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Radiation Chemistry of Ethanol: A Review of Data on Yields, Reaction Rate Parameters, and Spectral Properties of Transients

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Radiation Chemistry of Ethanol: A Review of Data on Yields, Reaction Rate Parameters, and Spectral Properties of Transients

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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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Radiation Chemistry of Ethanol: A Review of the Data on Yields, Reaction Rate Parameters, and Spectral Properties of Transients*

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The yields (*G*) for products and intermediates formed by irradiation of ethanol, in the solid, liquid and gaseous state, have been compiled and reviewed. Rates of reactions of transient ions and radicals and spectroscopic parameters, including optical and esr spectra, are also included.

Key Words: Chemical kinetics; data compilation; ethanol; *G*; radiation chemistry; rates; review; spectra.

1. Assessment Criteria and Data Code Numbers

When the investigation of a kinetic system is in the initial or the final stages, the experimental data can be evaluated according to mainly physical criteria. However, at intermediate stages a major criterion for evaluation is the extent to which the data fit a reaction mechanism.

The investigation of the liquid phase radiolysis of ethanol is at an intermediate stage, while the gas and solid phase studies are at late–initial stages. Matching the experimental results to a mechanism is therefore of great importance for the liquid phase; proposed mechanisms are useful but not stringent criteria for the evaluation of the gas and solid phase results.

Reaction mechanisms in the radiolysis of alcohols have recently been reviewed (700239) and do not require extensive discussion here. Relevant segments of mechanisms are presented where needed in the following sections.

Product yields are reported as G values, the number of molecules formed per 100 eV of energy absorbed by the system. The yields are usually lower when the system contains impurities. For this reason higher yields obtained at low doses are generally favored. A second criterion is self consistency; the yields of the various products should give a material balance.

In assessing rate constants, values obtained from pulse radiolysis are usually favored over those obtained from competition kinetics. Furthermore, the half life of solvated electrons is decreased by the presence of impurities, so the longer values of $t_{1/2}(e^-_{\text{solv}} \rightarrow \text{RO}^-_{\text{solv}} + \text{H})$ are probably more accurate than the shorter ones.

The text of each chapter should be read before the data sheets and figures of that chapter are used.

The data sheets and figures are numbered in such a way that additions to the compilation can conveniently be made in future revisions. In a code number such as **FP*g*1** the capital letters indicate the type of data, in this case Final Product Yields, the small letter indicates the phase, in this case gas, and the number is that of the sheet or figure. The codes are:

FP, final product yields; **PP**, primary product yields;
R, reaction rate parameters; **S**, spectroscopic parameters;
g, gas; *l*, liquid; *s*, solid.

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* This is a data review prepared for, and in cooperation with, the Radiation Chemistry Data Center of the Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556. The Laboratory is operated under contract with the Atomic Energy Commission. The work of the Center is supported in part by the National Bureau of Standards, Office of Standard Reference Data.

The term "primary product" is ambiguous in common usage and therefore requires definition. In the present data review a primary product is a transient intermediate or the final product of an "unscavengable" reaction. Its yield is in most cases not measured directly, but is derived from scavenging studies and a reaction mechanism.

The reference numbers are the code numbers assigned by the Radiation Chemistry Data Center at the University of Notre Dame.

Reference

700239 Freeman, G.R., ACTIONS CHIM. BIOL. RADIATIONS 14: 73–134 (1970).

2. Primary and Final Product Yields

2.1. Gas Phase

The product yields from ethanol vapor depend on the temperature, pressure and radiation dose (680521, 680522, 700231). Different reaction conditions have been used in different laboratories, so a comparison of results obtained by different workers is not straightforward. Reaction conditions are included in the tables.

One persistent difficulty with gas phase radiation chemistry is that no general agreement has been reached about a standard dosimeter. The Fricke dosimeter is reproducible, but its density is several orders of magnitude greater than that of vapors at the pressures usually used. The extrapolation from energy absorption in a Fricke solution to that in a low density vapor is somewhat uncertain, because the energy spectrum of the radiation (primary plus scattered) incident upon the samples is not accurately known in most laboratories.

The nitrogen yield from nitrous oxide has been used as a dosimeter, but the value of $G(N_2)$ depends upon reaction conditions and is not always reproducible (610103, 660434, 660747, 670027, 680318, 680403).

The saturation current method (620115, 640299) is good. It requires an accurate value of W, the average amount of energy expended in the gas per ion pair formed. The reproducibility of W values from one laboratory to the next is within about 4% (570050, 580061, 640177, 650795, 670437, 680390, 680843, 680844, 700510, 710122).

The radiation induced polymerization of acetylene, with $G(-C_2H_2) = 71.9$ (550037), is sometimes used.

A convenient and dependable gas phase dosimeter for γ–radiation in systems containing light atoms (H,C,N,O) is several hundred torr of ethylene at room temperature (~ 25°C). To obtain the same balance between secondary electrons from the cell walls and direct absorption from the γ rays, the pressure of ethylene chosen is that which gives an electron density the same as the sample under investigation. The value $G(H_2) = 1.31$ for ethylene at 25°C is probably accurate to within three percent (620115, 670149, 670398).

Causes of error in addition to dosimetry are likely to be impurities in the original ethanol and difficulties with the methods of microanalysis.

Product yields from the gas phase radiolysis of ethanol vapor at different temperatures, irradiation doses and pressures are given in the following data sheets and figures.

As the temperature is increased from 60°C to about 150°C most of the product yields increase gently and tend to reach plateau values (figs. **FP*g*1** and **2**). At temperatures above 200°C chain reactions begin to occur, causing a general increase in product yields. However, the butanediol yield decreases (fig. **FP*g*2**) due to the relative instability of its precursor radicals CH_3CHOH at high temperatures.

At 150°C, where chain reactions are negligible, the yields of hydrogen and acetaldehyde decrease with increasing dose (fig. **FP*g*3**). Those of methane and carbon monoxide increase slightly with dose (fig. **FP*g*3**). The yields of ethylene (1.1), ethane (0.3), butanediol (3.1), propanediol (0.4) and diethyl ether (0.15) were independent of dose up to 5×10^{20} eV/g (680521).

The yields of hydrogen, acetaldehyde and ethylene at 150°C decrease with increasing ethanol pressure (fig. **FP*g*4**). The *G* values of methane (3.3), ethane (0.3), and carbon monoxide (0.7) are independent of pressure. Those of 2,3–butanediol (3.1) and 1,2–propanediol (0.4) were too scattered to indicate whether they were pressure independent or not (680521).

The effect of ethanol pressure on the chain–product yields at 350°C is illustrated in figure **FP*g*5**. Some product yields increase while others remain constant or decrease as the pressure is increased (680522, 700231, 700239).

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DATA SHEET **FP*g*1**. *Ethanol gas. Final Product Yields*

Reference	610057	650027	650721	670096	670546	680521	(680493) 680522	700231
G (Product)								
H_2	7.6 (9.2)	7.5	10.8	10.3	9.2	9.9 (8.4)	47	
CH_3CHO	4.5	3.5	4.2			3.6 (3.2)	50	
$(CH_3CHOH)_2$	1.2	3.1	1.2			(3.1)	0.6	
CH_4	1.7 (2.4)	2.3	0.9	4.6	0.34	3.3 (3.3)	40	
CO	1.1 (0.9)	0.6	1.2			0.6 (0.7)	10.0	
C_2H_6	0.2 (0.2)	0.2	0.65			0.3 (0.3)	3.6	
C_2H_4	0.7 (1.4)	1.2	1.6			1.1 (1.1)	20	
C_2H_2	0.03	0.09	0.30			(0.26)	(~0.1)	
CH_2O			0.9			(0.8)	(13)	
CH_3OH							17.4	
$(C_2H_5)_2O$			0.07			0.15 (0.15)	(5.6)	~65 (~2.5)
$CH_3CH(OH)CH_2OH$	0.15	0.9	0.16			(0.4)	(1.8)	
$CH_3CH(OH)C_2H_5$							2.9	
Radiation	$^4He^{2+}$	γ	2MeV e^-	γ	γ	γ γ	γ	γ
Dose (10^{18}eV/g)	600(5)	400	70	30	200	10 (80)	120	40
Dose rate (10^{15}eV/gs)	3	17	~ 300	2	6	11	24	24
Dosimetry	Fricke *G*(Fe^{3+}) 15.5	$C_2H_4 \rightarrow H_2$ *G* 1.28	$(-C_2H_2)$ *G* 71.9	Fricke *G*(Fe^{3+}) 15.6	$N_2O \rightarrow N_2$ *G* 10.6	a	a	a
T (°C)	108	105	25	175	108	150	350	380
P (Torr)	660	800	45	3,040	760	860	560	85 (1630)
Cell size (cm^3)	1,000	500	2,040	50	130	500	300	500
Cell material	Pyrex	Pyrex	Al & Brass	hard glass	Pyrex	Pyrex	Pyrex	Pyrex

a. $C_2H_4 \rightarrow H_2$, *G* 1.31.

