6. Rates of reaction of Cl_2^- in aqueous solution—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
6.6	$Cl_2^- + Co(II) \rightarrow CoCl^{2+} + Cl^-$	$(1.4 \pm 0.2) \times 10^6$	~1	0.3	f.phot.	D.k. in Cl_3^- soln. (0.1 *M* Cl^-, 0.005 *M* Cl_2, 0.1 *M* H^+) contg. 0.1–0.5 *M* Co(II); $\Delta H^{\ddagger} = 29 \pm 4$ kJ mol^{-1} and $\Delta S^{\ddagger} = -31 \pm 10$ J K^{-1} mol^{-1} detd. at 13.5 to 41.5°C.; inner sphere substitution reaction.	73–7316
6.7	$Cl_2^- + CoL^{2+} \rightarrow Co^{III}$ L = 5,7,7,12,14,14–hexamethyl–1,4,8,11–tetraazacyclotetradeca–4,11–diene	$(1.0 \pm 0.4) \times 10^9$	1	1.1	f.phot.	D.k.	72–7506
6.8	$Cl_2^- + Cr_{aq}^{2+} \rightarrow [Cr(OH_2)_5Cl]^{2+} + Cl^-$	$(2.4 \pm 0.3) \times 10^9$	1	0.2	p.r.	D.k. in deaerated Cl^- soln.; $\Delta G^{\circ} = -263$ kJ mol^{-1}; reaction 50% inner sphere and 50% outer sphere.	74–1104
	$Cl_2^- + Cr_{aq}^{2+} \rightarrow [Cr(OH_2)_6]^{3+} + 2Cl^-$	$(2.4 \pm 0.3) \times 10^9$					
6.9	$Cl_2^- + Cu^{2+}$	$\leqslant 1.5 \times 10^8$	–	–	p.r.	–	75–1188
6.10	$Cl_2^- + CuL^{2+} \rightarrow Cu^{III}$ L = 5,7,7,12,14,14–hexamethyl–1,4,8,11–tetraazacyclotetradecane	6.5×10^8	2	0.02	p.r.	D.k.	78–1503
6.11	$Cl_2^- + CuL^{2+} \rightarrow Cu^{III}$ L = 5,7,7,12,14,14–hexamethyl–1,4,8,11–tetraazacyclotetradeca–4,11–diene	3.2×10^8	2	0.02	p.r.	D.k.	78–1503
6.12	$Cl_2^- + Fe^{2+} \rightarrow FeCl^{2+} + Cl^-$ (1)	$(3.8 \pm 0.3) \times 10^7$	2.1	0.04	p.r.	D.k.	68–0313
		$(1.4 \pm 0.2) \times 10^7$	1	0.1	p.r.	D.k. in soln. contg. 0.01 *M* NaCl and 0.1 *M* perchloric acid.	73–1039
	$Cl_2^- + Fe_{aq}^{2+} \rightarrow Fe_{aq}^{3+} + 2Cl^-$ (2)						
		$k_1 = (4.0 \pm 0.6) \times 10^6$	1	0.2	f.phot.	D.k. in $FeCl^{2+}$ soln. (10^{-3} *M* Fe^{3+}, 0.1 *M* H^+, 0.1 *M* Cl^-) in pres. of Fe^{2+}; $\Delta H^{\ddagger}$ for the inner sphere reaction (1) = 31.5 ± 4 kJ mol^{-1} and $\Delta S^{\ddagger} = -21 \pm 15$ J K^{-1} mol^{-1}; $\Delta H^{\ddagger}$ for the outer sphere reaction (2) = 22.7 ± 4 kJ mol^{-1} and $\Delta S^{\ddagger} = -42 \pm 15$ J K^{-1} mol^{-1}.	73–7159
		$k_2 = (1.0 \pm 0.2) \times 10^7$					
6.13	$Cl_2^- + Mn_{aq}^{2+} \rightarrow Mn^{III} + 2Cl^-$	8×10^6	1	0.25	f.phot.	D.k. in Cl_3^- soln. (0.1 *M* Cl^-, 0.005 *M* Cl_2, 0.1 *M* H^+) contg. 0.001–0.02 *M* Mn^{2+}; $E_a = 34 \pm 4$ kJ mol^{-1} (16 to 40°C); reaction is inner sphere electron transfer controlled; $\Delta H^{\ddagger} = 32 \pm 4$ kJ mol^{-1}, $\Delta S^{\ddagger} = -4 \pm 6$ J K^{-1} mol^{-1}.	73–7317
6.14	$Cl_2^- + N_2H_5^+$	8.0×10^6	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78–1093
		1.4×10^7	6.8	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78–1093
6.15	$Cl_2^- + NH_2OH$	9.3×10^6	6.7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78–1093
6.16	$Cl_2^- + NH_3OH^+$	$< 10^5$	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78–1093
6.17	$Cl_2^- + N_3^-$	1.2×10^9	7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78–1093

