

The Radiolysis of Methanol: Product Yields, Rate Constants, and Spectroscopic Parameters of Intermediates

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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.

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Reliable data on the properties of matter and materials is 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.



RICHARD W. ROBERTS, *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.

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Product yields and primary yields in the radiolysis of methanol in the solid, liquid and vapor phase have been compiled and reviewed. Preferred values for G of the major products in the vapor and liquid states are listed. Rates of reactions of solvated and trapped electrons and other transient ions and radicals, and optical absorption and esr parameters for e_s^- , e_t^- , $\dot{\text{C}}\text{H}_2\text{OH}$ and $\text{CH}_3\text{O}\cdot$ are also included.

Key words: Chemical kinetics; data compilation; methanol; radiation chemistry; rates; review.

Introduction

The presentation and evaluation of the numerical data summarized in this review attempts to bring together much of the published quantitative information concerning the radiation chemistry of methanol. Discussion of the mechanism of radiolysis is restricted only to explanation of the data. For further discussion of mechanistic detail see [690736, 690391 and 700239].¹

Reference to all the early work on the stable product yields from irradiated methanol has been included (even though more recent and more reliable data are often available), because the early references may contain qualitative information concerning the effects of additives which is not tabulated here but which may be of interest to the reader. However, some attempt to be critical in the selection of numerical values has been made. For example, since the reaction of the solvated electron with methanol is clearly no faster than observed in [710101], reference to earlier investiga-

tions (especially indirect estimates from the effects of nitrous oxide) do nothing but confuse the reader and are omitted.

The uncertainties listed in the tables of product yields and most of the rate parameters are those given in the original work. In many cases they are simply the reproducibility of the experiments and the true uncertainty may be much larger.

1. Gas Phase Radiolysis of Methanol

1.1. Final Products

At room temperature and low doses of ^{60}Co γ -irradiation, the final products are mainly hydrogen, formaldehyde, ethylene glycol, carbon monoxide and methane. $G(\text{H}_2)$ ² seems to increase at higher temperatures but this effect is offset at higher pressures, an observation attributed to ion-molecule clusters [670071].

1.2. Primary Products

At the time of reporting, few values for the unscavengable hydrogen and formaldehyde, and for hydrogen atoms and electrons are available. The latter give reasonable values for W ³ in methanol (see

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¹The coding of the Radiation Chemistry Data Center is used for references throughout this survey.

²The symbol G denotes yield of product per 100 eV (1.602×10^{-17} J) energy absorbed.

³The symbol W denotes the number of ion pairs produced per 100 eV energy absorbed.

[720441]), but confirmation and extension of such observations are required before reliable conclusions concerning the nature and yields of the primary products can be made.

1.3. Dosimetry

In comparing product yields from different investigations, note should be taken of the assumptions used in dosimetry, e.g. $G(\text{N}_2)$ from irradiated nitrous oxide.

TABLE 1. Methanol vapor: Product yields (molec. (100 eV)⁻¹)

Product \ Ref.	Preferred values	610021	630063	640154	650432	670071	670205	701047 ^k
H ₂ ^a	11.0 ± 0.5	10.4	11.8 ± 0.3	10 ± 2	11.2 ± 0.6	10 to 22	10.84 ± 0.07	11.1
(CH ₂ OH) ₂	3.4	3.1						
CH ₂ O		5.6						
CH ₄	0.38 ± 0.05	0.26		0.5 ± 0.1	0.35 ± 0.05	0.7 to 1.5	0.42 ± 0.01 ^j	0.42
CO	1.2 ± 0.1	0.84		1.0 ± 0.2	1.18 ± 0.06		1.41 ± 0.07 ^j	1.25
G(-CH ₃ OH) ^b		12.9						
e ⁻	4.5 ± 0.7			4.1 ± 0.7 ^h				4.0
H	5.4 ± 0.2	8.65 ^f		4.9 ± 0.2 ^h			8.48 ± 0.15 ^{g,j}	5.1
Unscavengeable H ₂	2.3 ± 0.2	1.75 ^f		1.9 ^g	2.1 ± 0.1 ⁱ		2.36 ± 0.05 ^{g,j}	2.0
Unscavengeable CH ₂ O		2.25 ^f						(SF ₆ , C ₃ H ₆)
Radiation ^c	γ	γ	γ	electrons (260 keV)	γ	γ	γ	γ
Dose ^d (10 ¹⁸ eV g ⁻¹)	5 to 50	5 to 50	5	0.4 to 5	3 to 90	350	< 800	30 to 600
Dose rate (10 ¹⁵ eV g ⁻¹ s ⁻¹)	0.02 to 0.4	0.017 and 0.17	0.08	5 × 10 ⁸	0.4	7	9	2.3 to 3.5
T(K)	295	295	389	314	293	323 to 523	room	290 ± 2
Pressure (Torr) ^e	~ 100	80	300	200	87	1900		80
Dosimetry	N ₂ O G(N ₂) = 10.6	N ₂ O G(N ₂) = 9.68	N ₂ O G(N ₂) = 11.0	N ₂ O G(N ₂) = 9.68	N ₂ O G(N ₂) = 9.68	N ₂ O G(N ₂) = 10.6		N ₂ O G(N ₂) = 9.7
Vessel		5 dm ³ soft glass	5 dm ³ soft glass	3 dm ³ Pyrex	0.5 dm ³ Pyrex	0.13 dm ³ Pyrex		0.25 dm ³ Pyrex

^a See table 2.1.2 for isotopic composition of hydrogen from deuterated methanols.

^b Calculated as 2G(glycol) + G(CH₄) + G(CH₂O) + G(CO).

^c All γ-irradiations use ⁶⁰Co sources.

^d Doses are approximate; 1 eV g⁻¹ = 1.602 × 10⁻¹⁶ J kg⁻¹; where the yields are dose dependent, extrapolation to zero dose is normally made.

^e 1 Torr = 133.3 Pa (N m⁻²).

^f With benzene.

^g With propylene.

^h With CH₃Br or CCl₄.

ⁱ With C₂H₄.

^j Measured yields were per ion pair, and were converted to G values by the authors using $W = 27.7$ ion pairs (100 eV)⁻¹; for a recent value of W see [720441].

^k [701014] is a preliminary report.

2. Liquid Phase Radiolysis of Methanol

2.1. Final Products

As in the gas phase, the final products of radiolysis are almost entirely made up of hydrogen, ethylene glycol, carbon monoxide, formaldehyde, and methane for irradiation at room temperature with low doses of ^{60}Co γ radiation. The yields in general decrease at lower temperatures [610015, 650507, 680189, 680397, 680407, 680610]. Small amounts of other products have also been reported [540005, 610020, 640121, 650507].

Low values of $G(\text{H}_2)$ are generally attributable to the presence of electron scavengers as impurities, scavenger concentrations as low as a few micromolar⁴ being sufficient to reduce $G(\text{H}_2)$ by several tenths of a G -unit. This effect was originally used [610015] to demonstrate the reactivity of the electron as a precursor of hydrogen. The removal of carbon dioxide by the degassing procedure is of prime importance [700947] because of the high solubility in methanol; the inadequate removal of CO_2 from the sample may cause difficulties even in the solid phase [690456]. In general, under similar conditions of dose, temperature and additive, the higher G values are to be preferred. Variations in other yields probably arise from errors in the methods of analysis.

There is little effect of dose or dose rate on the yields from ^{60}Co γ irradiations. Recoil nuclei from the $^{10}\text{B}(\text{n}, \alpha)^7\text{Li}$ reaction give similar values of $G(\text{H}_2)$ to γ -radiolysis, but give increased CH_2O and CO yields with a much reduced glycol yield. Interpretation of data from the recoil nuclei irradiations is complicated by the need to include ca. $0.1 M^4$ trimethyl borate in all the samples, but the gross effects of the different linear energy transfer of the radiation are apparent from the tables.

The addition of acid increases $G(\text{H}_2)$ and $G(\text{CH}_2\text{O})$ except at the lower concentrations but leaves the CO , CH_4 and glycol yields unchanged. An increase in hydrogen yield in the presence of small amounts of acid is often reported, but this effect arises from competition between the acid and impurities for the solvated electrons. Hydrogen yields as a

function of pressure (including the effects of acid) have been reported [730292].

2.2. Primary Products

The term "primary product" is applied to those species (ions, radicals, or atoms) which are precursors of the final products. The presence of precursors is usually established by the use of scavengers which affect the yields of the final products. However, conclusions as to their nature frequently require the assumption of a reaction mechanism which cannot be proven and only rarely can it be established that the precursor is truly a "primary product".