DATA SHEET **PP*g*1**. *Ethanol gas. Primary Product Yields*

Reference	670096[b]	670546[b]	700239[c]
G (Product)[a]			
e^-		3.5[f]	4.0[g]
H[d]			~ 4
H_2[d]	1.7		1.7
CH_3[d]			1.5
CH_4[d]	0.4		1.6
$CH_3CHO_{scavengable}$[e]			~ 2.5
$CH_3CHO_{unscavengable}$[d]			1.8
$(CH_3CHOH)_2$ scavengable[e]			3.1
$(CH_3CHOH)_2$ unscavengable			0.0
Method	C_2H_4 scavenger	temp. effect on H_2 & CH_4 yields	dose and scavenger effects

a. Yields derived from scavenging studies.
b. Reaction conditions same as on data sheet **FP*g*1**.
c. γ, 860 Torr, 150°C, extrapolated to zero dose.
d. Product that does not result from a neutralization reaction.
e. This is not a primary product because it results from free radical reactions.
$G(CH_3\dot{C}HOH) \cong 2G(CH_3CHO + (CH_3CHOH)_2)_{scavengable} \cong 11.$
f. Estimated from a mechanism that is probably not correct (see 700239).
g. The average amount of energy expended per ion pair formed is
$W = 25.1$ eV (650795).

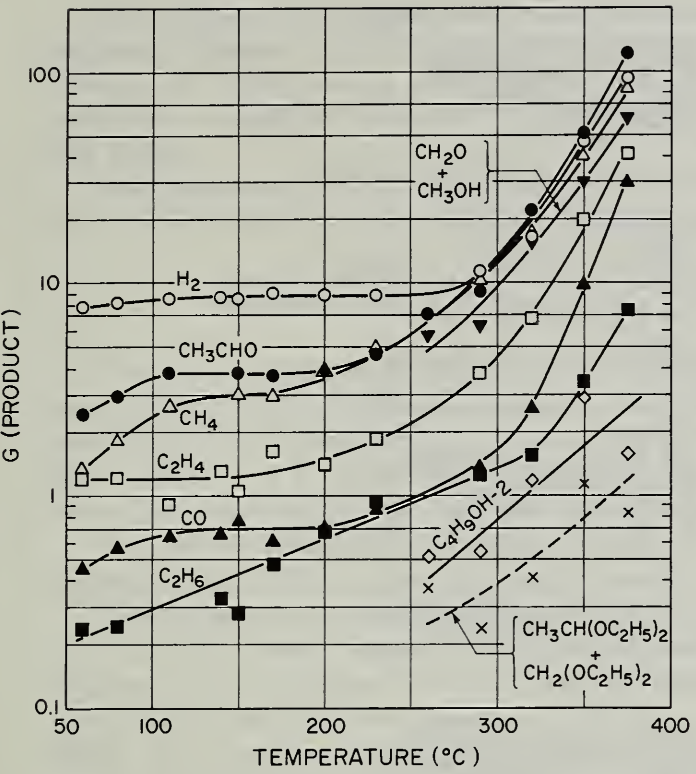

FIGURE FPg1. *Product yields from the γ–radiolysis of ethanol vapor as a function of temperature* (680493, 680521, 680522).
Ethanol density = 0.66g/l (385 Torr at 150°C).
Dose = 1.3 x 10^{20}eV/g. (×), the yields of $CH_3CH(OC_2H_5)_2$ and $CH_2(OC_2H_5)_2$ were approximately equal. ▼, see figure **FPg2** for the separate yields of CH_2O and CH_3OH.

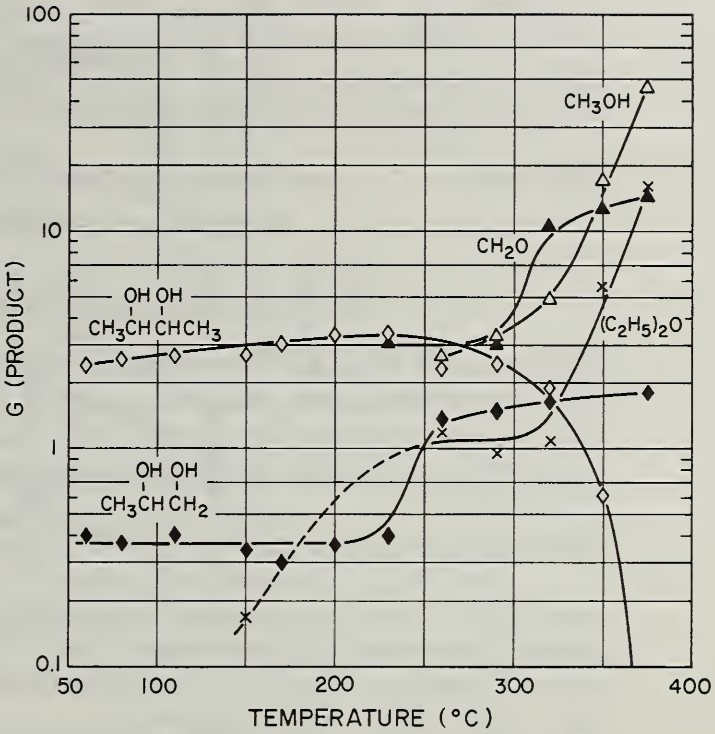

FIGURE FPg2. *Product yields from the γ–radiolysis of ethanol vapor as a function of temperature* (680493, 680287, 680521, 680522). Conditions same as in figure **FPg1**.

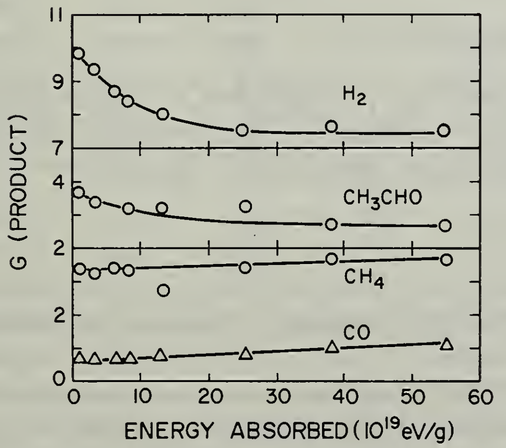

FIGURE FPg3. *Product yields from the γ–radiolysis of ethanol vapor as a function of dose at 150°C* (680521). Ethanol pressure = 860 Torr (1.50g/l).

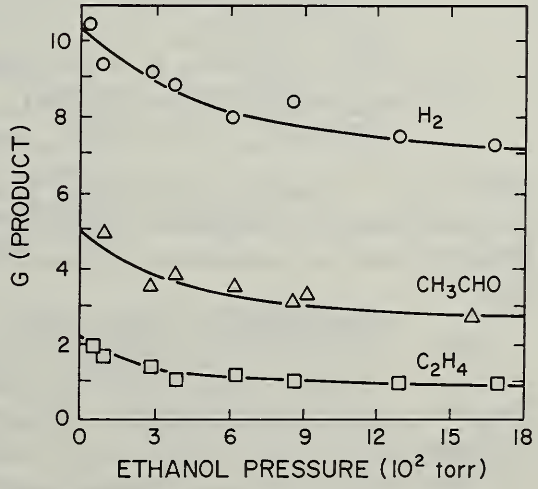

FIGURE FPg4. *Product yields from the γ–radiolysis of ethanol vapor as a function of pressure at 150°C* (680521). Dose = 8 x 10^{19}eV/g. The points represent experimental results; the solid lines were calculated from the proposed mechanism (680521).

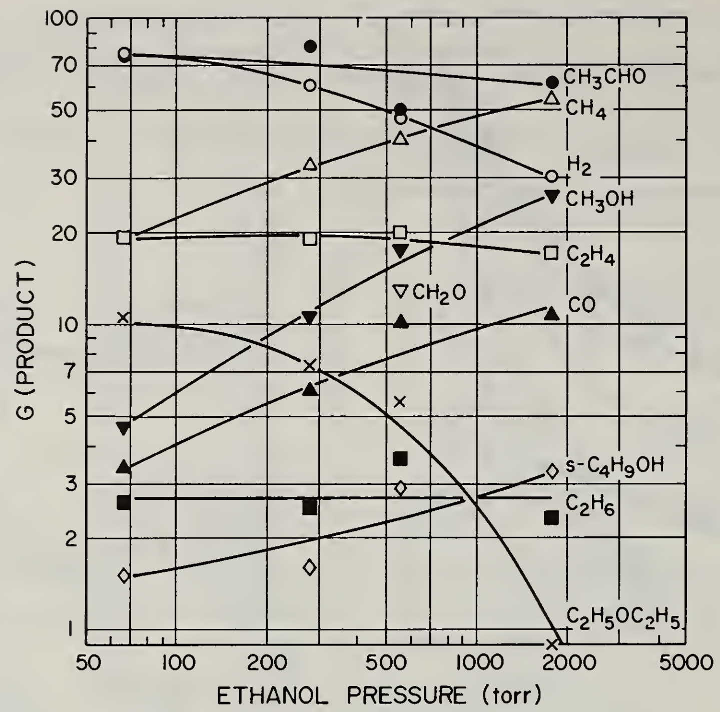

FIGURE **FPg5**. *Product yields from the radiation sensitized pyrolysis of ethanol, as a function of pressure* (680493, 680522). Temperature = 350°C. Dose = 8 x 10^{19}eV/g.