TABLE 6. Rates of reaction of Cl_2^- in aqueous solution—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
6.18	$Cl_2^- + NO_2^-$	2.5×10^8	7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78-1093
6.19	$Cl_2^- + NiL^{2+} \rightarrow Ni^{III}$ L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane	2.0×10^9	2	~0.02	p.r.	D.k. in 0.005 - 0.01 *M* Cl^- soln.	78-1502
6.20	$Cl_2^- + NiL^{2+} \rightarrow Ni^{III}$ L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene	9.6×10^9	2	~0.02	p.r.	D.k. in 0.005 - 0.01 *M* Cl^- soln.	78-1502
6.21	$Cl_2^- + NiL^{2+} \rightarrow Ni^{III}$ L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene	8.7×10^9	2	~0.02	p.r.	D.k. in 0.005 - 0.01 *M* Cl^- soln.	78-1502
6.22	$Cl_2^- + OH^-$	7.3×10^6	10-13	-	p.r.	Unpub. data from R.W. Fessenden.	78-1093
6.23	$Cl_2^- + H_2O_2$	1.4×10^5	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78-1093
6.24	$Cl_2^- + PtCl_4^{2-} \rightarrow$ Pt(III)	$(1.1 \pm 0.2) \times 10^9$	-	-	p.r.	D.k. in 0.5 *M* HCl; transient with ϵ(260 nm) $\cong$ 13000 $M^{-1}\ cm^{-1}$ was formed.	75-1188
		$(1.60 \pm 0.10) \times 10^9$	~1		p.r.	D.k. in 0.1 *M* HCl soln.; 1.0 *M* NaCl soln. gave $k = (1.25 \pm 0.3) \times 10^9$.	76-1055
6.25	$Cl_2^- + PtL_2^{2+} \rightarrow$ Pt(III) L = ethylenediamine	$(8.9 \pm 1.9) \times 10^9$	-	-	p.r.	D.k. in 0.5 *M* HCl; transient with ϵ(280 nm) = 15900 $M^{-1}\ cm^{-1}$ was formed.	75-1188
6.26	$Cl_2^- + PtLCl^+ \rightarrow$ Pt(III) L = diethylenetriamine	$(6.4 \pm 0.4) \times 10^9$	-	-	p.r.	D.k. in 0.5 *M* HCl; transient with ϵ(280 nm) = 17000 $M^{-1}\ cm^{-1}$ was formed.	75-1188
6.27	$Cl_2^- + PtLCl^+ \rightarrow$ Pt(III) L = tetraethyldiethylenetriamine	$(4.2 \pm 0.4) \times 10^8$	-	-	p.r.	D.k. in 0.5 *M* HCl; transient with ϵ(290 nm) = 7240 $M^{-1}\ cm^{-1}$ was formed.	75-1188
6.28	$Cl_2^- + SO_3^{2-}$	3.3×10^7	7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78-1093
6.28a	$Cl_2^- + Ti(III)$	$\sim 4 \times 10^8$	~1	-	p.r.	D.k. at 380 nm in 0.02 *M* HCl contg. formic acid.	73-1057
6.29	$Cl_2^- + Tl(I) \rightarrow Tl(II)$	5×10^9	-	1	p.r.	P.b.k. at 260 nm in 0.99 *M* HCl soln.	74-1038
6.30	$Cl_2^- + V^{2+} \rightarrow 2Cl^- + V^{3+}$	$(1.95 \pm 0.2) \times 10^9$	1	0.2	p.r.	D.k. in deaerated Cl^- soln.; ΔG° = -241 kJ mol^{-1}; outer sphere diffusion control.	74-1104
6.31	Acetanilide $Cl_2^- + C_6H_4NHCOCH_3$	$\sim 2.0 \times 10^7$	7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78-1093
6.32	Acetic acid	$< 10^4$	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78-1093
6.33	Acetone	1.4×10^3	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78-1093
6.34	Acriflavin	$\sim 4 \times 10^9$	-	1	p.r.	D.k. at 450 nm (dye) in N_2O-satd. 1 *M* KCl soln.	70-0241
6.35	Acrylate ion $Cl_2^- + CH_2{=}CHCOO^-$	1.9×10^7	7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78-1093
6.36	Acrylic acid $Cl_2^- + CH_2{=}CHCOOH$	5.4×10^6	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78-1093
6.37	Acrylonitrile $Cl_2^- + CH_2{=}CHCN$	2.2×10^6	7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78-1093
6.38	Adenine	$< 5 \times 10^6$	2.7	-	p.r.	D.k. in 0.1 *M* NaCl soln.	68-0313
6.39	Alanine	1.3×10^5	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78-1093

TABLE 6. Rates of reaction of Cl_2^- in aqueous solution—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
6.40	Allyl alcohol $Cl_2^- + CH_2{=}CHCH_2OH$	5.9×10^8	1,7	~1	p.r.	D.k. in 1 *M* Cl^- soln.; at pH 7 Cl_2^- was generated by SO_4^- from $S_2O_8^{2-}$.	78–1093
6.41	*p*–Aminobenzoate ion	1.1×10^9	7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78–1093
6.42	*p*–Aminobenzoic acid	2.2×10^7	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78–1093
6.43	Anilinium ion $Cl_2^- + C_6H_5NH_3^+$	1.2×10^7	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78–1093
6.44	Anthrasemiquinone–2,6–disulfonate radical ion $Cl_2^- + A^- \rightarrow A + 2Cl^-$	6.5×10^8	8.0	–	f.phot.	D.k.	73–7569
6.45	Ascorbic acid	6.8×10^8	2	–	p.r.	–	72–0266
	$Cl_2^- + AH_2 \rightarrow \cdot AH + H^+ + 2Cl^-$	$(6.0 \pm 1.0) \times 10^8$	2	–	p.r.	D.k. in N_2O–satd. 0.5 *M* Cl^- soln.	73–3006
6.46	Benzenesulfonate ion	$< 1 \times 10^5$	7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78–1093
6.47	Benzoate ion	2×10^6	7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78–1093
6.48	Benzonitrile	$< 1 \times 10^5$	1,7	~1	p.r.	D.k. in 1 *M* Cl^- soln.; at pH 7 Cl_2^- was generated by SO_4^- from $S_2O_8^{2-}$.	78–1093
6.49	*p*–Bromobenzoate ion	7×10^6	7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78–1093
6.50	*p*–Chlorobenzoate ion	3×10^6	7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78–1093
6.51	5–Chlorouracil	1.0×10^7	2.0	–	p.r.	D.k. in 0.01 *M* NaCl soln.	72–3107
6.52	*p*–Cyanobenzoate ion	5×10^6	7	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78–1093
6.53	*p*–Cyanophenol	4.0×10^7	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78–1093
6.54	Cysteine	$(8.5 \pm 0.8) \times 10^8$	1.8	–	p.r.	D.k. in 0.1 *M* Cl^- soln.	72–0036
6.55	Cytidine	4×10^6	2.0	–	p.r.	D.k. in 0.01 *M* NaCl soln.	72–3107
6.56	Cytosine	$(9.1 \pm 0.7) \times 10^7$	2.7	–	p.r.	D.k. in 0.1 *M* NaCl soln.	68–0313
		1.0×10^7	2.0	–	p.r.	D.k. in 0.01 *M* NaCl soln.	72–3107
6.57	Deoxyadenylic acid	$< 5 \times 10^6$	2.7	–	p.r.	D.k. in 0.1 *M* NaCl soln.	68–0313
6.58	Deoxycytidylic acid	$< 5 \times 10^6$	2.7	–	p.r.	D.k. in 0.1 *M* NaCl soln.	68–0313
6.59	Deoxyguanylic acid	$(1.2 \pm 0.1) \times 10^8$	2.7	–	p.r.	D.k. in 0.1 *M* NaCl soln.	68–0313
6.60	Dithiothreitol	$(3.0 \pm 0.3) \times 10^9$	2	–	p.r.	D.k.	73–1020
6.61	Dodecyl sodium sulfate	3.9×10^6	2.0	–	p.r.	D.k. in 0.5 *M* NaCl soln.	72–3107
6.62	Ethanol $Cl_2^- + CH_3CH_2OH$	4.5×10^4	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78–1093
6.63	Formate ion $Cl_2^- + HCO_2^-$	1.9×10^6	7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78–1093
6.64	Formic acid $Cl_2^- + HCOOH$	1.0×10^6	3.7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78–1093
		3×10^5	3	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78–1093
		6.7×10^3	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78–1093
6.65	Fumarate ion $Cl_2^- + {}^-OOCCH{=}CHCOO^- \rightarrow Cl^- + {}^-OOCCHCHClCOO^-$	4×10^9	7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$; adduct radical obs. by esr (75–5244).	78–1093
	$Cl_2^- + {}^-OOCCH{=}CHCOOH$	2.4×10^9	3.7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78–1093
6.66	Fumaric acid $Cl_2^- + HOOCCH{=}CHCOOH$	$\sim 2 \times 10^5$	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78–1093
6.67	Glutamic acid	2.3×10^5	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78–1093
6.68	Glycine	$\sim 5 \times 10^6$	9.8	~1	p.r.	D.k. in 1 *M* Cl^- soln.; at pH 9.8 Cl_2^- generated by SO_4^- from $S_2O_8^{2-}$.	78–1093
		$< 10^4$	1				
6.69	Guanine	$(8.1 \pm 0.6) \times 10^7$	2.3	–	p.r.	D.k. in 0.1 *M* NaCl soln.	68–0313