A demonstration of this uncertainty is provided by the data in [610015], which were analyzed to show the presence of two precursors of hydrogen. The more reactive precursor was correctly identified as the electron, and later direct observations of the solvated electron permit us to assign the readily scavengeable hydrogen to those electrons which escape the Coulombic field of the positive ions and are "free". The less reactive precursor of hydrogen was thought to be the hydrogen atom, but the analysis of the data cannot indicate the source of these atoms. It is impossible to say what fraction of these hydrogen atoms arise from the neutralization of electrons which do not diffuse a sufficient distance to become "free" but rather return to positive ions in the spur, and hydrogen atoms arising from the decomposition of excited molecules.

It is apparent that many atoms or radicals often described as primary products are in fact secondary products arising from the true primary ions or electronically excited molecules. Thus, "primary product" is rather an indefinite term in the present state of knowledge. The same uncertainty attaches to the numerical values of "primary" product yields, which again require the assumption of a reaction mechanism or model. It is important to realize in using tables 1 to 3 that a "primary" product may itself have a precursor.

A further complication arises because in general, scavenging kinetics depend on the concentration of scavenger used. At low concentrations, usually less than about $10^{-3} M$, the kinetics are usually in accord with the assumption that the species scavenged are homogeneously distributed throughout the medium. At higher concentrations, the

⁴Concentrations of additives are generally expressed in molar units throughout. $1 M = 1 \text{ mol dm}^{-3}$; $1 \text{ mM} = 10^{-3} \text{ mol dm}^{-3}$. Second order rate constants are also expressed in units of $M^{-1} \text{s}^{-1} = \text{dm}^3 \text{ mol}^{-1} \text{s}^{-1}$.

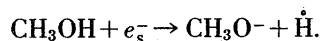
scavenger may react with species in high local concentrations ("spurs"), i.e. the reacting species are not homogeneously distributed. Simple kinetic treatment of the scavenging efficiency is no longer possible, and models accounting for the non-homogeneous distribution of radicals must contain an element of empiricism to a greater or lesser extent. It is seldom possible to establish experimentally that the total amount of primary product has been scavenged and recourse must be made to a model to calculate such yields. Values for the yields of primary products which are scavenged in the spurs are therefore somewhat empirical.

Although CH_2OH has been reported as a scavengable primary product, it is important to realize that much of the so-called "primary" yield arises from secondary abstraction by $\dot{\text{H}}$ atoms or by the $\text{CH}_3\text{O}\cdot$ radical, the latter being expected to be produced in significant yield in irradiated methanol [690456] and identified from its oxidizing properties [690045, 720115, 720122].⁵

These difficulties in assigning the true yields of the primary species in irradiated methanol unfortunately result in some confusion in interpreting the tables of primary yields. Because of the lack of a detailed understanding of many of the processes involved, a more rigorous nomenclature is not yet possible.

2.3. Reaction of the Solvated Electron with Methanol

Electrons which escape the Coulombic field of positive ions in the spur are observed to decay by first-order kinetics in either liquid [710101] or solid [675117] methanol. Although the decay is assumed to arise from reaction of e_s^- or e_t^- with methanol, it is not known whether the reaction is a simple bimolecular dissociative electron capture such as:



Accordingly in table 4.6 it is listed as a first-order decomposition. In the literature, several estimates have been made of the rate constant for this reaction by applying simple competition kinetics to the effects of scavengers on the hydrogen yield or to the nitrogen yield from solutions of nitrous oxide.

⁵ Confirmation that the oxidizing radical is indeed CH_3O has been provided by ESR using the spin trapping technique [725141].

This indirect method has been superceded by direct observation of e_s^- by pulse radiolysis, and the earlier approaches are now only of interest as a guide to the purity of the alcohol and reference to indirect estimates is omitted.

Experience with the analogous reaction in water showed that the early estimates of the rate of the decomposition of the solvated electron in water proved to be orders of magnitude too high. Further, it was only because considerable information was available concerning reactions of e_{aq}^- with other radicals that confident estimates of the rate of decomposition of e_{aq}^- could be made. It is clear that reliable measurements of the decomposition of e_s^- in alcohols can only be made by direct observation by pulse radiolysis, and that the lowest rate measured supercedes all higher values. In the present state of knowledge, this must only be an upper limit.

Only one study of the decomposition of e_s^- is listed in table 4.6. Longer lifetimes may be possible at high concentrations of alkali, but the structure of the solvent may be sufficiently changed that the rate constant may not be applicable to the pure solvent. There seems little doubt that further work will supercede the values listed in table 4.6, although the similar activation energies observed in the liquid and solid phases (the latter for the case with K^+ as the counter-ion) is noteworthy.

2.4. Determination of $G(e_s^-)_{\text{fi}}$ and $G(e_s^-)_{\text{gi}}$

We have already distinguished two kinds of ions: the "free ions", $(e_s^-)_{\text{fi}}$ which have diffused sufficiently from their geminate cations to be regarded as homogeneous and decaying by first-order kinetics at low dose rates, and the "geminate ions", $(e_s^-)_{\text{gi}}$ which, if left, would recombine with their geminate cations. The yields of these species have been the subject of several investigations, but it seems premature to recommend values of these important parameters.

The difficulty of the non-homogeneous distribution of the geminate ions has already been noted, but even the application of simple competition kinetics to the scavenging of the free ions is not without objection if only stable products are measured. Further information concerning the lifetime both of the free and geminate ions under the conditions used is necessary.

Thus if, under the conditions being studied, the half-life of the free ions is (typically) $2 \mu\text{s}$, then for 98% scavenging of the free ions a scavenger with concentration [S] is required such that $(k(e_s^- + S) \cdot [S]) = 2 \times 10^7 \text{s}^{-1}$ and the first-order half-life of $e_{s,fi}^-$ at this [S] is then $\approx 3 \times 10^{-8} \text{s}$. Direct observation of that fraction of the geminate ions which survive longer than ca. $1 \times 10^{-8} \text{s}$ has established that a yield of $G \approx 0.4$ of $e_{s,gi}^-$ survive longer than 10^{-8}s but have all decayed by $2 \times 10^{-7} \text{s}$.⁶ Thus the concentration region in which a scavenger will react with essentially all the free ions but remove a negligible fraction of the geminate ions is quite narrow.

Application of empirical models to scavenging of the geminate ions must consider the often neglected possibility that at high scavenger concentrations the electrons may be scavenged prior to the formation of the ionic atmosphere, when the electron mobility may be orders of magnitude greater than e_s^- . Such scavenging of "dry" electrons has been conclusively demonstrated [730087].

Direct observation of aromatic anions produced by electron attachment [650499, 700360] in principle provides a satisfactory method of determining $G(e_s^-)_{fi}$. The absence of an increase in $G(\text{diphenyl}^-)$ at high concentrations of diphenyl is attributed to spur neutralization of diphenyl^- at times less than 10^{-6}s . Measurement of the yield of a scavenger anion of uncertain extinction coefficient in polar solvents, with unknown rate constant for electron capture and at a single concentration of scavenger [700360] is quite insufficient to estimate $G(e_s^-)_{fi}$, and much further work is required.

The products from electron capture by N_2O , CH_3Br , or SF_6 appear a simple route to estimating scavengable electron yields, but the rate constants of e_s^- with these solutes have not been measured directly and are known to no better than $\pm 30\%$ at best. The N_2O system generally appears to predict $G(e_s^-)_{fi} \approx 1.9$ ⁷, e.g. [720197], whereas the CH_3Br or SF_6 systems suggest a value of about 1.05 [700064]. The halide systems suffer from the prob-

lem of buildup of acid at high doses, but this objection can readily be tested either by calculation or experiment. Unfortunately the doses used were not reported. The marked increase in $G(\text{CH}_2\text{O})$ at high concentrations of N_2O [700947] probably results from a secondary reaction (possibly the slow reduction of N_2O by CH_2OH radicals). The rate constant ratio for electron capture by N_2O and a second solute is independent of N_2O concentration even at high concentrations [670065, 670313] so this complication does not appear to interfere. The nitrous oxide technique seems to be useful as a reasonable guide to electron rate constants even though in principle the use of homogeneous kinetics is often not valid at the concentrations of scavenger used.