2.2. Liquid Phase

The main products from the radiolysis of liquid ethanol are hydrogen, acetaldehyde and 2,3–butanediol (sheets **FP*l*1** and **2**). Probable sources of error in the measured yields were impurities in the irradiated ethanol and difficulties with the methods of microanalysis. The error in the Fricke dosimetry used for all the γ radiolyses should have been $\leqslant 1\%$.

The yields of hydrogen and acetaldehyde decrease with increasing dose above 10^{17}eV/g (fig. **FP*l*1**), while that of 2,3–butanediol is independent of dose (650045, 660839, 680575).

Dose dependence of the hydrogen and acetaldehyde yields is caused by competition between the solvated electron reactions (1) and (3),

$$e^-_{solv} \rightarrow C_2H_5O^-_{solv} + H \qquad (1)$$
$$H + C_2H_5OH \rightarrow H_2 + CH_3CHOH \qquad (2)$$
$$e^-_{solv} + CH_3CHO \rightarrow CH_3CHO^-_{solv} \qquad (3)$$
$$CH_3CHO^-_{solv} + C_2H_5OH^+_{2\ solv} \rightarrow CH_3CHOH + C_2H_5OH \qquad (4)$$

where e^-_{solv} is actually $e^-(C_2H_5OH)_n$. The yield of 2,3-butanediol is independent of dose because the same number of precursor CH_3CHOH radicals result from either (1) or (3), through (2) and (4). Thus the rates of *formation* of butanediol and acetaldehyde are unaffected by the occurrence of (3).

$$2CH_3CHOH \rightarrow (CH_3CHOH)_2 \qquad (5)$$
$$\rightarrow CH_3CHO + C_2H_5OH \qquad (6)$$

The *net yield* (formation minus destruction) of acetaldehyde decreases because (3) destroys aldehyde.

The solvated electrons that undergo (3) at doses $\leqslant 10^{20}$eV/g are free ions. The aldehyde concentrations at these doses are $\leqslant 10^{-3}M$, and electrons that undergo geminate neutralization are too short lived to react appreciably with such low concentrations of scavenger (698025, 700239). At doses $\geqslant 10^{21}$eV/g the aldehyde is $\geqslant 10^{-2}M$, and by analogy with nitrous oxide solutions (680047, 698025) scavenging in spurs becomes significant at these concentrations.

The addition of a mineral acid to ethanol causes the yields of hydrogen and acetaldehyde to increase, whereas that of 2,3–butanediol remains unchanged (640279, 660839, 680047, 680575, 700239); as more acid is added $G(H_2)$ increases to a plateau of about 5.9 and $G(CH_3CHO)$ increases to a plateau of about 3.7 (660839, 680047). The plateau values are independent of dose (fig. **FP*l*1**).

Acid counteracts the effect of acetaldehyde formation in two ways: reaction (7) competes with (3), and (8) converts acetaldehyde into unreactive acetal.

$$e^-_{solv} + C_2H_5OH_2^+{}_{solv} \rightarrow C_2H_5OH + H \qquad (7)$$

$$CH_3CHO + 2C_2H_5OH\ (+\ H^+) \rightarrow CH_3CH(OC_2H_5)_2 + H_2O \qquad (8)$$

The upper, horizontal hydrogen curve in figure **FP*l*1** represents the values of $G(H_2)$ obtained when HCl or H_2SO_4 is added to ethanol. The lower hydrogen curve was calculated by assuming that $G(e^-_{solv})_{fi} = 1.7$ and $G(H_2)_0 = 5.9$ in neutral ethanol. The rate constants used were $k_1 = 1.2 \times 10^5 s^{-1}$ and $k_3 = 4 \times 10^9 dm^3 mol^{-1} s^{-1}$ (700172). The decrease in $G(H_2)$ at doses $> 4 \times 10^{20}$ eV/g is caused by acetaldehyde scavenging electrons in the spurs.

The curves through the acetaldehyde yields in figure **FP*l*1** are analogous to those through the hydrogen yields. The two sets are superimposable by a vertical displacement of 2.1 *G* units.

The hydrogen yield from liquid ethanol has been measured at temperatures from −112°C (mp = −117°C) to the critical temperature, 243°C (fig. **FP*l*2**). The increase of $G(H_2)$ from neutral ethanol at temperatures between 25° and 100°C is probably associated with the competition between reactions (1) and (3). The addition of acid removes the temperature effect in this region (fig. **FP*l*2**). The hydrogen yield increases gently as the temperature is increased above 150°C, and there is no discontinuity as the system passes through the critical temperature (fig. **FP*l*2**).

Yields of reactive intermediates and unscavengable yields of final products are given on sheets **PP*l*1** and **2**.

The free ion yield decreases gently with increasing temperature (698025), but is independent of pressure up to 5300 bar (720199). See sheets **PP*l*2** and **3**.

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DATA SHEET **FP/1**. *Ethanol liquid. Final Product Yields*

References	540005	560017	550032	610020	610098	640279	650045	690566
G(Product)								
H_2[a]	3.5	4.1	6.0	5.53	4.87	4.85	4.6, 5.0[d]	5.0
CH_3CHO[a]	1.7	3.0[c]	0.8(1)	(1.40)	3.14		(1.9), 2.8[d]	3.2
$(CH_3CHOH)_2$[a]	~0.7(1.0[b])	1.4[b]		(1.95)	1.67	2.80	(2.2)	1.7
CH_4[a]	0.43	0.43	0.1(0.2)	0.80	0.58	0.61	0.6, 0.6[d]	0.6
CO	0.11	0.09	0.2(0.3)	0.10	0.26		0.06	
H_2O	0.8		1.2(2.1)				(0.5)	0.30
C_2H_6	0.17	0.18		0.30		0.23	0.24	0.11
C_2H_4	0.17	0.22		0.27		0.1	0.14	0.19
C_2H_2	0.04						(≤0.02)	
C_3H_8	0.025						0.009	
C_4H_{10}	< 0.010						(0.0004)	
$CH_3CH(OH)C_2H_5$							(0.08)	
CH_2O	0.30						0.13	0.4
$(CH_2OH)_2$	~0.3						(0.01)	
$CH_3CH(OH)CH_2OH$							(0.13)	
$HO(CH_2)_3OH$	0.0						(0.002)	
$CH_3CH(OH)CH_2CH_2OH$							(0.05)	
$HO(CH_2)_4OH$							(0.01)	
Radiation	$^4He^{2+}$(28 MeV)	$^4He^{2+}$(28 MeV)	X(e^-)	γ(X)	γ	γ	γ	γ
Dose(10^{18}eV/g)	8000	300	–	10(200)	~ 1	3	10(100)	~ 1
Dose rate(10^{15}eV/gs)	1 x 10^6	3 x 10^4	300	3(40)	~ 1	0.6	0.3 – 17	2
Temp. (°C)	18	21	25	26	20	room	25	room

a. See data sheet **FP/2** for additional data and preferred values.
b. Total vicinal glycol.
c. Total carbonyl.
d. Extrapolated to zero dose.

Data Sheet **FP*l*2**. *Ethanol liquid. Final Product Yields*

Reference	$G(H_2)$	$G(CH_3CHO)$	$G(CH_3CHOH)_2$	$G(CH_4)$	Radiation	Dose (10^{18}eV/g)	Dose Rate (10^{15}eV/gs)	Temp. (°C)	Press. (bar)[c]
570024 570025	3.7	—	—	—	γ	500	—	room	—
590020	4.35	—	—	0.60	γ	5	0.1	18	—
620140	—	1.9	1.3	—	e^-(15MeV)	400	4 x 10^8	room	—
640228	—	—	—	0.45	γ	10	5	20	—
650501	4.9	—	—	—	γ	0.7	0.4	room	—
660133	4.87	2.18	—	—	γ	4	4	20	—
660839	4.2(5.0)	2.0	2.2	0.6(0.61)	γ	100(0.7)	10	room	—
670004	4.85	—	—	—	γ	1	2	room	—
670012 680047	5.1	—	—	—	γ	0.2	10	25	—
670223	4.2	—	—	0.4	γ	8	3	20	—
680336	—	—	2.8	—	γ	800	30	20	—
680575	5.0(4.0)	3.2(2.3)	1.7(1.6)	—	γ	1(100)	1	room	—
690651	4.5	—	—	—	γ	~ 5	2	room	—
700172	5.9[a]	3.7[a]	2.3[a]	—	γ	0[a]	—	25	—
710009	5.9[a]	—	—	—	γ	0[a]	7	20	—
720199	5.0	—	—	—	γ	1	2	23	1
720199	5.5	—	—	—	γ	1	2	23	5300
720199	5.7	—	—	—	γ	0[a]	2	23	1–5300
Preferred Values[b]	5.8 ± 0.1[a]	3.7 ± 0.2[a]	2.1 ± 0.4	0.61	γ	≤ 0.01	0.1–100	22 ± 4	0–5300
	5.1 ± 0.2	3.0 ± 0.2	2.1 ± 0.4	0.61	γ	1	0.1–100	22 ± 4	0–500
	4.15 ± 0.15	2.0 ± 0.2	2.1 ± 0.4	0.61	γ	100	0.1–100	22 ± 4	0–500

a. Extrapolated to zero dose.
b. See figure **FP*l*1** and discussion in section 2.2.
c. Pressure equals vapor pressure, ~ 50 Torr, unless otherwise stated.