TABLE 6. Rates of reaction of Cl_2^- in aqueous solution—Continued

Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
Hexadecyltrimethyl–ammonium chloride	1.2×10^7	2.0	–	p.r.	D.k. in 0.01 *M* HCl soln.	72–3107
Hexadienedioate ion *See* Muconate ion.						
Hexadienoate ion *See* Sorbate ion.						
Hexenedioate ion $Cl_2^- + {}^-OOCCH_2CH{=}CHCH_2COO^-$	1.0×10^7	7	~1	p.r.	D.k. in 0.1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78–1093
Histidine	$(1.4 \pm 0.1) \times 10^7$	1.8	–	p.r.	D.k. in 0.1 *M* Cl^- soln.	72–0036
Hydroquinone	1.4×10^9	1	~1	p.r.	D.k. in 0.1 *M* Cl^- soln.	78–1093
$Cl_2^- + OHC_6H_4OH \rightarrow 2Cl^- + 2H^+ + {\cdot}OC_6H_4O^-$	1.5×10^9	9.5	~1	p.r.	D.k. in 0.1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78–1093
p–Hydroxybenzoate ion $Cl_2^- + OHC_6H_4COO^- \rightarrow 2Cl^- + H^+ + {\cdot}OC_6H_4COO^-$	2.8×10^8	7	~1	p.r.	D.k. in 0.1 *M* Cl^- soln. contg. $S_2O_8^{2-}$; product radical obs. by esr.	78–1093
p–Hydroxybenzoic acid $Cl_2^- + OHC_6H_4COOH$	1.3×10^8	3.1	~1	p.r.	D.k. in 0.1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78–1093
	1.1×10^8	1	~1	p.r.	D.k. in 0.1 *M* Cl^- soln.	78–1093
Maleate ion	3×10^6	6.5	~1	p.r.	D.k. in 0.1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78–1093
Methanol	3.5×10^3	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78–1093
Methionine	$(7 \pm 0.7) \times 10^6$	1.8	–	p.r.	D.k. in 0.1 *M* Cl^- soln.	72–0036
p–Methoxybenzoate ion $Cl_2^- + CH_3OC_6H_4COO^- \rightarrow 2Cl^- + CH_3O^+C_6H_4COO^-$	2.0×10^8	7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$; product radical identified by optical p.r.	78–1093
p–Methoxyphenol	1.1×10^9	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78–1093
2–Methyl–2–propanol	$\sim 7 \times 10^2$	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78–1093
Muconate ion	3.1×10^9	7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78–1093
Phenol	2.5×10^8	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78–1093
p–Phenoxybenzoate ion	1.5×10^8	7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78–1093
Phenylalanine	$(6 \pm 0.6) \times 10^6$	1.8	–	p.r.	D.k. in 0.1 *M* Cl^- soln.	72–0036
Polyoxyethylene(15)nonyl phenol	2.1×10^8	2.0	–	p.r.	D.k. in 0.01 *M* NaCl soln.	72–3107
2–Propanol	1.2×10^5	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78–1093
	$(1.9 \pm 0.3) \times 10^5$	–	–	p.r.	D.k. in 0.5 *M* HCl.	75–1188
Propionic acid	2.2×10^4	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78–1093
Salicylic acid	1.1×10^8	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78–1093
Serine	1.2×10^5	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78–1093
Sorbate ion	6.8×10^8	7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78–1093
Succinic acid	$\sim 8 \times 10^2$	1	~1	p.r.	D.k. in 1 *M* Cl^- soln.	78–1093
Terephthalate ion	6×10^6	7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78–1093
Tetramethylpiperidone *N*–oxyl (TAN)	1.4×10^9	2	–	p.r.	D.k. at 350 nm.	71–0618
Thymidylic acid	$(4.4 \pm 0.3) \times 10^7$	2.7	–	p.r.	D.k. in 0.1 *M* NaCl soln.	68–0313
Thymine	$(1.2 \pm 0.1) \times 10^8$	2.7	–	p.r.	D.k. in 0.1 *M* NaCl soln.	68–0313
	7.0×10^7	2.0	–	p.r.	D.k. in 0.01 *M* NaCl soln.	72–3107
p–Toluate ion	5×10^6	7	~1	p.r.	D.k. in 1 *M* Cl^- soln. contg. $S_2O_8^{2-}$.	78–1093
Tryptophan	$(2.6 \pm 0.3) \times 10^9$	1.8	–	p.r.	D.k. in 0.1 *M* Cl^- soln.	72–0036
Tyrosine	$(2.7 \pm 0.3) \times 10^8$	1.8	–	p.r.	D.k. in 0.1 *M* Cl^- soln.	72–0036
Uracil	$(4.1 \pm 0.3) \times 10^7$	2.7	–	p.r.	D.k. in 0.1 *M* NaCl soln.	68–0313
	3.5×10^7	2.0	–	p.r.	D.k. in 0.01 *M* NaCl soln.	72–3107
	3.7×10^7	6	–	p.r.	–	75–5244