$G(e_s^-)_{fi}$ may in principle be estimated from the application of simple competition kinetics to the decrease in $G(\text{H}_2)$ on addition of electron scavengers. This approach is no less direct than the nitrous oxide or alkyl halide methods. The values obtained depend upon the extrapolation of $\Delta G(\text{H}_2)$ to infinite concentrations of scavenger. The reliability of the method depends upon the weight given to the values of $\Delta G(\text{H}_2)$ corresponding to high scavenger concentrations, values which for this purpose may be erroneously high due to spur scavenging and/or reaction with hydrogen atoms, both of which may lead to high values of $G(e_s^-)_{fi}$. On the other hand, the low concentration values, which are free from this objection, are subject to the greatest experimental uncertainty. Thus workers reporting the same $G(\text{H}_2)$ from pure methanol have estimated $G(e_s^-)_{fi}$ to be 1.3 [610015] or 1.8 (see [730292]) using this technique, and we can see no reason for preferring either value.

The importance of a reliable estimate of $G(e_s^-)_{fi}$ is that the ratio of free to geminate ions can be measured directly by pulse radiolysis. It has been shown [710101] that, at least at low temperature, for those electrons which survive long enough to establish the equilibrium ion atmosphere, $G(e_s^-)_{fi} = G(e_s^-)_{gi}$. It is now possible to make similar measurements at room temperature [730147].

⁶ J. H. Baxendale and P. Wardman, unpublished work, see [710101].

⁷ A value in accord with conductivity measurements [710064, 730042].

TABLE 2.1.1. *Liquid methanol: Product yields (molec. (100 eV)⁻¹)**

Product \ Ref.	Preferred values	530004	540005	550003	580003	580005	590017	590017
H ₂ ^a	5.4 ± 0.1	5.0 ± 0.3	3.46 ± 0.05	4.0 ± 0.3	4.1	5.39	4.57 ± 0.08	
(CH ₂ OH) ₂	3.2 ± 0.2		1.74 ± 0.04	3.0 ± 0.2	3.1	3.63	2.91 ± 0.11	2.96 ± 0.09 ^e
CH ₂ O	2.0 ± 0.1		1.67 ± 0.05	1.3 ± 0.1	2.05	1.84	1.91 ± 0.06	1.84 ± 0.12 ^e
CH ₄	0.43 ± 0.03	0.4	0.36	0.24 ± 0.06	1.23	0.54	}0.36	}0.36 ^e
CO	0.13 ± 0.03		0.23	0.16 ± 0.02	0.15	0.11		
Others			See below ^e					
G(-CH ₃ OH) ^b	9.0		5.5	7.7	9.6	9.8	8.1	8.1 ^e
Radiation ^c	γ	β (¹⁴ C)	He ⁺ (~ 28 MeV) ~ 4000	γ	γ	γ	γ	electrons (2 MeV)
Dose ^d (10 ¹⁸ eV g ⁻¹)				See below ^f	0.8 to 20	4 to 400	2 to 300	2 to 200
Dose rate (10 ¹⁵ eV g ⁻¹ s ⁻¹)				5	0.05 to 0.1	2	0.4	40 to 80
T (K)	293 to 303	room	289	room	room	room	293 to 298	room
Notes			Very high doses used					See below ^g

TABLE 2.1.1. *Liquid methanol: Product yields (molec. (100 eV)⁻¹)* - Continued*

Product \ Ref.	604001	610014	610015	610015	610020	610020	610027
H ₂ ^a	5.14 ± 0.02	4.1	5.40	4.15	5.66		~ 5.3
(CH ₂ OH) ₂	1.40 ± 0.10	2.43	3.7	4.0		2.10	~ 3.4
CH ₂ O	3.45 ± 0.10	1.41	2.15	0.65		1.0	~ 1.8
CH ₄	0.67 ± 0.04	0.39	0.80	0.45	0.57		~ 0.4
CO	0.92 ± 0.06	0.13	0.15	0.13	0.45		
Others					C ₂ H ₆ 0.14		
G(-CH ₃ OH) ^b	7.8	6.8	10.5	9.2	6.5		
Radiation ^c	recoils ¹⁰ B(n, α) ⁷ Li	γ	γ	γ	γ	X-rays (3 MeV pk.) ~ 200	γ
Dose ^d (10 ¹⁸ eV g ⁻¹)	30		0.1 to 0.5	0.1 to 0.5	10		600 to 6000
Dose rate (10 ¹⁵ eV g ⁻¹ s ⁻¹)		0.03	0.04 or 0.6	0.04 or 0.6	3.0	40	9
T (K)		293	292	195	299	room	
Notes	See below ^h						Very high doses used

* Footnotes follow the table.

TABLE 2.1.1. *Liquid methanol: Product yields (molec. (100 eV)⁻¹)** – Continued

Product \ Ref.	610029	610029	630056	630056	630056	630060	640121	640121
H ₂ ^a	4.79	9.68	4.60 ± 0.17	4.99 ± 0.36	4.81 ± 0.14	4.99	4.98 ± 0.08	5.53 ± 0.16
(CH ₂ OH) ₂	2.54	0.77	2.92 ± 0.4	0.60 ± 0.09	1.95 ± 0.26	2.99	3.23 ± 0.10	0.87 ± 0.07
CH ₂ O	2.28	3.6 ± 0.4	2.41 ± 0.28	3.15 ± 0.38	2.00 ± 0.17	1.96	2.2	3.04 ± 0.02
CH ₄	0.52	0.88	0.31 ± 0.05	0.57 ± 0.14	0.32 ± 0.04	0.41	0.43 ± 0.09	0.66
CO	0.30	2.98	0.15 ± 0.05	1.00 ± 0.13	0.15 ± 0.02	0.10	0.06	1.0
Others	See below ^l	See below ^l					See below ^l	C ₂ H ₄ 0.035
G(-CH ₃ OH) ^b	8.2	9.0	8.7	5.9	6.4	8.5	9.2	6.4
Radiation ^c	n, γ (pile)	fission ^j fragments	γ	recoils ¹⁰ B(n, α) ⁷ Li	γ	γ	γ	recoils ¹⁰ B(n, α) ⁷ Li
Dose ^d (10 ¹⁸ eV g ⁻¹)	600 to 800	500 to 1000	8 to 30	6 to 140	8 to 30	40	2 to 16	
Dose rate (10 ¹⁵ eV g ⁻¹ s ⁻¹)	~ 50		4	0.01 to 0.5	4	2.5 to 13	4	0.1 to 0.5
T (K)	373	373	~ 293	ambient	~ 293	room	293	ambient
Notes				See below ^k	See below ^k			See below ^k

 TABLE 2.1.1. *Liquid methanol: Product yields (molec. (100 eV)⁻¹)** – Continued

Product \ Ref.	640166	650230	650501	650507	650507	650773	660013	660259
H ₂ ^a	5.1 to 5.6	4.24 ± 0.30	5.26 ± 0.1	4.6 ± 0.2	3.4 to 6.5	4.92 ± 0.03	5.3	4.32
(CH ₂ OH) ₂	0.6 to 0.8	2.72 ± 0.19		5.7 ± 0.3	3.2 to 8.4	2.95	3.24	
CH ₂ O	3.0 to 3.6	1.34 ± 0.07		0.57 ± 0.06	1.0 to 0.33 ⁿ	2.2		
CH ₄	0.58 to 0.64	0.24 ± 0.03		1.5 ± 0.1	0.9 to 2.2		~ 0.6	
CO	1.0 to 1.1	0.20 ± 0.06		0.09 ± 0.01	0.08 to 0.11			
Others				CH ₃ OCH ₃ 0.074	CH ₃ OCH ₃ 0.10 to 0.055			
G(-CH ₃ OH) ^b	~ 6.4	7.2		13.6				
Radiation ^c	recoils ¹⁰ B(n, α) ⁷ Li	γ	γ	γ	γ	γ	γ	γ
Dose ^d (10 ¹⁸ eV g ⁻¹)	10 to 20	< 60	0.7	15 to 200	15 to 200		600	10 to 300
Dose rate (10 ¹⁵ eV g ⁻¹ s ⁻¹)	0.01 to 0.5	1.5	0.4	3	3	3	0.35	0.8
T (K)		293	room	295	213 to 398 ^o		room	293 ± 5
Notes	See below ^k			See below ^m	See below ^m			

*Footnotes follow the table.