Data Sheet **PP*l*1**. *Ethanol liquid. Primary Product Yields.* (*contd.* on **PP*l*2**)

Reference	590020	610098	640113 650499	640155	640279	650045	650501	660308
G(Product)								
Intermediates								
e^- (total)[a]							1.65[d]	
$(e^-_{solv})_{fi}$[b]		1.4	1.0[c]		1.02	0.9	0.9	
$H_{spur,\ scavengable}$	2.7				2.25	2.7	2.7 – 3.0	
CH_3	0.44					0.4		
$CH_3\dot{C}HOH$						6.4		
radicals (total)	6.9			7.76				6.5
triplet states								
Unscavengable								
H_2	1.65				1.65	1.5		
CH_4	0.16					0.2		0.28(0.26)
CH_3CHO						1.9		
Radiation	γ	γ	pulse 14MeV e^-	γ	γ	γ	γ	γ(X)
Dose(10^{18}eV/g)	5	1	0.14	~ 10	3	2 – 100	0.7	10(0.5)
Dose rate(10^{15}eV/gs)	0.1	0.3	3 x 10^8	3	0.6	0.3 – 17	0.4	4(2)
Temp. (°C)	18	20	25	25	room	25	room	
Scavenger	benzoquinone	$HOCH_2COOH$ $ClCH_2COOH$ $ClCH_2CH_2OH$	biphenyl	DPPH	H_2SO_4 CH_3CHO CH_3COCH_3 $ClCH_2COOH$ anthracene	C_6H_6 pentadiene-1,3	$LiNO_3$ $ClCH_2COOH$ Ni^{2+}, Co^{2+}	I_2

Data Sheet **PPl2**. *Ethanol liquid. Primary Product Yields*

Reference	670004	670012	670173 (680575)	680047	698025	700064	700172	700360	710009	Preferred Values
G(Product)										
Intermediates										
e^-(total)[a]		3.1		4.0	4.3	4.1	(4.3)			4.3
$(e^-_{solv})_{fi}$[b]	0.9	1.2	0.95	1.5	1.5[h]	1.05	1.7	1.0	1.7	1.7[f]
$H_{spur,\ scavengable}$	2.3	2.0	2.33	2.2						2.6
CH_3										0.4
$CH_3\dot{C}HOH$			6.3				(8.4)[e]			~ 8[g]
radicals (total)										
triplet states								(~ 0.07)		
species X		0.8		0.8					0.0	0.0[f]
Unscavengable										
H_2	1.7		1.72							1.6
CH_4										0.2
CH_3CHO			1.7							1.8
Radiation	γ	γ	γ	γ	γ	γ	pulse 2MeV e^- (γ)	pulse 2MeV e^-	γ	γ or e^-
Dose(10^{18}eV/g)	1	0.2	~ 1	0.2	0.2	0.2	0.08	0.9	0.1	
Dose rate(10^{15}eV/gs)	2	10	2	10	10	~ 1	2 x 10^8	3 x 10^{10}	7	
Temp. (°C)	room	25	25	25	25[h]	room	25	room	20	25
Scavenger	acetone	N_2O, HCl	$ClCH_2COOH$ (O_2, Fe^{3+})HCl	N_2O H_2SO_4	N_2O	SF_6, CH_3Br	terphenyl, $C_2H_5O^-$	anthracene (+ N_2O for triplets)	H_2SO_4, N_2O, CH_3CHO	

Footnotes to *Data Sheets* **PPl1** and **2**.

a. Derived from an assumed model.

b. The free ions are those that escape neutralization in the spurs.

c. Used ϵ(biphenylide) = (1.1 ± 0.4) x $10^4 M^{-1}cm^{-1}$ at 546 nm and 1.5 x $10^4 M^{-1}cm^{-1}$ at 700 nm.

d. This value is much too low, because it was derived from results obtained from dilute electron–scavenger solutions, *e.g.* $10^{-2} M$ chloroacetic acid.

e. Estimated from the listed yields of scavengable products.

f. See also sheet no. **PPl3**. Lower values of $G(e^-_{solv})_{fi}$ apparently result from the use of impure ethanol or high irradiation doses (> 10^{17}eV/g). Values of $G(e^-_{solv})_{fi} \cong 1.0$ are associated with reported values of $k(e^-_{solv} \rightarrow C_2H_5O^-_{solv} + H) \geqslant 2 \times 10^5 s^{-1}$, which are too high (see sheet **Rl1**).

g. The values of $G(CH_3\dot{C}HOH) \cong 6 - 7$ correspond to a value of $G(e^-_{solv})_{fi} \cong 1.0$. The $CH_3\dot{C}HOH$ yield has to be increased by 2(1.7 − 1.0) = 1.4 units to match $G(e^-_{solv})_{fi} = 1.7$.

h. $G(e^-_{solv})_{fi}$ = 1.7, 1.4 and 1.2, at −112, 90, and 145°C, respectively.

Data Sheet **PPl3**. *Ethanol liquid. Free Ion Yields*[a]

Reference	710064	710531	710759	720199
G (Free Ion)				
e^-_{solv}	1.95 ± 0.4[b]	1.8 ± 0.2[b]	1.05	1.7
$C_2H_5O^-$		1.8 ± 0.1[b]		
X^-		0.34 ± 0.04[b]		
Total		3.4 ± 0.1[b]		
Radiation	pulse 10 MeV e^-	pulse 2 MeV e^-	pulse 5 MeV e^-	γ
Dose (10^{18}eV/g)	0.1	0.01	0.1	1
Dose rate (10^{15}eV/gs)	10^8	10^7	10^8	2
Temp. (°C)	26 ± 4	17	room	23
Press. (bar)	1	1	1	1, 5300
Scavenger	N_2O, $HClO_4$, NaOH	$C_6H_5CH_2Cl$, $HClO_4$	KOH, $NaOC_2H_5$	$C_6H_5NO_2$, CH_3COCH_3, naphthalene

a. See also data sheet no. **PPl2**.

b. Measured by a radiation induced electrical conductance method.

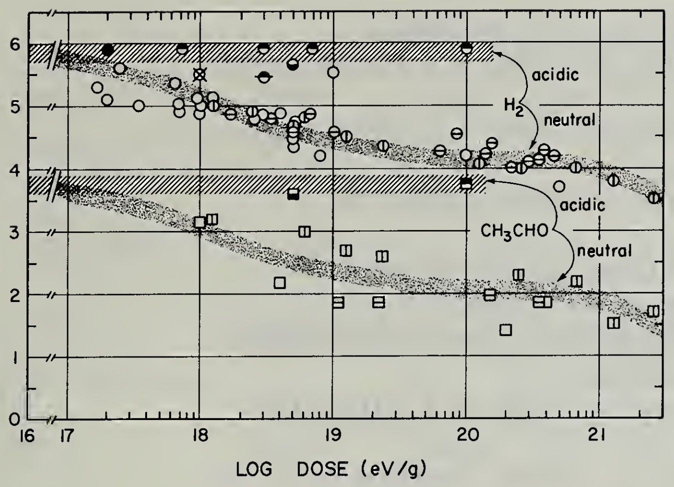

Figure FP*l*1. *Yields of hydrogen and acetaldehyde as functions of absorbed γ–ray dose in liquid ethanol at 22 ± 4°C.*
Circles, H_2; squares, CH_3CHO. The neutral ethanol curves are calculated (see section 2.2).
Neutral ethanol: ⊖, ⊟, 650045; ⦶, ◫, 680575; ○, □, all other references in sheets **FP*l*1** and **2**.
$10^{-2}M$ *HCl* or H_2SO_4: ◓, ⬒, 660839; ◒, ⬓, 680575; ●, 680047; ⦵, 640279.
The yield of 2,3–butanediol is 2.1 ± 0.4, (sheets **FP*l*1** and **2**), independent of dose (650045, 680575) and of the presence or absence of acid (640279, 650045, 660839).
5300 bar: ⊠; all other experiments were done at the vapor pressure, ~ 50 Torr.