TABLE 7. Rates of reaction of Br_2^- in aqueous solution

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment
7.1	$Br_2^- + Br_2 \rightarrow Br_3^- + Br^-$	$k = 1.8 \times 10^9$	2	0.03	p.r.	D.k. in aerated 10^{-4} *M* Br $- 10^{-3}$ *M* Br_2; $k/\epsilon = 2.2 \times 10^5$ cm s^{-1}; ϵ(360 nm) $= 8200\ M^{-1}\ cm^{-1}$.
		$k = (1.8 \pm 0.3) \times 10^9$	7	0.01	p.r.	D.k. in N_2O–satd. 10^{-3} *M* Br ; ϵ(360 nm) $= 9000 \pm 600\ M^{-1}\ cm^{-1}$.
		$2k = (3.3 \pm 1.0) \times 10^9$	7	<0.01	p.r.	D.k. in $10^{-3} - 10^{-2}$ *M* Br^- soln.; ϵ(365 nm) $= 7800 \pm 2000\ M^{-1}\ cm^{-1}$.
		$2k = (3.7 \pm 0.6) \times 10^9$	6	0.02	f.phot.	D.k. in 0.02 *M* Br^- or $HgBr_2 - HgBr_3^-$ soln.; ϵ(360 nm) $= (7.8 \pm 0.2) \times 10^3\ M^{-1}\ cm^{-1}$.
		$k = 2.8 \times 10^9$	12	0.02	p.r.	D.k. in N_2O–satd. 10^{-2} *M* Br^- soln.; ϵ(360 nm) $= 8200\ M^{-1}\ cm^{-1}$.
		$2k = 5.3 \times 10^9$	1	0.2	f.phot.	D.k. in $FeBr^{2-}$ soln. (10^{-3} *M* Fe^{3+}, 0.1 *M* H^+, 0.1 *M* Br); ϵ(366 nm) $= 7.8 \times 10^3\ M^{-1}\ cm^{-1}$.
		1.0×10^9	–	–	f.phot.	Calcd. from assumed mechanism for d.k. at 350 nm in Br soln. 10^{-5} to 10^{-1} *M*.
		$2k = (3.1 \pm 0.9) \times 10^9$	–	–	p.r.	D.k. in Br^- soln.; ϵ(360 nm) $= (8.56 \pm 0.24) \times 10^3\ M^{-1}\ cm^{-1}$.
		2.4×10^9	–	0.02	p.r.	D.k. in N_2O–satd. Br soln.; ϵ(360 nm) $= 9600\ M^{-1}\ cm^{-1}$; rates in micellar systems also detd.
7.1a	$Br_2^- \rightarrow Br + Br^-$	$k_f = (2.5 \pm 1) \times 10^4\ s^{-1}$	2	–	p.r.	Calcd. from dependence of $[Br_2^-]$ on $[Br^-]$; $k_r = (5.4 \pm 3) \times 10^9$ and $K^{-1} = (2.2 \pm 1) \times 10^5\ M^{-1}$.
		$k_f = (7 \pm 2) \times 10^5\ s^{-1}$	~2	0.12	f.phot.	Calcd. from buildup of Br_2^- in $Br^- - Br_2$ soln.; $k_r = (1.1 \pm 0.1) \times 10^{10}$.
7.2	$Br_2^- + Br \rightarrow Br_3^-$	1.37×10^9	~7	–	f.phot.	Calcd. from assumed mechanism for d.k. at 350 nm in Br soln. 10^{-5} to 10^{-1} *M*.
7.3	$Br_2^- + H \rightarrow H^+ + 2Br^-$	$(7 \pm 1) \times 10^9$	2	–	p.r.	–
7.4	$Br_2^- + HO_2 \rightarrow Br_2 + HO_2^-$	$(1.6 \pm 0.5) \times 10^9$	2	–	p.r.	D.k. in air–satd. 0.1 *M* Br^- soln.
7.5	$Br_2^- + BrO^- \rightarrow BrO + 2Br^-$	$(8.0 \pm 0.7) \times 10^7$	–	0.02	p.r.	D.k. in $Br^- - BrO^-$ soln.
7.6	$Br_2^- + BrO_2^- \rightarrow BrO + BrO^- + Br^-$	$(8.0 \pm 0.8) \times 10^7$	–	1	p.r.	D.k. in $Br^- - BrO_2^-$ soln.
7.7	$Br_2^- + BrO_3^-$	no reaction	–	–	p.r.	D.k. of Br_2^- unaffected by BrO_3^-.
7.8	$Br_2^- + ClO_2$	$(1.2 \pm 0.1) \times 10^9$	–	–	f.phot.	D.k. in $Br^- - ClO_2$ soln.
7.9	$Br_2^- + Co^{1+} \rightarrow Co^{2+} + 2Br^-$	$(1.0 \pm 0.3) \times 10^{10}$	–	–	f.phot.	D.k. in Br^- soln. contg. Co^{2+}; $e_{aq}^- + Co^{2+} \rightarrow Co^{1+}$.
7.10	$Br_2^- + Co^{2+}$	–	–	–	f.phot.	No reaction.
7.11	$Br_2^- + CoL^{2+} \rightarrow Co^{III}$	$(1.4 \pm 0.1) \times 10^9$	1	0.2	f.phot.	D.k. in Br^- soln.
		2.0×10^9	9.2	0.1	p.r.	D.k. in N_2O–satd. Br^- soln.

L = 5,7,7,12,14,14–hexamethyl–1,4,8,11–tetraazacyclotetradeca–4,11–diene

TABLE 7. Rates of reaction of Br_2^- in aqueous solution—Continued

Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
$Br_2^- + Cr_{aq}^{2+} \rightarrow [Cr(OH_2)_5Br]^{2+} + Br^-$	$(1.9 \pm 0.2) \times 10^9$	1	0.2	p.r.	D.k. in deaerated Br^- soln.; $\Delta G^\circ = -213$ kJ mol^{-1}; inner sphere diffusion controlled mechanism.	74–1104
$Br_2^- + CuL^{2+} \rightarrow Cu^{III}$ L = 5,7,7,12,14,14–hexamethyl–1,4,8,11–tetraazacyclotetradecane	2×10^7	6	0.02	p.r.	D.k.	78–1503
$Br_2^- + CuL^{2+} \rightarrow Cu^{III}$ L = 5,7,7,12,14,14–hexamethyl–1,4,8,11–tetraazacyclotetradeca–4,11–diene	1×10^7	6	0.02	p.r.	D.k.	78–1503
$Br_2^- + Fe_{aq}^{2+} \rightarrow Br^- + FeBr^{2+}$	$(3.6 \pm 0.4) \times 10^6$	1	0.2	f.phot.	D.k. at 366 nm (Br_2^-) or p.b.k. at 405 nm ($FeBr^{2+}$); $\Delta H^\ddagger = 25.2 \pm 2$ kJ mol^{-1}; $\Delta S^\ddagger = -42 \pm 12$ J k^{-1} mol^{-1}; inner sphere substitution controlled mechanism.	73–7159
Br_2^- + ferricenium ion → ferrocene	3×10^8	–	–	p.r.	–	74–1182
$Br_2^- + H_2O_2 \rightarrow H^+ + 2Br^- + HO_2$	$\leqslant 10^3$	7	–	p.r.	D.k. in N_2O–satd. 1 *M* NaBr soln.	78–1093
$Br_2^- + Mn^{2+} \rightarrow 2Br^- + Mn^{3+}$	6.3×10^6	1	0.25	f.phot.	D.k. in Br_3^- soln. (0.1 *M* Br^-, 5×10^{-5} *M* Br_2 and 0.1 *M* H^+); $E_a = 36 \pm 4$ kJ mol^{-1}; $\Delta H^\ddagger = 33.6 \pm 4$ kJ mol^{-1}; $\Delta S^\ddagger = -3 \pm 6$ J K^{-1} mol^{-1}; inner sphere electron transfer.	73–7317
$Br_2^- + NiL^{2+} \rightarrow Ni^{III}$ L = 5,7,7,12,14,14–hexamethyl–1,4,8,11–tetraazacyclotetradecane	3.4×10^9	2	–	p.r.	D.k. in 0.005 – 0.01 *M* Br^- soln.	78–1502
$Br_2^- + NiL^{2+} \rightarrow Ni^{III}$ L = 5,7,7,12,14,14–hexamethyl–1,4,8,11–tetraazacyclotetradeca–4,11–diene	9.8×10^9	2	–	p.r.	D.k. in 0.005 – 0.01 *M* Br^- soln.	78–1502
$Br_2^- + NiL^{2+} \rightarrow Ni^{III}$ L = 5,7,7,12,14,14–hexamethyl–1,4,8,11–tetraazacyclotetradeca–1,4,8,11–tetraene	9.5×10^9	2	–	p.r.	D.k. in 0.005 – 0.01 *M* Br^- soln.	78–1502
$Br_2^- + PtCl_4^{2-} \rightarrow$ Pt(III)–D	$(2.8 \pm 0.2) \times 10^8$	–	→0	p.r.	D.k. in N_2O–satd. 0.1 or 0.01 *M* Br^- soln. contg. $PtCl_4^{2-}$; Pt(III)–D ($\epsilon_{310\ nm} = 8.4 \times 10^4\ M^{-1}$ cm^{-1}) may be $PtBr_nCl_{4-n}^-$.	76–1055
$Br_2^- + Ru(bipy)_3^{2+} \rightleftharpoons [Ru(bipy)_3^{3+}Br^-] + Br^-$	$(3.1 \pm 0.5) \times 10^9$	1 *M* H_2SO_4	–	f.phot.	D.k. in 10^{-3} *M* Br^- soln.	73–7066
$Br_2^- + SCN^- \rightarrow 2Br^- + SCN$ or → $Br^- + BrSCN^-$	1.9×10^9	–	–	p.r.	D.k. in N_2O–satd. 5×10^{-3} *M* Br^- soln. contg. $10^{-5} - 2 \times 10^{-4}$ *M* SCN^- as well as p.b.k. at 500 nm $(SCN)_2^-$; $K(BrSCN^- + SCN^- \rightleftharpoons Br^- + (SCN)_2^-) = 1.1 \times 10^2$.	69–0180
$Br_2^- + Tl^+$		1	0.01	f.phot.	no reaction	74–7625
$Br_2^- + UO_2^+ \rightarrow 2Br^- + UO_2^{2+}$	$0.33 \times 10^3\ s^{-1}$	1.7	–	f.phot.	D.k. in Br^- – U(VI) soln.; react. probably reoxid. of U(V) to U(VI).	76–7279
$Br_2^- + V^{2+} \rightarrow 2Br^- + V^{3+}$	$(1.48 \pm 0.2) \times 10^9$	1	0.2	p.r.	D.k. in Br^- soln.: $\Delta G^\circ = -191$ kJ mol^{-1}; outer sphere diffusion control.	74–1104