TABLE 2.1.1. *Liquid methanol: Product yields (molec. (100 eV)⁻¹)** – Continued

Product \ Ref.	660260	670018	670030	670044	670313	674005	680140
H ₂ ^a	4.5	4.92	4.48	4.4	4.98	5.3 to 6.6	4.89
(CH ₂ OH) ₂	2.8	3.0		3.1		0.5 to 0.6	2.82
CH ₂ O	1.8	2.0		1.5		2.9 to 3.4	
CH ₄		0.35			0.3 to 0.4	0.8 to 1.0	
CO		0.12				0.9 to 1.2	
G(–CH ₃ OH) ^b		8.5				6.2	
Radiation ^c	γ	γ	γ	γ	γ	recoils ¹⁰ B(n, α) ⁷ Li	γ
Dose ^d (10 ¹⁸ eV g ⁻¹)		30	0.4 to 60	2 to 30	12	20 to 40	1 to 3
Dose rate (10 ¹⁵ eV g ⁻¹ s ⁻¹)	0.4	3	1.5	1.3	7		
T(K)	298	room		296	room	ambient	
Notes		See below ^p		Values read from graph		See below ^q	

TABLE 2.1.1. *Liquid methanol: Product yields (molec. (100 eV)⁻¹)** – Continued

Product \ Ref.	680397	680397	680397	680397	680407	680407	680594
H ₂ ^a	4.88	3.17	6.28	5.84	5.30	4.44 to 6.00	4.92
(CH ₂ OH) ₂	3.25	0.36	0.49	0.54	3.24	3.82 to 4.65	2.95
CH ₂ O	1.44	1.59	2.17	2.01	1.88	1.40 to 2.00	2.15
CH ₄			0.70	0.61	0.46	0.35 to 0.50	
CO			1.74	1.50			
G(–CH ₃ OH) ^b			5.6		~ 8.9	~ 9.5 to 11.9	
Radiation ^c	γ	⁴ He ⁺ (3 MeV)	²⁰ Ne ⁺ (22 MeV)	²⁰ Ne ⁺ (22 MeV)	γ	γ	γ
Dose ^d (10 ¹⁸ eV g ⁻¹)	10	10	160 to 180	160 to 180	600	600	
Dose rate (10 ¹⁵ eV g ⁻¹ s ⁻¹)					5	5	3
T(K)	295 to 298	295 to 298	295 to 298	195	303	195 to 383 ^o	room
Notes							

*Footnotes follow the table.

TABLE 2.1.1. *Liquid methanol: Product yields (molec. (100 eV)⁻¹)—Continued*

Product \ Ref.	680610	680610	690089	690146	700947	730292
H ₂ ^a	5.4	4.5 to 8.0	4.5	4.92	5.25 ± 0.2	5.45 ^f
(CH ₂ OH) ₂			2.8	2.66 ± 0.02	3.2	
CH ₂ O			1.8	2.12 ± 0.03	2.0	
CH ₄	0.45			0.5	0.43	
CO	0.2				0.13	
G(-CH ₃ OH) ^b				8.0	9.0	
Radiation ^c	γ	γ	γ	γ	γ	γ
Dose ^d (10 ¹⁸ eV g ⁻¹)	0.6	0.6		0.8 to 1.0	0.4 to 6	2
Dose rate (10 ¹⁵ eV g ⁻¹ s ⁻¹)	5	5	4	2	1.5	1.7
T(K)	298	176 to 513 ^e	room	296	room	296
Notes						

^a See table 2.1.2 for isotopic composition of hydrogen from deuterated methanols.

^b Calculated as 2G(glycol) + G(CH₄) + G(CH₂O) + G(CO).

^c All γ irradiations use ⁶⁰Co source.

^d Doses are approximate; 1 eVg⁻¹ = 1.602 × 10⁻¹⁶ J kg⁻¹; where the yields are dose dependent, extrapolation to zero dose is normally made.

^e G(H₂O) = 0.93 ± 0.03; G(C₂H₆) = 0.014 ± 0.001. Note 2 to 3% decomposition of methanol.

^f Dose ~ (4.5 to 18) × 10¹⁸ eV g⁻¹ to measure gaseous products. Dose ~ (0.4 to 2) × 10²¹ eV g⁻¹ to measure liquid products (very high).

^g All product yields are normalized assuming G(H₂) = 4.57 under these conditions.

^h All solutions contained 0.2 M B(OCH₃)₃.

ⁱ Data for higher hydrocarbons.

^j 84 MeV recoils. Data for 4 different types of ²³⁵U source.

^k All radiolysis samples for recoil nuclei irradiations contain ~0.1 M B(OCH₃)₃. The data in column 2 [630056] are for γ-radiolysis of a similar sample.

^l C₂H₄, 0.004; C₂H₆, 0.006.

^m Glycol and CH₂O yields clearly in error.

ⁿ CH₂O found as CH₂(OCH₃)₂ at 398 K.

^o Data for several temperatures over this range.

^p [650187] is a preliminary report of these data.

^q Samples contained 0.24 to 0.27 M B(OCH₃)₃.

^r Independent of pressure in the range 1 to 5400 bar (10⁵ to 5.4 × 10⁸ Pa). Independent of HClO₄ up to 0.5 mM.

 TABLE 2.1.2. *Isotopic composition of hydrogen from methanol^a deuterated in the methyl or hydroxyl positions*

Reference	Phase	Alcohol	T (K)	% H ₂	% HD	% D ₂	Notes
610021	vapor	CH ₃ OD	295	56	44	0.2	
701047	vapor	CD ₃ OH	290	31	38	30	Also data with added SF ₆ and C ₃ H ₆ .
570027	liquid	CH ₃ OD	room	36	60	4	
630060	liquid	CD ₃ OH	room	11	78	11	See below ^b
650507	liquid	CH ₃ OD	195	29	68	3	
650507	liquid	CH ₃ OD	295	34	63	3	
650507	liquid	CH ₃ OD	398	33	66	2	
650507	liquid	CD ₃ OH	295	15	73	12	
650507	liquid	CD ₃ OH	398	13	75	12	
680167	liquid	CH ₃ OD	room	38	59	3	See below ^c

^a All samples irradiated with ⁶⁰Co-γ-rays.

^b Also data with added LaCl₃, KI; also CD₄/CD₃H = 2.4.

^c Also data with added FeCl₃, N₂O. Also data for samples after recoil nuclei irradiations (¹⁰B(n,α)⁷Li).

TABLE 2.2. *Liquid methanol: Primary yields ((100 eV)⁻¹)**

Product		Ref.	580003	580005	580026	590029	600011	610015
Scavengeable radicals	Total Scavengeable		6.55 ^a		6.3	6.6	6.8	6.3 ^c
	Total e ⁻		3.8 ^b					1.3
	(e ₂ ⁻) _{fl}							2.5
	(e ₂ ⁻) _{st}							
	H·							
CH ₂ OH		2.7						
CH ₃ O·								
CH ₃		1.0						
Unscavengeable ('molecular') products	H ₂		1.7	2.0				1.6 to 1.7 ^d
	(CH ₂ OH) ₂		0.2	0.1				
	CH ₂ O		2.05 ^h	0.36				0.65 ^e
	CH ₄		0.2	0.2				0.22 ^f
	CO		0.15	~0.1				0.12
Radiation ^h		γ	γ	γ	γ	γ	γ	γ
T(K)		room	room	room	room	room	room	room
Notes			With I ₂ (0.04 M)	With FeCl ₃	With 0.01 M C(NO ₂) ₄	2 × G(I ₂) with ICN		

TABLE 2.2. *Liquid methanol: Primary yields ((100 eV)⁻¹)* – Continued*

Product		Ref.	630060	640121	640121	640155	650499	650501	
Scavengeable radicals	Total Scavengeable			6.2		6.26			
	Total e ⁻			3.1	3.1		1.1 ⁿ	1.85 ± 0.1 ^o	
	(e ₂ ⁻) _{fl}								1.05 ± 0.05 ^p
	(e ₂ ⁻) _{st}								
	H·								
CH ₂ OH									
CH ₃ O·									
CH ₃				0.25	0.1				
Unscavengeable ('molecular') products	H ₂			1.9	2.4			1.82 ^a	
	(CH ₂ OH) ₂		~0.4 ^{i,j}	0.1	0.4				
	CH ₂ O		~0.1 ^{i,k}						
	CH ₄			0.18	0.6				
	CO			0.09	0.8				
Radiation ^h		γ	γ	recoils ^l	γ	electrons	γ		
T (K)		room	293	¹⁰ B(n,α) ⁷ Li ambient	room	~ 15 MeV room	room	room	
Notes			With O ₂ (2 to 3mM)	With O ₂ (2 to 3mM)	With DPPH ^m	Pulse radiolysis			

*Footnotes follow the table.