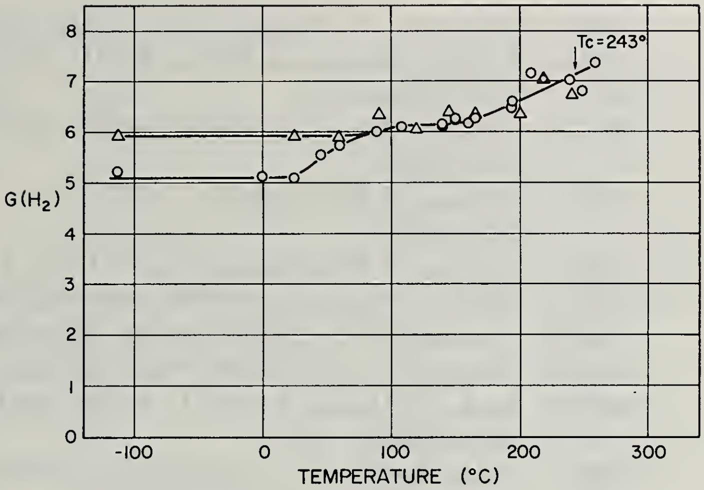

Figure FP*l*2. *Yield of hydrogen from the γ–radiolysis of liquid ethanol at different temperatures* (680047). ○, neutral; △, 3 x $10^{-4}M$ HCl. Dose = 2 x 10^{17}eV/g. 7.9 g ethanol in a 30 ml bulb. Critical density = 0.276 g/cm^3.

2.3. Solid Phase

There are many similarities between the liquid and solid phase product yields (see sheets **FP*l*2** and **FP*s*1**). In both phases electron reactions make the hydrogen and acetaldehyde yields sensitive to the radiation dose and to the presence or absence of a mineral acid (670023).

Electrons and neutral free radicals are trapped in solid ethanol when it is irradiated at 77 K (620100, 625003). The presence of a solute such as sodium hydroxide in the ethanol increases the yield of trapped electrons (635001), whereas the presence of a mineral acid decreases it (645001). Addition of an aromatic hydrocarbon to the alcohol increases the yield of trapped negative charges by capturing electrons to form anions. The same yield of trapped negative charge is obtained, $G(e^-_{\mathrm{trap}} + \text{anion}) \cong 3.0$, whether the solute is sodium hydroxide or an aromatic hydrocarbon (sheets **PP*s*1** and **2**). In the absence of an added solute, $G(e^-_{\mathrm{trap}}) \cong 2.3$. In both the presence and absence of a solute, $G(\text{anions} + \text{neutral radicals})_{\mathrm{trap}} \cong 9$.

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DATA SHEET **FP*s*1**. *Ethanol solid. Final Product Yields*[g]

Reference	590044	610020	610098		660133	660195	670023	670272	680336
G (Product)[a]									
H_2	4.7, 5.9[b]	4.6, 5.9[b]	6.0	4.5	4.4		4.0[c], 4.9[d]	4.4, 4.9[f]	
CH_3CHO		*2.4, 4.2[b]	3.5	3.6	3.1	2.6	2.8, 3.8[d]		
$(CH_3CHOH)_2$		*0.8, 1.4[b]	2.6	0.95		0.94	0.85, 1.0[d]		0.7
CH_4	0.28, 0.46[b]	0.30, 0.42[b]	0.22	0.45			0.3, 0.3[d]		
CO	0.01, 0.30[b]	0.01, 0.30[b]	0.11	0.20			0.3, 0.3[d]		
C_2H_6	0.29, 0.28[b]	0.41, 0.28[b]					0.3, 0.3[d,e]		
C_2H_4	0.32, 0.33[b]	0.35, 0.33[b]					0.20, 0.23[d]		
C_2H_2							0.01, 0.01[d]		
C_3H_8							0.02, 0.02[d]		
H_2O		*2.2[b]							
Radiation	γ	γ	200kv Xrays	γ	γ	3MeV Xrays	γ	γ	γ
Dose(10^{18}eV/g)	10	10, *200	1	1	5	420	100	4	800
Dose rate(10^{15}eV/gs)	3	3 – 40	3	0.3	4	—	8	3	30
T(K)	83	77	77	77	77	77	77	77	77

a. Measured after melting the sample.
b. Photobleached with visible light.
c. $G(H_2) = 4.4$ at 5×10^{17}eV/g.
d. Photobleached with light of $\lambda > 520$ nm. The same yields, except that of ethane, were obtained without photobleaching when the alcohol contained 0.2*M* HCl. Exposing the acidic samples to light of $\lambda > 520$ nm had no effect on the yields.
e. 0.2*M* HCl increased $G(C_2H_6)$ to 0.6.
f. 10^{-3}*M* H_2SO_4.
g. Preferred values similar to those in the liquid phase.

Data Sheet **PP*s*1**. *Ethanol solid. Primary Product Yields*[a]

Reference	640229	620100	625003	635001	645001	660132	670023	670272
G (Product)								
e^-_{trap}	0.14	(3)		2 (3)	2.3(0.0[a], 3.1[b])		> 0.9[a]	0.85
H_{trap}							0.0[b]	
$CH_3\dot{C}HOH_{trap}$				6	6(9.7[a], 5.5[b])			
$radicals_{trap}$			9.0			7.3		
Radiation	$^{10}B(n,\alpha)^7Li$	γ	γ, X	γ	γ	γ	γ	γ
Dose(10^{18}eV/g)	5	1	1	19	70	10	100	4
Dose rate(10^{15}eV/gs)	1	2	~ 1	—	20	4	8	3
T(K)	77	77	77	77	77	77	77	77
Method	optical	optical (ϕ_2)	esr	esr (1*N* NaOH)	esr (a, 1*N* H_2SO_4) (b, 2*N* NaOH)	esr	a. kinetics b. esr	C_6H_6, kinetics of $\Delta G(H_2)$

a. See data sheet **PP*s*2** for additional data and preferred values.

b. The values in parentheses were measured with the solute listed at the bottom of the column, opposite Method. The values without parentheses were obtained without the addition of a solute.

Data Sheet **PP*s*2**. *Ethanol solid. Primary Product Yields*[a]

Reference	670650	675183	700097	700276	700328	710389	720198	Preferred Values	
G(Product)									
e^-_{trap}[b]		2.4(3.0)	2.2	(2.35)		3.55	c	2.3(3.0)	0.14
H_{trap}					< 0.1			0.0	
$CH_3\dot{C}HOH_{trap}$		5.5						6(5.5)	
$radicals_{trap}$	6.3					8.25		~ 8.3 (8.5)	
Radiation	1.6MeV e^-	γ	γ	γ	γ	γ	γ	γ	$^{10}B(n,\alpha)^7Li$
Dose(10^{18}eV/g)	300	100	4	6	20	10	15	1–100	5
Dose rate(10^{15}eV/gs)	—	10	3	35	5	—	6	1–100	1
T(K)	120	77	107	77	77	77	4, 77	77	77
Method	esr	esr (C_6H_6)	optical	optical (RSSR)	esr EtOH–H_2O	optical esr	optical esr	(NaOH or aromatic hydrocarbon)	

a. See data sheet **PP*s*1** for additional data.

b. The values in parentheses were measured with the solute listed at the bottom of the column, opposite Method. The values without parentheses were obtained without the addition of a solute.

c. Same yield of e^-_{trap} at 4 and 77 K.

3. Reaction Rate Parameters

The reactions are listed according to phase. Estimates of accuracy are not given because it is not yet possible to evaluate the systematic errors. Reference to accuracy is sometimes made in the footnotes or comments under the Tables.

Temperatures are given in °C for the gas phase and in K for the liquid and solid phases, which corresponds to the most general usage.

DATA SHEET **R*g*1**. *Ethanol gas.* C_2H_5OH*

Reaction	$k(s^{-1})$	Method	Reference
(1) $C_2H_5OH* \rightarrow CH_3\dot{C}HOH + H$	6×10^{9} [a]	γ–rad., pressure dependence of H_2 and C_2H_4 yields at 150°C.	680521
(2) $C_2H_5OH* \rightarrow CH_3CHO + H_2$			
(3) $C_2H_5OH* + M \rightarrow C_2H_5OH + M$	a		
(4) $C_2H_5OH^{\dagger} \rightarrow C_2H_4 + H_2O$	3×10^{9} [a]		
(5) $C_2H_5OH^{\dagger} + M \rightarrow C_2H_5OH + M$	a		

a. Relative to assumed value of $k_3 = k_5 = 3 \times 10^{11} dm^3/mol \cdot s$ calculated from collision rate at 150°, assuming the collision efficiency to be unity. However, the collision efficiencies of 3 and 5 might be less than unity.

Reference to Sheet No. R*g*1

680521 Bansal, K.M.; Freeman, G.R., J. AM. CHEM. SOC. 90: 7183–9 (1968).

DATA SHEET **R*g*2**. *Ethanol gas.* $e^- + C_2H_5OH$

$e^- + C_2H_5OH \rightarrow C_2H_5O^- + H$

$\Delta H = 63$ kcal/mol [a]

This reaction is highly endothermic and is negligible in radiolysis systems. However, the equivalent reaction in the liquid phase does occur (sheet no. **R*l*1**).