TABLE 7. Rates of reaction of Br_2^- in aqueous solution—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment
7.28	Acriflavin	$(3.7 \pm 0.6) \times 10^9$	–	–	p.r.	D.k. of Br_2^- in N_2O–satd. 10^{-3} *M* Br^- soln. as well as dye bleaching at 450 nm.
7.29	Alcohol dehydrogenase (yeast)	2.6×10^9	7	–	p.r.	D.k. in 0.05 *M* Br^- soln.; $k = 1.0 \times 10^9$ for horse liver enzyme (79–3007).
7.30	Ascorbic acid $Br_2^- + AH_2 \rightarrow$ $\cdot AH + H^+ + 2Br^-$	$(1.1 \pm 0.4) \times 10^8$ $(1.1 \pm 0.4) \times 10^9$ $(8.7 \pm 0.9) \times 10^8$	2 7 7.2	– 0.5	p.r. p.r.	p*K* = 4.17, 11.57. D.k. in N_2O–satd. Br^- soln.
7.31	*p*–Bromophenoxide ion	2.75×10^8	12.5	–	p.r.	–
7.32	Carboxypeptidase A	$(1 \text{ to } 2.5) \times 10^9$	8–11	–	p.r.	D.k. in 0.05 *M* Br^- soln.
7.33	*p*–Chlorophenoxide ion	1.73×10^8	12.5	–	p.r.	–
7.34	α–Chymotrypsin	1.6×10^9	6.7	–	p.r.	D.k. in N_2O–satd. 0.04 *M* Br^-; mol. wt. = 20,000.
7.34a	Concanavalin A	7×10^9	7.1	–	p.r.	P.b.k. at 530 nm in N_2O–satd. 10^{-2} *M* KBr soln.
7.35	*p*–Cyanophenoxide ion	1.8×10^8	12.5	–	p.r.	–
7.36	Cysteamine	3×10^8	–	–	p.r.	–
7.37	Cysteine	$(1.8 \pm 0.2) \times 10^8$	6.6	0.1	p.r.	D.k. in N_2O–satd. Br^- soln.; *k* increases with pH.
7.38	Cytochrome C (ferro) $Br_2^- + Fe^{2+}\text{cytC} \rightarrow 2Br^- + Fe^{3+}\text{cytC}$	1.5×10^9	7	–	p.r.	–
7.39	Diethyl disulfide $Br_2^- + RSSR \rightarrow 2Br^- + RSSR\cdot^+$	1.8×10^9	4–5	0.02	p.r.	D.k. in N_2O–satd. Br^- soln., as well as p.b.k. at 430 nm ($RSSR\cdot^+$).
7.39a	Diethyl sulfide $Br_2^- + (C_2H_5)_2S \rightarrow (C_2H_5)_2SBr\cdot + Br^-$	$\sim 2 \times 10^9$	3.9	0.2	p.r.	D.k. at 360 nm in N_2O–satd. KBr soln.
7.40	3,5–Diiodotyrosine	$< 1 \times 10^8$ $\sim 1.3 \times 10^9$	6 8	–	p.r.	D.k. in N_2O–satd. 0.04 *M* Br^- soln.; values from graph.
7.41	Dimethyl disulfide	2.2×10^9	4–5	0.02	p.r.	D.k. in N_2O–satd. Br soln., as well as p.b.k. at 430 nm ($RSSR\cdot^+$).
7.42	*m*–Fluorotyrosine	$< 1 \times 10^8$ $\sim 1.2 \times 10^9$	6 11	–	p.r.	D.k. in N_2O–satd. 0.04 *M* Br^- soln.; values from graph.
7.43	Formate ion	$\leq 10^7$	7		p.r.	D.k. in N_2O–satd. 1 *M* Br^- soln.
7.44	d–Guanylic acid $Br_2^- + GMP \rightarrow 2Br^- + GMP\cdot^+$	4×10^7 2×10^8	– 12	–	p.r.	–
7.45	Histidine	$(1.5 \pm 0.2) \times 10^7$	7.6	0.1	p.r.	D.k. in N_2O–satd. Br^- soln.
7.46	Hydroquinone	1×10^8	–	–	p.r.	–
7.47	*p*–Hydroxybenzoate ion	2.28×10^8	12.5	–	p.r.	–
7.48	Lactate dehydrogenase	$(5.5 \pm 0.5) \times 10^9$	7.2	0.005	p.r.	D.k. in N_2O–satd. Br^- soln.
7.49	Methionine	$(1.1 \pm 0.1) \times 10^7$	7.3	0.1	p.r.	D.k. in N_2O–satd. Br^- soln.; *k* increases with pH.
7.50	*p*–Methylphenoxide ion	3.74×10^8	12.5	–	p.r.	–
7.51	Nicotinamide–adenine dinucleotide, reduced $Br_2^- + NADH \rightarrow 2Br^- + H^+ + NAD\cdot$	9.0×10^8	–	–	p.r.	P.b.k. at ~ 400 nm in N_2O–satd. 0.1 *M* Br^- soln.
7.52	Papain	1.05×10^9 2.30×10^9	7 11.5	–	p.r.	D.k. in 0.05 *M* Br^- soln.; activated enzyme used.