TABLE 2.2. *Liquid methanol: Primary yields ((100 eV)⁻¹)* – Continued*

Product		Ref.	660259	670018	670030	670313	680594	680610
Scavengeable radicals	Total Scavengeable							
	Total e ⁻ (e _s ⁻) _{fl} (e _s ⁻) _{st} H· CH ₂ OH CH ₃ O· CH ₃			2.0 ^r	1.05 } 2.8	1.1 ^t		4.6 2.0 ± 0.2
Unscavengeable ('molecular') products	H ₂ (CH ₂ OH) ₂ CH ₂ O CH ₄ CO		1.7		1.4 to 1.9		1.7 0.3	
	Radiation ^a T(K) Notes		γ room With pyridine	γ room See also 650187	γ room See below ^s	γ room	γ room With FeCl ₃	γ 176 to 423 See below ^u

TABLE 2.2. *Liquid methanol: Primary yields ((100 eV)⁻¹)* – Continued*

Product		Ref.	690146	700064	700360	700947	710064	720115 ^{aa}	730042	730292
Scavengeable radicals	Total Scavengeable									
	Total e ⁻ (e _s ⁻) _{fl} (e _s ⁻) _{st} H· CH ₂ OH CH ₃ O CH ₃		2.02 ± 0.18 } 3.96 ± 0.27	4.15 1.05	1.10 ^x	4.9 ~ 1.3	2.0 ± 0.2 ^z	2.5 ^{bb}	1.8 ± 0.2 ^{cc}	1.7 ± 0.1 ^{dd}
Unscavengeable ('molecular') products	H ₂ (CH ₂ OH) ₂ CH ₂ O CH ₄ CO		1.81 ± 0.27							
	Radiation ^b T(K) Notes		γ 296 See below ^v	γ room See below ^w	electrons room Pulse radiolysis	γ room See below ^y	electrons 298 Pulse radiolysis	electrons room Pulse radiolysis	electrons room Pulse radiolysis	γ 296

*Footnotes follow the table.

TABLE 2.2. *Liquid methanol: Primary yields ((100 eV)⁻¹)—Continued*

Footnotes for table 2.2.

- ^a With 1 *M* FeCl₃ in neutral CH₃OH. *G*(Fe(II)) increased to 7.6 at 0.1 *M* FeCl₃.
- ^b In presence of acid to convert all e_s⁻ to H.
- ^c With FeCl₃, benzoquinone, duroquinone (see also 590020).
- ^d With FeCl₃, benzoquinone, duroquinone, benzene, aromatic polycyclic hydrocarbons.
- ^e With anthracene, benzene, and naphthalene at 195 K.
- ^f With FeCl₃.
- ^g With benzene.
- ^h All γ -irradiations use ⁶⁰Co source.
- ⁱ Read from graph.
- ^j With 0.1 *M* KI.
- ^k With 0.5 *M* LaCl₃.
- ^l All radiolysis samples for recoil nuclei irradiations contain ~ 0.1 *M* B(OCH₃)₃.
- ^m 1,1-diphenyl-2-picrylhydrazyl.
- ⁿ *G*(diphenyl⁻) from solutions of diphenyl. Assumed *G*(diphenyl⁻)=1.0 in ethanol($\epsilon_{\text{diphenyl}^-}$)=5.8 × 10⁴ M⁻¹ cm⁻¹ at 405 nm). Uncertainty ± 30%. See discussion.
- ^o This conclusion not apparent from results.
- ^p $\Delta G(\text{H}_2)$ with 0.1 to 0.5 *mM* NiCl₂.
- ^q With 1.0 *M* LiNO₃.
- ^r Total electrons scavenged with ~ 5 *mM* N₂O (see discussion).
- ^s From theoretical treatment of *G*(H₂) in presence of N₂O, O₂, I₂ or FeCl₃. Low *G*(H₂) in absence of solute.
- ^t From $\Delta G(\text{H}_2)$ with 1 to 10 *mM* N₂O. Low *G*(H₂) in absence of solute.
- ^u From theoretical treatment of *G*(H₂) and *G*(N₂) in presence of N₂O.
- ^v From theoretical treatment of *G*(H₂) in presence of O₂ and H₂SO₄.
- ^w From theoretical treatment of *G*(product) in presence of CH₃Br or SF₆.
- ^x *G*(pyrene⁻) in presence of 10 *mM* pyrene using $\epsilon_{\text{max}}=4.95 \times 10^4$ M⁻¹ cm⁻¹. See discussion.
- ^y From theoretical treatment of *G*(N₂) in presence of N₂O.
- ^z Total negative free ion yield as measured by conductivity.
- ^{aa} [690045] is a preliminary report of these data.
- ^{bb} Of which *G*=2.0 escapes spurs.
- ^{cc} Negative ion yield with 1 to 10 *mM* benzyl chloride, measured by conductivity. *G*(CH₃O⁻)=0.35 ± 0.15.
- ^{dd} From effect of nitrobenzene or acetone on *G*(H₂). *G*(e_s⁻)_n=1.9 ± 0.1 at 5.4 kbar (5.4 × 10⁸ Pa).

3. Radiolysis of solid methanol

Methanol frozen to 77 K may be either polycrystalline (when anhydrous) or glassy (e.g. with 2 to 3% v/v water or propanol as an additive which can be considered inert for most purposes). Depending on the degree of crystallinity, major differences are found in the nature and yields of the species trapped at 77 K or measured after melting. Electrons are trapped only in glassy methanol and the red-purple color of e_t⁻ can be removed by illumination with visible light (photobleaching), changing the yield of the radicals trapped in the glass or measured after melting.

Differences in yields in the solid (anhydrous) methanol probably reflect differences in macro-

scopic structure, since regions where the alcohol is glassy may be produced by rapid freezing even of anhydrous methanol. This will be especially true of small diameter sample tubes where more rapid cooling is obtained.

In glassy methanol *G*(e_t⁻) ≈ 2.5 and an increased yield of H₂ and glycol is observed if the trapped electrons are photobleached prior to melting, when the net decomposition *G*(-CH₃OH) is similar to that observed in the liquid. Much lower yields of formaldehyde are observed after irradiation of solid methanol than in the liquid or vapor phase radiolysis.

TABLE 3. Solid methanol: Product yields (molec. (100 eV)⁻¹)*

Reference	610014	610020	610020	625003	630220	645001
Polycrystalline or glassy?	cryst.	cryst.	cryst.	cryst.	cryst.	glass
Additive ('inert')	none	none	none	none	none	H ₂ O 5% (v/v ?)
H ₂	3.84	3.60				
(CH ₂ OH) ₂	3.31		1.77			
CH ₂ O	0		0.8			
CH ₄	0.51	1.56				
CO	0.25	0.33				
Others		C ₂ H ₆ 0.10	H ₂ O 2.5			
C(-CH ₃ OH) ^a	7.4	6.4				
e ₁ ⁻						2.2 ^e
CH ₂ OH						4.5 ^e
Total radicals				5.5 ^e	5.0 ± 0.8 ^e	6.7 ^e
Radiation ^b	X rays 200 keV	γ	X rays 3 MeV pk. ~ 200	γ or X rays	electrons 1.6 MeV ~ 50 to 300	γ
Dose ^c (10 ¹⁸ eV g ⁻¹)		10	~ 200	0.1 to 10	~ 50 to 300	20 to 150
Dose rate (10 ¹⁵ eV g ⁻¹ s ⁻¹)	0.24	3.0	40	0.3 to 0.5		19
T (K) ^q	77	77	77	77	87 to 93	77
Notes		See below ^d	See below ^d			

 TABLE 3. Solid methanol: Product yields (molec. (100 eV)⁻¹)* - Continued

Reference	650204	650218	650230	660609	670110	670110
Polycrystalline or glassy?	glass	cryst.	cryst.	glass	glass	cryst.
Additive ('inert')	H ₂ O 5% (v/v?)	none	none	H ₂ O 2.4% v/v	H ₂ O 5 mol %	none
H ₂		3.2 ^f	2.41 ± 0.05	3.2 ± 0.1 (4.4 ± 0.1) ^g	3.4	2.8
(CH ₂ OH) ₂			2.12 ± 0.17	2.9 ± 0.2 (4.1 ± 0.2) ^g		
CH ₂ O			0.47 ± 0.05	0.1 (0.1) ^g		
CH ₄		0.15 ^f		0.34 (0.41) ^g	0.50	1.60
CO		0.22 ^f		0.08 (0.15) ^g	0.06	0.08
Others						
C(-CH ₃ OH) ^a		HCO 0.15 ^e		6.3 (8.9) ^g		
e ₁ ⁻	3 ^e			2.9 ± 0.3 ^h		
CH ₂ OH	2 ^e					
Total radicals		5 ^{e,f}	3.8 ^a			
Radiation ^b	γ	γ	γ	γ	X rays 3 MeV pk. 10 to 100	X rays 3 MeV pk. 10 to 100
Dose ^c (10 ¹⁸ eV g ⁻¹)	~ 60 to 120	~ 300	≤ 50	0.07 to 5	10 to 100	10 to 100
Dose rate (10 ¹⁵ eV g ⁻¹ s ⁻¹)		30	0.7 or 1.2	~ 8		
T (K) ^q	77	77	77	77	77	77
Notes				See below ⁱ		

*Footnotes follow the table.