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a. Estimated from the bond dissociation energy $D(C_2H_5O\text{–}H) = 102$ kcal/mol[b] and the electron affinity $EA(C_2H_5O) = 39$ kcal/mol.[c]

b. 659052 Benson, S.W., J. CHEM. EDUC. 42: 502 (1965).

c. 689041 Williams, J.W.; Hamill, W.H., J. CHEM. PHYS. 49: 4467–77 (1968).

DATA SHEET **R*g*3**. *Ethanol gas.* $e^- + (C_2H_5OH)_nH^+$

Reaction	t(°C)	$k(dm^3/mol \cdot s)$	Reference
$e^- + (C_2H_5OH)_nH^+ \rightarrow nC_2H_5OH + H$	50 – 200	estimated 10^{14}–10^{15} [a] at several hundred torr pressure	680133 680522

a. Assumed to be equal to the rate constant in other molecular gases at pressures in the vicinity of 1 atm (679028, 679027, 679029, 670319, 700046).

Comment:

The reaction

$$e^- + (C_2H_5OH)_nH^+ \rightarrow (n-1)C_2H_5OH + CH_3\dot{C}HOH + 2H$$

is endothermic and highly improbable for n > 1 (680521). It can be neglected under all radiolysis conditions that have been reported (700239).

References to Sheet No. R*g*3

670319 Wood, C.J.; Back, R.A.; Dawes, D.H., CAN. J. CHEM. 45: 3071–8 (1967).
679027 McGowan, S.M., CAN. J. PHYS. 45: 439–48 (1967).
679028 Fisk, G.A.; Mahan, B.H.; Parks, E.K., J. CHEM. PHYS. 47: 2649–58 (1967).
679029 Kasner, W.H., PHYS. REV. 164: 194–200 (1967).
680133 Freeman, G.R., RADIATION RES. REV. 1: 1–74 (1968).
680521 Bansal, K.M.; Freeman, G.R., J. AM. CHEM. SOC. 90: 7183–9 (1968).
680522 Bansal, K.M.; Freeman, G.R., J. AM. CHEM. SOC. 90: 7190–6 (1968).
700046 Wilson, D.E.; Armstrong, D.A., CAN. J. CHEM. 48: 598–602 (1970).
700239 Freeman, G.R., ACTIONS CHIM. BIOL. RAD. 14: 73–134 (1970).

Data Sheet **R*g*4**. *Ethanol gas.* $e^- + CH_3CHO$

Reaction	t(°C)	P(Torr)	k(dm^3/mol·s)	Method	Reference
(1) $e^- + CH_3CHO \rightarrow CH_3CHO^-$ postulated	150	860 C_2H_5OH	10^8 [a]	γ–rad. of ethanol, dose dependence of yields.	680521

a. Relative to $k(e^- + (C_2H_5OH)_nH^+) = 10^{14}$ dm^3/mol·s (Sheet no. R*g*3). The authors state that a high pressure (~ 1 atm) of alcohol vapor is required to obtain the high value of k, which might indicate that the charged species are clustered by ethanol molecules.

References to Sheet No. R*g*4

680521 Bansal, K.M.; Freeman, G.R., J. AM. CHEM. SOC. 90: 7183–9 (1968).
700239 Freeman, G.R., ACTIONS CHEM. BIOL. RAD. 14: 73–134 (1970).

Data Sheet **R*g*5**. *Ethanol gas.* $CH_3\dot{C}HOH + CH_3\dot{C}HOH$

Reaction	t(°C)	P(Torr)	k_1/k_2	Method	Reference
(1) $2CH_3\dot{C}HOH \rightarrow CH_3CHO + C_2H_5OH$	25	10 – 60	~ 1	Hg($^3P_1$) photosens.	677127
(2) $2CH_3\dot{C}HOH \rightarrow (CH_3CHOH)_2$	150	$10^2 - 10^3$	≤ 2.0	γ–rad.	680521

References to Sheet No. R*g*5

677127 Kato, A.; Cvetanovic, R.J., CAN. J. CHEM. 45: 1845–61 (1967).
680521 Bansal, K.M.; Freeman, G.R., J. AM. CHEM. SOC. 90: 7183–9 (1968).

Data Sheet **R*g*6**. *Ethanol gas.* $C_2H_5O\cdot + C_2H_5O\cdot$

$C_2H_5O\cdot + C_2H_5O\cdot \rightarrow CH_3CHO + C_2H_5OH$ (1)
$C_2H_5O\cdot + C_2H_5O\cdot \rightarrow C_2H_5OOC_2H_5$ (2)
$k_1/k_2 = 12$ at 25°C (627003)
Reactions of $C_2H_5O\cdot$ and other alkoxy radicals are discussed in 670780.

References to Sheet No. R*g*6

627003 Heicklen, J.; Johnston, H. S., J. AM. CHEM. SOC. 84: 4394–403 (1962).
670780 Gray, P.; Shaw, R.; Thynne, J. C. J., PROG. REAC. KIN. 4: 63–117 (1967).

Data Sheet R*g*7. *Ethanol gas.* H + C_2H_5OH

(I) $H + C_2H_5OH \rightarrow H_2 + CH_3\dot{C}HOH$

Reaction	k/k_I	t(°C)	k_I, dm³/mol·s	Method	Reference
$\log k_I = 10.1 - (8100 \pm 600)/4.6T$		570 – 690	1.5×10^8 at 650°C (calc. 3×10^5 at 108°)	ignition	659047
(1) $D + C_2H_5OH \rightarrow HD + CH_3\dot{C}HOH$ $\log k_I = 9.7 - (6900 \pm 1000)/4.6T$		570 – 670	1.1×10^8 at 650°C (calc. 8×10^5 at 108°C)	ignition	689067
(2) $H + C_6H_6 \rightarrow H_2 + C_6H_5$	0.9	108	$(1 - 7) \times 10^7$ [a]	α rad.	610046
(3) $H + C_6H_6 \rightarrow C_6H_7$	4.2	108		α rad.	610046
(4) $H + c{-}C_6H_{10} \rightarrow H_2 + c{-}C_6H_9$	20	108		α rad.	610046
(5) $H + c{-}C_6H_{10} \rightarrow c{-}C_6H_{11}$	50	108		α rad.	610046
(6) $H + C_3H_6 \rightarrow C_3H_7$	80	150	1×10^7 [b]	γ rad.	680521

a. Assuming: $k_2 = 6 \times 10^7$ (610026); $k_3 = 1.8 \times 10^8$ (620067); $k_4 = 1.1 \times 10^8$ (620061); $k_5 = 4.9 \times 10^8$ (620061).

b. Assuming $k_6 = 1.0 \times 10^9$ (620117).

Comment: There is uncertainty about the degree to which hydrogen atoms are thermalized before they react in radiolysis systems. The value $k_I = 1 \times 10^7$ dm³/mol·s at 108° might be somewhat higher than that for thermal hydrogen atoms at the same temperature.

References to Sheet No. R*g*7

610026	Hardwick, T.J., J. PHYS. CHEM. 65: 101–8 (1961).
610046	Ramaradhya, J.M.; Freeman, G.R., CAN. J. CHEM. 39: 1843–7 (1961).
620061	Hardwick, T.J., J. PHYS. CHEM. 66: 291–5 (1962).
620067	Hardwick, T.J., J. PHYS. CHEM. 66: 117–25 (1962).
620117	Yang, K., J. AM. CHEM. SOC. 84: 719–21 (1962).
659047	Oganesgan, K.T.; Nal'andyan, A.B.; Parsamyan, N.I., DOKL. AKAD. NAUK ARMYANSKII, SSSR 40: 159–63 (1965) (RUSSIAN).
680521	Bansal, K.M.; Freeman, G.R., J. AM. CHEM. SOC. 90(26): 7183–89 (1968).
689067	Dzotsenidze, Z.G.; Oganesyan, K.T.; Nal'andyan, A.B., ARM. KHIM. ZHURNAL 21: 370–4 (1968) (RUSSIAN).