TABLE 7. Rates of reaction of Br_2^- in aqueous solution—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
7.53	Phenol	6×10^6	6	–	p.r.	–	74–3003
7.54	Phenoxide ion	5×10^8	10	–	p.r.	–	74–3003
		2.88×10^8	12.5	–	p.r.	–	74–3052
7.55	Phenylalanine	$< 1 \times 10^6$	7.0	0.1	p.r.	D.k. in N_2O–satd. Br^- soln.	72–0036
7.56	Promethazine	4×10^9	–	–	p.r.	–	74–1168
7.57	Pyrene (triplet state) $Br_2^- + {}^3Py \rightarrow 2Br^- + Py^+$	1×10^9	–	–	p.r.	D.k. at 414 nm (^3Py) or 360 nm (Br_2^-) or p.b.k. at 448 nm (Py^+) in 0.02 *M* Br^- contg. 10^{-2} *M* hexadecyltrimethyl ammonium bromide; triplet state formed by f.phot.	76–1181
7.58	Ribonuclease	4.6×10^9	4.5	–	p.r.	D.k. in 10^{-2} *M* Br^- soln.	72–0037
7.59	Subtilisin (serine protease)	1×10^9	7	–	p.r.	D.k. in N_2O–satd. 0.04 *M* Br^- soln.; *k* increases with pH in alk. soln.	73–1147, 74–1119
7.60	Superoxide dismutase	$(0.44 \pm 0.03) \times 10^9$	<10	–	p.r.	Bovine enzyme; $k = (1.18 \pm 0.04) \times 10^9$ for human enzyme; *k* decreases at higher pH.	73–1148, 74–3081
7.61	Tetramethylpiperidone *N*–oxyl (TAN)	1.6×10^9	5–6	–	p.r.	D.k. at 380 nm.	71–0618
7.62	Thymine	$< 1 \times 10^7$	–	–	p.r.	–	74–1168
		2×10^8	12				
7.63	Trypsin	$(2.55 \pm 0.3) \times 10^9$	7.0–8.0	–	p.r.	D.k. in N_2O–satd. 0.04 *M* Br^-.	73–1067
		$(5.30 \pm 0.5) \times 10^9$	11.5				
7.64	Tryptophan	$(7.7 \pm 0.8) \times 10^8$	7.0	0.1	p.r.	D.k. in N_2O–satd. Br^- soln.	72–0036
7.65	Tyrosine $Br_2^- + HOC_6H_4CH_2CHNH_2COOH \rightarrow 2Br^- + H^+ + {\cdot}OC_6H_4CH_2CHNH_2COOH$	$(2.0 \pm 0.2) \times 10^7$	7.5	0.1	p.r.	D.k. in N_2O–satd. Br^- soln.; *k* increases with pH.	72–0036
		$< 1 \times 10^7$	6	–	p.r.	D.k. in N_2O–satd. 0.04 *M* Br^- soln.; values from graph.	73–1067
		$\sim 1.4 \times 10^9$	12				
		5×10^8	12	–	p.r.	–	74–1168
7.66	Uracil	$< 1 \times 10^7$	–	–	p.r.	–	74–1168
		2×10^8	12				

TABLE 8. Rates of reaction of I_2^- in aqueous solution

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
8.1	$I_2^- + I_2^- \rightarrow I_3^- + I^-$	$2k = (7.7 \pm 1.5) \times 10^9$	1.4–6	–	f.phot.	D.k. at 404.7 nm in 3×10^{-5} to 10^{-3} M I^- soln.; ϵ(404.7 nm) = 11,700 M^{-1} cm^{-1}.	57–7007
		$2k = (1.17 \pm 0.2) \times 10^{10}$	6.0	–	f.phot.	D.k. at 385 nm in N_2O–satd. 10^{-3} M I^- soln., or HgI_4^{2-} soln. (10^{-4} M HgI_2 + 10^{-2} M I^-); ϵ(385 nm) = 1.4×10^4 M^{-1} cm^{-1}.	67–7171
		$(8.7 \pm 0.5) \times 10^9$	1.1				
		$(6.7 \pm 0.6) \times 10^9$	6.5				
		$2k = (9.0 \pm 2.0) \times 10^9$	alk.	–	p.r.	Computer analysis of abs. at 335 and 390 nm in N_2O–satd. I^- soln.; ϵ(390 nm) = 15,600 M^{-1} cm^{-1}; ϵ(335 nm) = 8200 M^{-1} cm^{-1}.	76–1105
8.2	$I_2^- \rightleftharpoons I + I^-$	$k_f = 6 \times 10^4\ s^{-1}$	–	–	p.r.	$K^{-1} = 1.13 \times 10^5\ M^{-1}$; $k_r = 7.6 \times 10^9\ M^{-1}\ s^{-1}$ detd. by effect of $[I^-]$ on $[I_2^-]$.	68–0375
		$k_f = 1.7 \times 10^6\ s^{-1}$	–	–	f.phot.	D.k. at 385 nm in HgI_2–I^- soln.	74–7224
		$k_f = (9 \pm 1) \times 10^5\ s^{-1}$	–	–	f.phot.	Detd. in I_3^- soln.	74–7554
8.3	$I_2^- + Co^{2+}$	–	–	–	f.phot.	no reaction	73–7316
8.4	$I_2^- + CoL^{2+} \rightarrow CoLI_2^{+}$ L = 5,7,7,12,14,14–hexamethyl–1,4,8,11–tetraazacyclotetradeca–4,11–diene	$(7.2 \pm 0.8) \times 10^9$	2	0.03	f.phot.	D.k.; I_2^- from ion pair $Co(NH_3)_6^{3+}$, I^-.	72–7506
8.5	$I_2^- + Co(NH_3)_5I^{2+}(+H^+) \rightarrow I_2 + Co^{2+} + 5NH_4^+$	$\sim 2.5 \times 10^4$	–	–	f.phot.	Estd. from intensity dependence of $\Phi(Co^{II})$.	72–7506
8.6	$I_2^- + Cr_{aq}^{2+} \rightarrow [Cr(OH_2)_5I]^{2+} + I^-$	$(1.5 \pm 0.2) \times 10^9$	1	0.2	p.r.	D.k.; ΔG° = –138 kJ mol^{-1}; inner sphere diffusion control.	74–1104
8.7	$I_2^- + Fe_{aq}^{2+} \rightarrow FeI^{2+} + I^-$	3.6×10^6	–	–	–	ΔG° = –22 kJ mol^{-1}; unpub. work cited; inner sphere substitution.	74–1104
8.8	$I_2^- + IO^- \rightarrow IO + 2I^-$	$(5.0 \pm 0.6) \times 10^7$	13.6	–	f.phot.	D.k. in (1–3) $\times 10^{-4}$ M IO^- and I^- soln.	70–0018
8.9	$I_2^- + IOH^- \rightarrow I_3^- + OH^-$	$(1.8 \pm 0.8) \times 10^{10}$	alk	–	p.r.	Computer anal. of abs. at 335 nm and 390 nm in N_2O–satd. I^- soln.	76–1105
8.10	$I_2^- + V^{2+} \rightarrow 2I^- + V^{3+}$	$(1.43 \pm 0.2) \times 10^8$	1	0.2	p.r.	D.k.; ΔG° = –116 kJ mol^{-1}; outer sphere.	74–1104
8.11	Acriflavin	$< 2 \times 10^8$	–	–	p.r.	Decay of I_2^- only slightly increased in presence of dye.	70–0241
8.12	Alcohol dehydrogenase (yeast)	$\sim 1.2 \times 10^9$	–	–	p.r.	Est. from d.k. in N_2O–satd. I^- soln.	73–1C