TABLE 3. Solid methanol: Product yields (molec. (100 eV)⁻¹)—Continued*

Reference	680407	685054	685054	685146	690089	690089	690456 ⁿ
Polycrystalline or glassy?	cryst.	glass	glass		glass	cryst.	glass
Additive ('inert')	none	H ₂ O 5.8 mol %	H ₂ O 5.8 mol %		H ₂ O 5.8 mol %		H ₂ O 5.3 mol %
H ₂	2.30				2.9 ^k (4.2) ^g	2.9	3.2 ± 0.1 ^o (4.4 ± 0.1) ^g
(CH ₂ OH) ₂	2.84				2.8 (3.9) ^g	2.7	2.9 ± 0.2 (4.1 ± 0.2) ^g
CH ₂ O	1.48				0.2 (0.3) ^g	0.7	0.1 (0.1) ^g
CH ₄	0.60						0.4 (0.4) ^g
CO							0.1 (0.1) ^g
Others G(-CH ₃ OH) ^a							See below ^p 6.4 (8.8) ^g
e ₁ ⁻		2.61 ^e ± 0.12	2.22 ^e ± 0.05		2.3 ¹		2.7 ± 0.3 ^r
CH ₂ OH Total radicals		(6.12 ± 0.31) ^{e,g}	(5.14 ± 0.16) ^{e,g}	7.5 ^e			
Radiation ^b	γ	γ	β (³ H/HTO) ^j	γ	γ	γ	γ
Dose ^c (10 ¹⁸ eV g ⁻¹)	600	0.8 to 5	0.8 to 5				0.007 to 5
Dose rate (10 ¹⁵ eV g ⁻¹ s ⁻¹)	5	0.0043	0.0042	60	3	3	10
T (K) ^q	77	77	77	77	77	77	77
Notes					See below ^m		See below ^o

^a Calculated as 2 G(glycol) + G(CH₄) + G(CH₂O) + G(CO).

^b All γ irradiations use ⁶⁰Co source.

^c Doses are approximate; 1 eV g⁻¹ = 1.602 × 10⁻¹⁶ J kg⁻¹; where the yields are dose dependent, extrapolation to zero dose is normally made.

^d UV illumination at 77 K after irradiation increased yields of all products.

^e By electron spin resonance (ESR).

^f Read from figure.

^g Yields in parentheses are after photobleaching e₁⁻ with visible light at 77 K prior to melting.

^h Estimated from G(C(NO₂)₂) with 0.1 M C(NO₂)₄ measured at 80 K.

ⁱ Stable products after rapidly melting the sample.

^j [680599] also gives the total radical yields (ESR) after ³H-β irradiation (also γ and ²¹⁰Po-α) but all the samples contained 4 vol % 1 M HNO₃. See also [700418] for ²¹⁰Po-α

^k G(H₂) increased by ~0.8 if e₁⁻ thermally bleached at 102 to 104 K prior to melting.

^l From G(H₂) with I₂ or C(NO₂)₄.

^m G(H)_{scavengeable} = 0.5 (allyl alcohol); G(H)_{unscavengeable} = 1.1; G(H₂)_{unscavengeable} = 0.3.

ⁿ [680370] is a preliminary report of these data.

^o Yields from rapidly melted samples. G(H₂) increased by 0.2 to 0.6 if slowly warmed without photobleaching.

^p Very low G values (~0.001 to 0.01) of C₂, C₃ and C₄ hydrocarbons.

^q Temperatures given are those of irradiation; irradiated solids are melted to room temperature to measure the stable products.

^r From G(C(NO₂)₂) measured at ~80 K in samples containing C(NO₂)₄; see also [660609].

4. Reaction Rate Parameters

See tables 4.1 to 4.8.

TABLE 4.1. *Hydrogen atom reaction rates in methanol vapor*

Reference	S	T (K)	k_2/k_1	Notes
610021	benzene	295	100 ± 20	With CH ₃ OD (HD yield)
610021	benzene	295	100 ± 20	
610021	benzene	295	(k_2/k_{1a}) 65 ± 20	With CH ₃ OD (HD yield)
			(k_2/k_{1b})	
650432	ethylene	293	1300 ± 200	
650432	propylene	293	3000 ± 700	
670205	propylene	room	2700 ± 100	
701047	propylene	290 ± 2	4300	

Method: Application of simple competition kinetics to the decrease in hydrogen yield caused by various concentrations of additive S. Assumes reaction (2) does not produce hydrogen.

TABLE 4.2. *Hydrogen atom reaction rates in methanol liquid*

Reference	S	T (K)	k_2/k_1	Notes
580003	benzoquinone	292	1730 ^a	See below ^b In n-hexane solvent Data from 660259 ^c
610015	benzoquinone	292	1700 ^a	
580003	FeCl ₃	292	3170 ^a	
610015	FeCl ₃	292	3600 ^a	
610015	diphenyl	292	600	
610015	naphthalene	292	940	
610015	anthracene	292	4000	
610015	benzene	292	140	
610015	benzene	195	330	
620067	n-hexane	296	5.6 ± 1.0	
670030	pyridine	room	1900	
670030	I ₂	room	21000	
690146	O ₂	296	5800 ± 700	

^a Estimated from graph.

^b Estimated that $E_2 - E_1 = 4$ kJ.

^c Also values of k_2/k_1 for other H atom scavengers, recalculations of data from [610015] using same method as [610015], not original data.

TABLE 4.3. Solvated electron reaction rates in methanol: relative rates

Reference	S	T (K)	k_4/k_3	Ionic strength	$[\text{N}_2\text{O}]$ (mM)	Notes
670018	H ⁺	room	3.0 ^a	(0.4 to 3) $\times 10^{-3}$	4 to 6	
670018	H ⁺	room	~ 4.5 ^{a, b}	0	4 to 6	
670065	H ⁺	273	7.9	0 ^c	~ 9 or 90	
670313	H ⁺	room	~ 11.7 ^a	0	1 and 50	Read from graph
700947	H ⁺	room	4.5	0.013	7 to 70	
700947	H ⁺	room	~ 10.1 ^b	0	7 to 70	
Recommended value	H ⁺	room	9 ± 2	0		
670065	Ag ⁺	273	2.4	0 ^c	~ 9 or 90	
670313	toluene	room	5.9×10^{-4}	0	0.5	
670313	benzene	room	2.3×10^{-3}	0	0.5 to 5	
670313	fluorobenzene	room	5.8×10^{-3}	0	1.0	
670313	chlorobenzene	room	0.093 ^a	0	10	
670313	acetophenone	room	1.9 ^a	0	1.0	
670313	benzotrile	room	2.1 ^a	0	1.0	
670313	benzyl chloride	room	0.75 ^a	0	1.0	
670313	acetone	room	0.83 ^a	0	1.0	
670313	CCl ₄	room	6.3 ^a	0	1.0	
690456	benzyl chloride	298	0.36 ± 0.04	0	10	
700064	CH ₃ Br	room	1.5 ^a	0	0.1 to 2.5	CH ₄ yield measured ^d
700064	SF ₆	room	3.2 ^a	0	2.7 to 181	F ⁻ yield measured ^d
700064	acetone	room	0.57 ^a	0		See below ^{d, e}
670313	nitrobenzene	room	4.0 ^a	0	1.0	

^a N₂O concentration may have been $\sim 18\%$ higher than authors assumed (see [690456] and discussion). This possibility taken into account in recommending values, but not in tabulating authors' original data or for simple ionic strength corrections to the original data, as on this sheet. This would increase k_4/k_3 by $\sim 18\%$.

^b Estimated by Reviewer assuming effect of ionic strength on reaction (4) given by the Brønsted-Bjerrum/extended Debye-Hückel treatments (see [670065]).

^c Data over full range of ionic strengths.

^d Data fitted to Schuler-Asmus-Warman scavenging curve to account for geminate ion scavenging as well as free ions.

^e Indirectly compared via SF₆ (F⁻ yield).