Data Sheet R*g*8. *Ethanol gas.* CH_3 + C_2H_5OH

Reaction	log *A* (dm³/mol·s)	*E* (kcal/mol)	t(°C)	log *k* (dm³/mol·s) at 150°C	Method	Reference
(1) $CH_3 + C_2H_5OH \rightarrow CH_4 + R\cdot$	8.3	8.7	189–341	3.8[a]	phot. $(+CD_3COCD_3)$	517000
			150	3.2[b]	γ–rad. $(+C_3H_6)$	680521
	8.7	9.6	130–250	3.7[a]	phot. $(+CD_3COCD_3)$	687266
(2) $CH_3 + C_2H_5OH \rightarrow CH_4 + CH_3\dot{C}HOH$	8.6	9.7	130–250	3.6[a]	phot. $(+CD_3COCD_3)$	687266
(3) $CH_3 + C_2H_5OH \rightarrow CH_4 + CH_3CH_2O\cdot$	7.9	9.4	130–250	3.0[a]	phot. $(+CD_3COCD_3)$	687266
(4) $CH_3 + C_2H_5OH \rightarrow CH_4 + \dot{C}H_2CH_2OH$			130–250	2.5[a]	phot. $(+CD_3COCD_3)$	687266
(5) $CH_3 + CH_3CD_2OH \rightarrow CH_4 + [C_2OH_3D_2]\cdot$	7.8	9.0	130–250	3.2[a]	phot. $(+CD_3COCD_3)$	687266
(6) $CH_3 + CH_3CD_2OH \rightarrow CH_3D + CH_3\dot{C}DOH$	8.6	11.4	130–250	2.7[a]	phot. $(+CD_3COCD_3)$	687266
(7) $CD_3 + C_2H_5OD \rightarrow CD_3H + C_2H_4OD$	8.6	9.7	130–250	3.6[a]	phot. $(+CD_3COCD_3)$	687266
(8) $CD_3 + C_2H_5OD \rightarrow CD_4 + C_2H_5O\cdot$	7.8	10.1	130–250	2.6[a]	phot. $(+CD_3COCD_3)$	687266
$k_2/k_3 = 2.7$ (scavengable CH_4) and 1.8 (unscavengable CH_4)[c]			105		γ–rad. (deuterated ethanols + 1,3–pentadiene)	650027
$k_2/k_4 = 8.0$ (scavengable CH_4) and 6.4 (unscavengable CH_4)			105			650027

a. Based on $k(CH_3 + CH_3 \rightarrow C_2H_6) = 2.2 \times 10^{10}$ dm³/mol·s (568001).

b. Based on $k(CH_3 + C_3H_6 \rightarrow C_4H_9) = 5.3 \times 10^4$ dm³/mol·s (677501).

c. The isotope effect per C–H or C–D bond for abstraction by methyl radicals was $k_H/k_D = 3.9$ for scavengable methane and 2.5 for unscavengable methane (650027).

References to Sheet No. R*g*8

517000	Trotman–Dickensen, A.F.; Steacie, E.W.R., J. CHEM. PHYS. 19: 329–36 (1951).
568001	Shepp, A., J. CHEM. PHYS. 24: 939–43 (1956).
650027	Myron, J.J.J.; Freeman, G.R., CAN. J. CHEM. 43: 1484–92 (1965).
677501	Cvetanovic, R.J.; Irwin, R.S., J. CHEM. PHYS. 46: 1694–702 (1967).
680521	Bansal, K.M.; Freeman, G.R., J. AM. CHEM. SOC. 90: 7183–9 (1968).
687266	Gray, P.; Herod, A.A., TRANS. FARADAY SOC. 64: 1568–76 (1968).

DATA SHEET Rg9. *Ethanol gas.* $O(^3P) + C_2H_5OH$; $O(^3P) + CH_3CHO$

Reaction	t(°C)	k(dm^3/mol·s)	Method	Reference
(1) $O(^3P) + C_2H_5OH \rightarrow OH + CH_3\dot{C}HOH$	25	6 x 10^7[a]	$Hg(^3P_1) + N_2O$[b] $+ C_4H_8\text{-}1$	677127
(2) $O(^3P) + CH_3CHO \rightarrow OH + CH_3\dot{C}O$	25	2 x 10^8[a]	$Hg(^3P_1) + N_2O$[b] $+ C_4H_8\text{-}1$	639015

a. Relative to $k_3 = 2 \times 10^9$dm^3/mol·s at 25° (639015).

$$O(^3P) + C_4H_8\text{-}1 \rightarrow C_4H_8O\cdot \qquad (3)$$

b. $Hg(^3P_1) + N_2O \rightarrow Hg + N_2 + O(^3P)$. The N_2 yield was used to monitor the amount of $O(^3P)$ formed. Rate constant ratios were obtained from product analyses.

References to Sheet No. Rg9

677127 Kato, A.; Cvetanovic, R.J., CAN. J. CHEM. 45: 1845–61 (1967).
639015 Cvetanovic, R.J., ADV. PHOTOCHEM. 1: 115–82 (1963).

DATA SHEET Rg10. *Ethanol gas.* $(C_2H_5OH)_2H^+$

Reaction[a]	E(kcal/mol)	t(°C)	P(Torr)	ΔH(kcal/mol)	Reference
$(C_2H_5OH)_2H^+ \rightarrow (C_2H_5)_2OH^+ + H_2O$	~ 43	300–400	10^2–10^3	~ 25	680287 700231 710449

a. Method: γ–radiation sensitized pyrolysis of ethanol.

References to Sheet No. Rg10

680287 Bansal, K.M.; Freeman, G.R., J. AM. CHEM. SOC. 90: 5632–3 (1968).
700231 Bansal, K.M.; Freeman, G.R., J. AM. CHEM. SOC. 92: 4173–5 (1970).
710449 Bansal, K.M.; Freeman, G.R., RADIAT. RES. REV. 3: 209–77 (1971).

DATA SHEET Rg11. *Ethanol gas.* $CH_3\dot{C}HOH$, $\cdot CH_2CH_2OH$, $CH_3CH_2O\cdot$

Reaction	log A(s^{-1})	E(kcal/mol)	t(°C)	P(Torr)	Method	ΔH(kcal/mol)	Reference
(1) $CH_3\dot{C}HOH \rightarrow CH_3CHO + H$		$\geqslant 30$[a]	290–375	~ 500 (0.66g/dm^3)	γ-rad. ethanol	30	680522
(2) $\cdot CH_2CH_2OH \rightarrow C_2H_4 + OH$		27[a,b]	320–375	"	"	~ 30	"
(3) $CH_3CH_2O\cdot \rightarrow CH_3 + CH_2O$		20[a]	290–375	"	"	12	"
	9.6	13[c]	19–195	~ 20	phot. ethyl propionate	11	607002
(4) $CH_3CH_2O\cdot \rightarrow CH_3CHO + H$[d]		21[d]	~ 100		phot. $C_2H_5ONO_2$	19	670780

a. The reaction appeared to be in its pressure dependent rate region at the temperatures and pressures used, so the "infinite pressure" value of E is probably a little higher than this.

b. The infinite pressure value of E_2 is at least equal to the endothermic heat of reaction, $\Delta H_2 \cong 30$ kcal/mol.

c. Calculated from the values $E_3 - E_5 = 7.5 \pm 1$ kcal/mol and $E_5 = 5.5$ kcal/mol (607002).

$$C_2H_5O\cdot + C_2H_5COOC_2H_5 \rightarrow C_2H_5OH + [C_5H_9O_2]\cdot \quad (5)$$

However, the value of E_5 seems too low by comparison with the value $E_6 = 9.8$ kcal/mol (587001), so E_3 may be greater than 13 kcal/mol.

$$CH_3 + C_2H_5COOC_2H_5 \rightarrow CH_4 + [C_5H_9O_2]\cdot \qquad (6)$$

d. The evidence for the occurrence of this reaction is somewhat tenuous.

References to Sheet No. Rg11

587001 Wijnen, M.H.J., J. AM. CHEM. SOC. 80: 2394–400 (1958).
607002 Wijnen, M.H.J., J. AM. CHEM. SOC. 82: 3034–40 (1960).
670780 Gray, P.; Shaw, R.; Thynne, J.C.J., PROG. REAC. KIN. 4: 63–117 (1967).
680522 Bansal, K.M.; Freeman, G.R., J. AM. CHEM. SOC. 90: 7190–6 (1968).

Data Sheet **Rg12**. *Ethanol gas*. $CH_2O + C_2H_5OH$

Reaction[a]	*E* (kcal/mol)	t(°C)	P(Torr)	Δ*H*(kcal/mol)	Reference
$CH_2O + C_2H_5OH \rightarrow CH_3OH + CH_3CHO$	~ 16	200–380	C_2H_5OH ~ 600 CH_2O ~ 40	–4	700231

a. Method: Thermal. Mechanism unknown; not inhibited by propylene. Overall rate constant at 380°C, $k = 1.6 \times 10^{-2} dm^3/mol \cdot s$.