TABLE 8. Rates of reaction of I_2^- in aqueous solution—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
8.13	Aldolase (rabbit muscle)	$\sim 3 \times 10^8$	–	–	p.r.	Est. from d.k. in N_2O-satd. I^- soln.	73-1065
8.14	Ascorbate ion	$(1.4 \pm 0.3) \times 10^8$	7	–	p.r.	–	72-0266
8.15	Ascorbic acid	5×10^6	2	–	p.r.	–	72-0266
8.16	*p*-Bromophenoxide ion	5.0×10^7	12.5	–	p.r.	At pH 7 $k \cong 5 \times 10^6$.	74-3052
8.17	*p*-Chlorophenoxide ion	5.8×10^7	12.5	–	p.r.	–	74-3052
8.18	Cysteine	$(1.1 \pm 0.1) \times 10^8$	6.8	0.1	p.r.	D.k. in N_2O-satd. I^- soln.; k increases with pH.	72-0036
8.19	Dithiothreitol	$(1.9 \pm 0.2) \times 10^7$	7	–	p.r.	D.k.	73-1020
8.20	Histidine	$< 1 \times 10^6$	7.0	0.1	p.r.	D.k. in N_2O-satd. I^- soln.	72-0036
8.21	Lactate dehydrogenase	$(4.3 \pm 0.5) \times 10^9$	7.2	0.005	p.r.	D.k. at N_2O-satd. I^- soln.	77-1132
8.22	Methionine	$< 1 \times 10^6$	7.0	0.1	p.r.	D.k. at N_2O-satd. I^- soln.	72-0036
8.23	*p*-Methylphenoxide ion	9.8×10^7	12.5	–	p.r.	–	74-3052
8.24	Nicotinamide-adenine dinucleotide, reduced $I_2^- + NADH \rightarrow 2I^- + NAD\cdot + H^+$	$\sim 5 \times 10^7$	–	0.1	p.r.	D.k. at 370 nm in N_2O-satd. I^- soln.	71-0158
8.25	Phenoxide ion	5.7×10^7	12.5	–	p.r.	–	74-3052
8.26	Phenylalanine	$< 1 \times 10^6$	7.0	0.1	p.r.	D.k. in N_2O-satd. I^- soln.	72-0036
8.27	Tetramethylpiperidone *N*-oxyl (TAN)	1.7×10^9	5-6	–	p.r.	D.k. at 390 nm; final product may be I_3^-.	71-0618
8.28	Trypsin	$(1 \text{ to } 6) \times 10^8$	11-12	–	p.r.	D.k. in N_2O-satd. 0.04 M I^- soln.; values from graph.	73-1067
8.29	Tryptophan	$< 1 \times 10^6$	7.0	0.1	p.r.	D.k. in N_2O-satd. I^- soln.; k increases with pH.	72-0036
8.30	Tyrosine	$< 1 \times 10^6$	7.0	0.1	p.r.	D.k. in N_2O-satd. I^- soln.	72-0036

TABLE 9. Rates of reaction of $(SCN)_2^-$ in aqueous solution

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
9.1	$2(SCN)_2^- \rightarrow (SCN)_2 + 2SCN^-$	$2k = 2.9 \times 10^9$	7	0.01	p.r.	D.k. in presence or absence of O_2; ϵ(500 nm) = 7100 M^{-1} cm^{-1}.	65–0386
		$2k \cong 3 \times 10^9$	–	$\rightarrow 0$	p.r.	Second order decay in N_2O–satd. CNS^- soln.; value from graph; ϵ = 7600 M^{-1} cm^{-1}.	68–0375
		$2k = (2.4 \pm 0.4) \times 10^9$	~5.7	0	p.r.	D.k. in O_2–satd. soln. of $\leqslant$ 0.5 M CNS^-; ϵ not given.	72–0475
		$2k = (2.5 \pm 0.2) \times 10^9$	–	0.005	p.r.	Addn. of Cl^- increases k to 3.3×10^9 at 5 M LiCl.	75–1119
9.1a	$(SCN)_2^- \rightleftharpoons SCN + SCN^-$	$k_f = 3.4 \times 10^4\ s^{-1}$	–	–	p.r.	$K^{-1} = 2 \times 10^5$ M, k_r = 7.0×10^9 M^{-1} s^{-1} detd. by effect of $[SCN^-]$ on $[(SCN)_2^-]$.	68–0375
		$k_f \cong 3 \times 10^3\ s^{-1}$	1,6	–	f.phot.	First-order decay in N_2 or N_2O–satd. 2.5×10^{-5} to 2×10^{-4} M CNS^- soln.; second order in presence of O_2 with $2k/\epsilon = 2.0 \times 10^6$.	68–7072
9.2	$(SCN)_2^- + I^- \rightarrow ISCN^- + SCN^-$	1.6×10^9	–	0.005	p.r.	D.k. in N_2O–satd. CNS^- soln.	70–0164
9.3	$(SCN)_2^- + NiL^{2+} \rightarrow Ni^{III}$ L = 5,7,7,12,14,14–hexamethyl–1,4,8,11–tetraazacyclotetradecane	$(1.0 \pm 0.4) \times 10^9$	2	~0.02	p.r.	D.k. in 0.005–0.01 M SCN^- soln.	78–1502
9.4	$(SCN)_2^- + UO_2^+ \rightarrow 2SCN^- + UO_2^{2+}$	$(1.46 \pm 0.34) \times 10^9$	1.0	–	f.phot.	D.k. in CNS^- – U(VI) soln.; reaction probably reoxid. of U(V) to U(VI); assume $[(SCN)_2^-] = [UO_2^+]$.	76–7279
9.5	Alcohol dehydrogenase (yeast)	9.6×10^8	7	–	p.r.	D.k.; $k = 5.6 \times 10^8$ in horse liver enzyme (78–3007).	74–1125
9.6	Aldolase	$< 5 \times 10^9$	7	0.1	p.r.	D.k. in SCN^- soln.; value from graph; k increases with pH.	75–3058
9.7	D–Amino acid oxidase	6.6×10^8	–	–	p.r.	D.k. in N_2O–satd. 0.05 M SCN^- soln.; mol. wt. 50,000.	77–1198
9.8	Ascorbic acid $(SCN)_2^- + AH_2 \rightarrow H^+ + 2SCN^- + \cdot AH$	$(1.0 \pm 0.5) \times 10^7$	1.8	–	p.r.	P.b.k. at 380 nm in 0.1 M SCN^- soln.	72–0266
		$\leqslant 1.0 \times 10^7$	–	–	p.r.	D.k. in N_2O–satd. 10^{-2} M SCN^- soln.	73–3006
	$(SCN)_2 + AH^- \rightarrow H^+ + 2SCN^- + A\cdot^-$	$(6.0 \pm 1) \times 10^8$	7	0.1	p.r.	D.k. in SCN^- soln., as well as p.b.k. at 360 nm.	72–0266
		$(4.8 \pm 0.8) \times 10^8$	6.7	0.01	p.r.	D.k. in N_2O–satd. 10^{-2} M SCN^- soln.	73–3006
9.9	*p*–Bromophenoxide ion	3.10×10^8	12.5	–	p.r.	–	74–3052
9.10	Carboxypeptidase A	(4 to 12) $\times 10^8$	8–11	–	p.r.	D.k.; values from graph.	73–1060
9.11	*p*–Chlorophenoxide ion	3.40×10^8	12.5	–	p.r.	–	74–3052
9.12	α–Chymotrypsin	9×10^8	6.7	0.04	p.r.	D.k. in N_2O–satd. SCN^- soln.	74–1096
9.13	*p*–Cyanophenoxide ion	6.3×10^7	12.5	–	p.r.	–	74–3052
9.14	Cysteamine	8×10^7	–	–	p.r.	–	74–1168
9.15	Cysteine	$(5 \pm 0.5) \times 10^7$	6.6	0.1	p.r.	D.k. in N_2O–satd. SCN^- soln.; k increases with pH.	72–0036
9.16	3,4–Dihydroxyphenyl–alanine	3×10^7	–	–	p.r.	–	74–1168
9.17	Dithiothreitol	$(2.1 \pm 0.2) \times 10^7$	7	0.1	p.r.	D.k. in SCN^- soln.	73–1020