TABLE 4.4. Solvated electron reaction rates in methanol by pulse radiolysis

Reference	S	T(K)	$10^{-10} \cdot k_5(M^{-1}s^{-1})$
630059	H ⁺	296	3.9 ± 0.9
630059	O ₂	296	1.9 ± 0.4
630059	benzyl chloride	296	0.50 ± 0.12
640080	naphthalene	293	0.2
710064	H ⁺	298	6.81 ± 0.63 ^b
710644	NO ₂ ^{-a}	room	0.13
710644	NO ₂ ^{-a}	room	0.05 ± 0.01
710644	ClCH ₂ CO ₂ ^{-a}	room	0.035 ± 0.004
710644	diphenyl	room	0.13
710644	naphthalene	room	0.27
710644	acetone	room	0.25
717394	N ₂ O	room	1.3 ^c
720062	H ⁺	293 ± 2	5.2 ± 0.2
720194	H ⁺	293	6.5
730292	nitrobenzene	295	2.0
730292	acetone	295	0.42
730292	hexene-1	295	1 × 10 ⁻⁵
730292	benzene	295	1 × 10 ⁻⁴
730292	phenol	295	7 × 10 ⁻⁴
730292	c-hexene	295	< 10 ⁻⁶

^a Ionic strength effects may have been substantial because of the relatively high concentration of scavenger required. True rate constant may be at least 30% smaller than reported, when extrapolated to zero ionic strength.

^b Conductivity method.

^c See note a, table 4.3. This value not consistent with $k(e_s^- + H^+)$, now known to 20% or better, and the measured ratio $k(e_s^- + H^+)/k(e_s^- + N_2O)$ (see table 4.5).

TABLE 4.5. Solvated electron reaction rates in methanol: Recommended values

Reaction(s) Recommended values for reaction (5): $e_s^- + S \rightarrow$ products at room temperature in liquid methanol.					
S	$10^{-10} \cdot k$ ($M^{-1} s^{-1}$) ^b	References	S	$10^{10} \cdot k$ ($M^{-1} s^{-1}$)	References
H ⁺ ^a	5.6 ± 0.8	710064, 720062, 720194	C ₆ H ₅ COCH ₃	1.4 ± 0.4	670313
N ₂ O	0.62 ± 0.16	See table 4.3 (cf. to H ⁺)	C ₆ H ₅ NO ₂	2.0	670313, 730292
Ag ⁺ ^a	1.5 ± 0.5	670065	(C ₆ H ₅) ₂	~0.13	710644
O ₂	1.9 ± 0.4	630059, 690146	naphthalene	0.2 to 0.3	640080, 710644
SF ₆	2.3 ± 0.8	700064	C ₆ H ₅ F	~0.004	670313
NO ₃ ^{-a}	~0.10	710644	C ₆ H ₆	10 ⁻⁴	730292
NO ₂ ^{-a}	~0.03	710644 (690456)	C ₆ H ₅ CH ₃	~0.0004	670313
ClCH ₂ CO ₂ ^{-a}	~0.02	710644 (690456)	C ₆ H ₅ OH	7 × 10 ⁻⁴	730292
CCl ₄	4.6 ± 1.5	670313			
CH ₃ Br	0.9 ± 0.3	700064			
(CH ₃) ₂ CO	~0.42	670313, 700064, 710644, 730292			
C ₆ H ₅ CH ₂ Cl	~0.5	630059, 670313 ^c			
C ₆ H ₅ CN	1.5 ± 0.5	670313			
C ₆ H ₅ Cl	0.07 ± 0.02	670313			

^a At zero ionic strength. Corrections for ionic strength effects made by reviewer (see [670065]) to data reported in [710644].

^b The uncertainties are provided by the reviewer; experience will prove some of them to be optimistic.

^c Data in [690456] suggest a lower value.

TABLE 4.6. Rate of disappearance of solvated and trapped electrons in methanol

Reaction(s)	$(e_s^-)_n \rightarrow$ products (liquid) } $e_t^- \rightarrow$ products (glass) } . . . (6)					
Method: In the liquid, direct observation of e_s^- by pulse radiolysis. In the solid, by observation of the decay of e_t^- by ESR or optical spectroscopy.						
Reference	Phase	T (K)	k_6 (s ⁻¹)	log ₁₀ A	E (kJ)	Notes
710101	liquid	298	≤ 1.0 × 10 ⁶			
710101	liquid	195	≤ 1.9 × 10 ³			
710101	liquid	179 to 333		8.70 ± 0.11 (s ⁻¹)	20.2 ± 0.5	Max. value of k_6
650460	glass (5.3 mol % water)	101 to 105		13.9 ± 1.5 (s ⁻¹)	32 ± 3	
675117	solid ^a	88 to 98		7.0 (s ⁻¹)	20 ± 2	

^a Preparation of e_t^- by reaction of K with CH₃OH on rotating cryostat. The counter ion is therefore K⁺ rather than the proton as in radiolysis experiments.

TABLE 4.7. Methyl radical reactions in methanol vapor or solid

Reference	Reaction and phase	T(K)	$k(M^{-1}s^{-1})$	$\log_{10}A$	E(kJ)	Notes
687279	(7) vapor	413 to 523		8.26 ($M^{-1}s^{-1}$)	41	See below ^a
687279	(7a) vapor (with CH ₃ OD)	413 to 523		8.29 ($M^{-1}s^{-1}$)	42	
687279	(7a) vapor (CD ₃ OH)	408 to 523		8.34 ($M^{-1}s^{-1}$)	50	
687279	(7b) vapor (CD ₃ OH)	408 to 523		7.5 ($M^{-1}s^{-1}$)	40	
637003	(7) solid	77	$\sim 2.2 \times 10^{-5}$			Complex kinetics ^b
670110	(7) solid	77	$\sim 3.7 \times 10^{-5}$			
697036	(7) solid	77	$\sim 8 \times 10^{-6}$			
725012	(7) solid	77	$\sim 7 \times 10^{-8}$			
725140	(CH ₃ OH/H ₂ O, 1:1) (7) solid	77	$\sim 9 \times 10^{-5}$			
725140	(7) solid (CH ₃ OD)	77	$\sim 1.1 \times 10^{-4}$	- 3.46	~ 3.6	
725140	(7) solid (CH ₃ OD)	67	$\sim 4.5 \times 10^{-5}$			

^aSee references in this paper for further work on vapor phase reactions.

^bData for full range of methanol-water mixtures. Considerable effect of matrix.

TABLE 4.8. Rates of reactions of other transients in methanol liquid

Reaction	Other reactions in methanol	Kinetic parameters	Reference
Ar ⁻ + CH ₃ OH → ArH + CH ₃ O ⁻ (8)			
Ar = diphenyl		$k_8 = (6.9 \pm 1.2) \times 10^4 M^{-1}s^{-1}$ at 298 K.	640084
Ar = anthracene		$k_8 = (8.1 \pm 2.0) \times 10^4 M^{-1}s^{-1}$ at 298 K.	640084
Ar = <i>p</i> -terphenyl		$k_8 = (4 \pm 1) \times 10^2 M^{-1}s^{-1}$ at 298 K.	640084
Ar = anthracene		$k_8 = 3.7 \times 10^6 \cdot \exp(-8.8\text{kJ}/RT) M^{-1}s^{-1}$	670188
Ar = diphenyl		$k_8 = 6.2 \times 10^6 \cdot \exp(-11.3\text{kJ}/RT) M^{-1}s^{-1}$	670188
CH ₃ O ⁻ + CH ₃ OH ₂ ⁺ → 2 CH ₃ OH..... (9)		$k_9 = (7.1 \pm 0.3) \times 10^{10} M^{-1}s^{-1}$ at 298 K.	710064 ^a
		$E_9 = 12.6 \pm 0.6$ kJ	710064 ^a
2 e _s ⁻ → products..... (10)		$k_{10} = (3.3 \pm 2) \times 10^9 M^{-1}s^{-1}$ in CH ₃ OD at 298 K	719165 ^b
CH ₃ O + S → CH ₃ O ⁻ + S ⁺ (11)		$k_{11}/k_{12} = (1.4 \pm 0.1) \times 10^4$ at ~ 293 K	720115
CH ₃ O + CH ₃ OH → [*] CH ₃ OH + CH ₂ OH..... (12)		S = I ⁻ or TMPD ^c	
CH ₃ O + TMPD ^c → CH ₃ O ⁻ + TMPD ⁺ (13)		$k_{13} = (6.10 \pm 0.05) \times 10^9 M^{-1}s^{-1}$ at ~ 293 K	720122
		$k_{11} = 3.7 \times 10^9 M^{-1}s^{-1}$ (S = I ⁻) at ~ 293 K	720122
		$k_{12} = (2.63 \pm 0.1) \times 10^5 M^{-1}s^{-1}$	

^aBy conductivity measurements.

^bTheoretical treatment of evolution of hydrogen from the dissolution of sodium in methanol.