TABLE 9. Rates of reaction of $(SCN)_2^-$ in aqueous solution—Continued

No.	Reaction	$k(M^{-1}\ s^{-1})$	pH	I	Method	Comment	Ref.
9.18	Formate ion	$\leqslant 2 \times 10^3$	7	~1	p.r.	D.k. in N_2O-satd. 1 *M* SCN^- soln.	78-1093
9.19	Histidine	$< 1 \times 10^6$	7.0	0.1	p.r.	D.k. in N_2O-satd. SCN^- soln.	72-0036
9.20	Hydroquinone	6×10^7	–	–	p.r.	–	74-1168
9.21	*p*-Hydroxybenzoate ion	2.65×10^8	12.5	–	p.r.	–	74-3052
9.22	Lactate dehydrogenase	1.5×10^9	7.2	0.005	p.r.	D.k. in N_2O-satd. SCN^- soln.	77-1132
9.23	Lysozyme	6.6×10^8	–	0.1	p.r.	D.k. in N_2O-satd. SCN^- soln.	69-3039, 70-0967
9.24	Methionine	$(2 \pm 0.2) \times 10^6$	7.0	0.1	p.r.	D.k. in N_2O-satd. SCN^- soln.; k increases with pH.	72-0036
9.25	*p*-Methylphenoxide ion	5.52×10^8	12.5	–	p.r.	At pH 7 $k \cong 10^7$.	74-3052
9.26	Nicotinamide-adenine dinucleotide, reduced $(SCN)_2^- + NADH \rightarrow 2SCN^- + NADH^+$	4.7×10^8	–	0.1	p.r.	D.k. in N_2O-satd. SCN^- soln.	71-0158
9.27	*p*-Nitrophenoxide ion	3.9×10^7	12.5	–	p.r.	–	74-3052
9.28	Papain	9.5×10^9 1.75×10^9	7 11.5	–	p.r.	D.k.; activated enzyme used.	74-1026
9.29	Phenol	$< 1 \times 10^7$	–	–	p.r.	–	74-1168
9.30	Phenoxide ion	3×10^8 3.42×10^8	12 12.5	– –	p.r. p.r.	– –	74-1168 74-3052
9.31	Phenylalanine	$< 1 \times 10^6$	7.0	0.1	p.r.	D.k. in N_2O-satd. SCN^- soln.	72-0036
9.32	Promethazine	2×10^9	–	–	p.r.	–	74-1168
9.33	Ribonuclease	3.4×10^7	7	0.05	p.r.	D.k. in N_2O-satd. SCN^- soln.; k increases at pH > 9.5.	72-0037
9.34	Serum albumin	1×10^9 (bovine) 5×10^8 (human)	6.0 6.5	0.01	p.r.	D.k. in SCN^- soln.; also detd. reactivity with alkyl sulfate complexes.	76-1185
9.35	Subtilisin (serine protease)	1×10^8	7	–	p.r.	D.k. in N_2O-satd. 0.04 *M* SCN^- soln.; k increases with pH in alk. soln.	73-1147, 74-1119
9.36	Tetramethyl-piperidone-*N*-oxyl (TAN)	1.1×10^9 1.0×10^9 1.1×10^9	2 5-6 12	0.1	p.r.	D.k. in 0.1 *M* CNS^- soln.	71-0618
9.37	Thymine	$< 1 \times 10^6$ 3×10^7	6 12	–	p.r.	–	74-1168
9.38	Trypsin	$(5.1 \pm 0.5) \times 10^8$ $(3.06 \pm 0.3) \times 10^9$	7-8 11.5	0.04	p.r.	D.k. in N_2O-satd. SCN^- soln.	73-1067
9.39	Trypsinogen	$(2.6 \pm 0.3) \times 10^8$ $(3.6 \pm 0.4) \times 10^9$	7-8 12.1	–	p.r.	–	73-1067
9.40	Tryptophan	3×10^8	7	–	p.r.	–	69-3039
	$(SCN)_2^- + TrpH \rightarrow 2SCN^- + Trp\cdot + H^+$	$(2.7 \pm 0.3) \times 10^8$	7.0	0.1	p.r.	D.k. in N_2O-satd. SCN^- soln.; k increases with pH.	72-0036
	(pK of $TrpH^+ = 4.3$, ref. 76-1151)	4.6×10^8	11.2	–	p.r.	–	73-1147
9.41	Tyrosine	$(5 \pm 0.5) \times 10^6$	7.0	0.1	p.r.	D.k. in N_2O-satd. SCN^- soln.; k increases with pH.	72-0036
		3.2×10^8	11.2	–	p.r.	–	73-1147

Formula Index

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