^cN,N,N',N'-tetramethyl-*p*-phenylene diamine.

5. Spectroscopic Parameters

5.1. Optical Absorption of Trapped Electrons in Methanol Glass

See table 5.1

TABLE 5.1. Spectroscopic parameters of $e_{\bar{1}}$ in CH_3OH glass

Reference	T (K)	additive	λ_{max} (nm) ^a	$W_{1/2}(+)^b$ (eV)	$W_{1/2}(-)^c$ (eV)	$10^{-4} G\epsilon^d$	Notes
620028	77	2 M CH_3ONa	540				
650298	77		496	0.68	0.35		
650460	80	H_2O 5.3 mol %	533			3.46	
660188	77	<i>n</i> -propanol 4 vol. %	520				
660609	80-85	H_2O 5.3 mol %	526	0.64 ± 0.04	0.36 ± 0.03	3.0 ± 0.3	See also [690456]
670230	77	H_2O 10 mol %	514	0.83			Also data for 30 to 70 mol % water
670651	77		513 (518)	1.28 to 1.44 (0.99)			Data for CH_3OD in parentheses
685130	77	isopropanol 1 mol %	521				
700096	80	H_2O 5.8 mol %	528	0.74 ± 0.01	0.36 ± 0.01	3.17 ± 0.07	
700096	80	NaOCH_3 (1 M)	541	0.74	0.38	3.65	
710091 ^e	4.2	H_2O 5 mol %	605	1.5			Also data for 4-80 K.
720145	77	H_2O 5 mol %	520				Also data for 25 and 60% water.
720428	77	none	519	1.02			

^a Wavelength of maximum absorption.

^b Energy separation between λ_{max} and half-height on high energy side of λ_{max} .

^c Energy separation between λ_{max} and half-height on low energy side of λ_{max} .

^d Units are $M^{-1} \text{cm}^{-1} (100 \text{ eV})^{-1}$. Product of G and ϵ at absorption maximum.

^e For data for methanol/ethanol mixtures at 4 K see [710526].

5.2. Optical Absorption of Solvated Electrons in Methanol Liquid

See table 5.2.

TABLE 5.2. Spectroscopic parameters of e_s^- in liquid methanol

Reference	T (K)	additive	λ_{\max} (nm) ^a	$W_{1/2}$ (+) ^a (eV)	$W_{1/2}$ (-) ^a (eV)	$10^{-4}G\epsilon$ (fi)	$10^{-4}G\epsilon$ (gi)	Notes ^{a,b}
640113	~ 295	none				1.1 ± 0.1 (546 nm)		
640080	~ 295	none	650	0.93 ^d	0.33 ^d	1.39		
650499	~ 295	none	630	0.78 ^d	0.48 ^d	1.9		
650397	~ 295	none	630 ^d	0.88 ^d	0.41 ^d			See below ^e
660082	195	none	580 ^d	1.25 ^d				
700246	~ 295	~ 0.1 M NaI	730 ^d	0.2 ^d	0.2 ^d			
710101	293	none				1.79 ± 0.11	0.43	
710101	187	none				1.83 ± 0.11	1.94 ± 0.2	
710727	~ 295	none	640					
720197	183	none	557	0.69 ^d	0.43 ^d	1.9 (176 K)		
720197	294	none	635	0.87 ^d	0.43 ^d	1.9		
720197	358	none	710					
720197	423	none				1.9		
720293	303	none	640					
720437	~ 295	none	640	1.23 ± 0.04				

^a See footnotes on table 5.1 for definition of symbols.

^b fi = free ions; gi = geminate ions (see discussion). $G\epsilon$ product at λ_{\max} unless stated.

^c Also data for solutions containing CH_3O^- or OH^-

^d Estimated from figure.

^e Also data for mixtures of methanol with tetrahydrofuran or cyclohexane.

5.3. Optical Absorption of $\dot{\text{C}}\text{H}_2\text{OH}$ and $\text{CH}_3\dot{\text{O}}$ in Methanol

Few quantitative studies have been reported; there are some difficulties in interpretation and recommended data cannot be given.

In irradiated glassy methanol, an absorption in the ultra-violet remains after photobleaching the trapped electrons, but the absorption at ca. 200 nm does not change significantly during photobleaching [690456]; an earlier report to the contrary [640080] has not been substantiated [700096]. Since the ESR signal of $\dot{\text{C}}\text{H}_2\text{OH}$ increases considerably during photobleaching, positive assignment of this UV absorption wholly to $\dot{\text{C}}\text{H}_2\text{OH}$ cannot be made [690456].

A similar UV absorption has been reported in liquid methanol after pulse radiolysis [690456, 690419], and at times longer than ca. 1 μs (when

$\text{CH}_3\dot{\text{O}}$ has completely decayed [720122]) this can confidently be ascribed to $\dot{\text{C}}\text{H}_2\text{OH}$. The early spectrum reported with $\lambda_{\max} = 290$ nm appears to be erroneous [640080]. Data for the $G\epsilon$ product and decay constant k/ϵ have been reported [690456, 690418] for $\dot{\text{C}}\text{H}_2\text{OH}$ in liquid methanol and aqueous methanol solutions. The latter studies permit estimation of the extinction coefficient. With 0.5 M methanol in water saturated with N_2O , $G\epsilon(\dot{\text{C}}\text{H}_2\text{OH}) = (1.8 \pm 0.2) \times 10^3 M^{-1}\text{cm}^{-1}$ (100 eV)⁻¹ at 300 nm [690456], giving $\epsilon = 250 \pm 40 M^{-1}\text{cm}^{-1}$ at 300 nm if $G(\dot{\text{O}}\text{H}) = 7.3$ in this solution. The data read from the graph in [690418] appear not inconsistent with this estimate, but the assumed $G(\text{OH})$ was not reported.

The possibility of an absorption ascribable to $\text{CH}_3\dot{\text{O}}$ at times shorter than 1 μs in pulse-irradiated liquid methanol has been explored [720122] but it was concluded that the absorption spectra of $\dot{\text{C}}\text{H}_2\text{OH}$ and $\text{CH}_3\dot{\text{O}}$ may be similar.

5.4. Electron Spin Resonance Parameters for $e_{\bar{1}}$ and $\dot{\text{C}}\text{H}_2\text{OH}$ in Irradiated Solid Methanol

In irradiated solid (glassy) methanol the ESR absorption of $e_{\bar{1}}$ is difficult to establish precisely because of the underlying signal from $\dot{\text{C}}\text{H}_2\text{OH}$. The line shape may be characterized by the parameter ΔH_{ms} , the line width between points of maximum slope on the absorption curve. Values of ΔH_{ms} for $e_{\bar{1}}$ range from 1.1 mT (11 gauss)⁸ to 2.0 mT [625001, 645001, 685088, 685130, 695078]. Electrons trapped in solid methanol on the rotating cryostat by reaction of K atoms with methanol (there being no $\dot{\text{C}}\text{H}_2\text{OH}$ to obscure the spectra) have $\Delta H_{\text{ms}} = 1.12 \pm 0.1$ mT and $g = 2.0018$ at 77 K [675117].

The $\dot{\text{C}}\text{H}_2\text{OH}$ radical is observed in irradiated polycrystalline or glassy methanol, with line shape characteristic of a $\dot{\text{C}}\text{H}_2\text{X}$ species with restricted rotation and anisotropic proton hyperfine coupling. In solids the average splitting is often reported, presumably $(A_{\parallel} + 2A_{\perp})/3$. An average coupling $A_{\text{CH}_2}^{\text{H}} = 1.8$ mT is observed [585000, 625001, 640080, 650230] with $g = 2.001$ [585000]. In solution the $\dot{\text{C}}\text{H}_2\text{OH}$ radical is well characterized, e.g. from the photolysis of hydrogen peroxide in liquid methanol, $A_{\text{CH}_2}^{\text{H}} = 1.784$ to 1.726 mT, $A_{\text{OH}}^{\text{H}} = 0.175$ to 0.100 mT, and $g = 2.00333$ in methanol at 223 to 314 K [660840].

The radical $\dot{\text{C}}\text{H}_2\text{O}^-$ has been reported in solid alkoxides [645013] with $A_{\text{CH}_2}^{\text{H}} = 1.6$ mT.

In sulfuric acid glass the $\dot{\text{C}}\text{H}_2\dot{\text{O}}\text{H}_2$ radical has been identified, with $A_{\text{CH}_2}^{\text{H}} = 2.22$ mT and $A_{\text{OH}_2}^{\text{H}} = 0.5 \pm 0.1$ mT [695130].

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⁸ 1 gauss corresponds to 10^{-4} tesla.

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