Reference to Sheet No. Rg12

700231 Bansal, K.M.; Freeman, G.R., J. AM. CHEM. SOC. 92: 4173–5 (1970)

Data Sheet **Rl1**. *Ethanol liquid*. e^-_{solv}

Reaction[a]	log *A* (s^{-1})	*E* (kcal/mol)	k_1 ($10^5 s^{-1}$)	$t_{1/2}(\mu s)$	T(K)	dose (10^{17}eV/g)	Method	Ref.
(1) $e^-_{solv} \rightarrow C_2H_5O^-_{solv} + H$			2	3	room	1.4	pulse rad.	630059
($\Delta H \leq 0$ kcal/mol)			0.33	21	room		flash phot. I^-_{solv}	647006
($\Delta S\ddagger = -21$ cal/deg mol) (698025)			2.1[b]	3.3	298		γ–rad., dose dependence of H_2 yield.[b]	650045
			0.35	20	195	1.4	pulse rad.	660082
			1[c]	7	298		γ–rad., N_2O scav.[c]	670012 680047
			~ 2	~ 3[d]	room		pulse rad.	670126
			(~ 2)	(3–4)	room		(0.1 N NaOH)	670126
			2.1[e]	3.3	293		γ–rad., RCl scav.	670173
	8.4	4.6			173–433		γ–rad., N_2O scav.	698025
			1	7	298			698025
			2.6	2.7	room		γ–rad., CH_3Br scav.	700064
			1.2	6	298	< 0.1	pulse rad.	700172
				1.8	room	~ 10	pulse rad. (+ LiCl)	700246
				4.5–6.8	room	~ 10	pulse (+ KOH or $NaOC_2H_5$)	700246
			1.1	6.1	293	1	pulse rad., (1m*M* NaOH)	710009
	8.45	4.86	0.8	9	298	?	pulse (+1m*M* NaOEt)	710101
Preferred Values	8.4	4.6	1.1	6.1	293	0		

a. For those who prefer the alternate formulation (2), $k_2 = (k_1/17)$ dm³/mol·s.

$$e^-_{solv} + C_2H_5OH \rightarrow C_2H_5O^-_{solv} + H \qquad (2)$$

However, see the footnotes on sheet no. **Rs1**.

b. Assumed $k(e^-_{solv} + CH_3CHO) = 1.6 \times 10^9 dm^3/mol \cdot s$.

c. Assumed $k(e^-_{solv} + N_2O) = 7 \times 10^9 dm^3/mol \cdot s$, as in water at 298 K.

d. This reaction was preceded by the fast decay of an initial portion with $t_{1/2} \cong 0.08\mu s$, attributed to reaction of e^-_{solv} with $C_2H_5OH_2^+$ and other intermediates in spurs. The initial fast decay did not occur in the presence of 0.1*N* NaOH.

e. Assumed $k(e^-_{solv} + ClCH_2COO^-) = 1.2 \times 10^9 dm^3/mol \cdot s$, as in water.

Comment:

The pulse technique gives $t_{1/2} \cong 3\mu s$ for solvated electrons in neutral ethanol when the pulse dose is about 10^{17}eV/g. At such a dose the concentration of the sibling ions $C_2H_5OH_2^+$ is great enough that the rate of (3) is appreciable (700172).

$$e^-_{solv} + C_2H_5OH_2^+ \rightarrow C_2H_5OH + H \qquad (3)$$

A more accurate value of the half life of (1) at room temperature is 6μs. Associated with this higher value of $t_{1/2}$ are higher values of the free ion yield, $G_{fi} \cong 1.7$, and initial hydrogen yield, $G(H_2)_0 \cong 5.9$ (sheets **PPl2** and **FPl2**).

References to Sheet No. Rl1

630059 Taub, I.A.; Sauer, M.C.Jr.; Dorfman, L.M., DISCUSS. FARADAY SOC. 36: 206–13 (1963).
647006 Dobson, G.; Grossweiner, L.I., RADIAT. RES. 23: 290–9 (1964).
650045 Myron, J.J.J.; Freeman, G.R., CAN. J. CHEM. 43: 381–94 (1965).

660082 Arai, S.; Sauer, M.C.Jr., J. CHEM. PHYS. 44(6): 2297–305 (1966).
670012 Russell, J.C.; Freeman, G.R., J. PHYS. CHEM. 71: 755–62 (1967).
670126 Thomas, J.K.; Bensasson, R.V., J. CHEM. PHYS. 46: 4147–8 (1967).
670173 Basson, R.A., J. CHEM. SOC. PT. A (7): 1179–82 (1967).
680047 Russell, J.C.; Freeman, G.R., J. PHYS. CHEM. 72(3): 816–21 (1968).
698025 Jha, K.N.; Freeman, G.R., J. CHEM. PHYS. 51(7): 2846–50 (1969).
700064 Rzad, S.J.; Fendler, J.H., J. CHEM. PHYS. 52(10): 5395–403 (1970).
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700246 Arai, S.; Kira, A.; Imamura, M., J. PHYS. CHEM. 74(10): 2102–7 (1970).
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710101 Baxendale, J.H.; Wardman, P., CHEM. COMMUN. (9): 429–30 (1971).

DATA SHEET **R*l*2**. *Ethanol liquid.* e^-_{solv} + *solute* → *(solute)*$^-$

Solute	$k(10^9 dm^3/mol \cdot s)$	T(K)	Reference
e^-_{solv}	5	room	700172
H^+_{solv}	$20^{a,b}$	296	630059, 640113, 659018
	29^c	296	710009
	39^a, 36^a	293	710064, 720194
	53^a	290	710531
O_2	19^a	296	659018
N_2O	8^c	298	690883
NO_3^-	$2.8^{d,e}$	room	650501
CH_3CHO	4.0^a	298	700172
$(CH_3)_2CO$	4.0^a	294	730001
$C(NO_2)_4$	35^a	293	710009
$c-C_6F_{12}$	2.5^a	298	700172
$ClCH_2COOH$	3.0^a	293	730001
	$20^{d,e}$	room	650501
C_3H_7Cl	$0.48^{d,f}$	room	700248
$C_6H_5CH_2Cl$	5.1^a	296	659018
CCl_4	11^a	293	710009
$n-C_3H_7Br$	3.0^a	293	710009
$c-C_5H_9Br$	$9.5^{d,f}$	room	700248
C_6H_6	0.005^g	room	690651
biphenyl	4.3^a	296	659018
naphthalene	5.4^a, 4.5^a, 4.1^a	295 ± 1	659018, 710009, 730001
p-terphenyl	7.2^a	296	659018
naphthacene	10.2^a	296	659018
$(C_6H_5)_3COH$	0.2^a	296	659018

a. Pulse radiolysis.
b. The ethanol possibly contained water, which reduces the diffusion coefficient of H^+ (710064).
c. Relative to $k(e^-_{solv} + CH_3CHO) = 4 \times 10^9 dm^3/mol \cdot s$ (710009).
d. Relative to $k(e^-_{solv} + H^+_{solv}) = 2.0 \times 10^{10} dm^3/mol \cdot s$.
e. Obtained by normalization to earlier results that now appear to have been affected by impurities.
f. γ–radiolysis of 95% ethanol + 0.2 – 1*M* HCl + solute.
g. Relative to assumed $k(e^-_{solv} \rightarrow RO^-_{solv} + H) = 1 \times 10^5 s^{-1}$ and $k(e^-_{solv} + \text{impurity})[\text{impurity}] = 5 \times 10^4 s^{-1}$.

References to Sheet No. R*l*2

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640113 Taub, I.A.; Harter, D.A.; Sauer, M.C.Jr.; Dorfman, L.M., J. CHEM. PHYS. 41(4): 979–85 (1964).
650501 Hayon, E.; Moreau, M., J. PHYS. CHEM. 69: 4053–7 (1965).
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690651 Holcman, J.; Karolczak, S.; Kroh, J.; Mayer, J.; Mienska, M., INT. J. RADIAT. PHYS. CHEM. 1(4): 457–64 (1969).
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710064 Fowles, P., TRANS. FARADAY SOC. 67(2): 428–39 (1971).
710531 Rabani, J.; Graetzel, M.; Chaudhri, S.A., J. PHYS. CHEM. 75(25): 3893–4 (1971).
720194 Jha, K.N.; Bolton, G.L.; Freeman, G.R., CAN. J. CHEM. 50: 3073–5 (1972).
730001 Bolton, G.L.; Jha, K.N., Freeman, G.R., (unpublished).

DATA SHEET R/3. *Ethanol liquid.* e^-_{solv} + *solute*

(1) e^-_{solv} + solute → products
(2) $e^-_{solv} \rightarrow C_2H_5O^-_{solv} + H$

Solute	k_1/k_2[a] ($10^4 dm^3/mol$)	T(K)	Reference
H^+_{solv}	24, 12	293, 296	710009, 640279
N_2O	6.7	418	698025
	3.4	363	698025
	4.2	298	698025
	6	293	710009
	4.0	161	698025
	3.6	room	700064
SF_6	5.4	room	700064
CH_3Br	5.5	room	700064
CH_3Cl	1.4	room	700064
CCl_4	9.	293	710009
	0.06(?)	296	640279
CH_3CHO	3, 0.93	293, 296	710009, 640279
$(CH_3)_2CO$	4.1	296	640279
	2	296	670004
	1.9	room	700064
	3.5	296	720199
$ClCH_2COOH$	0.64	room	640279
	0.58	293	670173
	0.29	273	670173
	0.041	253	670173
	0.022	201	670173
$CH_3COOC_2H_5$	0.064	296	640279
$C_6H_5NO_2$	12.2	296	720199
anthracene	14	296	640279
naphthalene	4.2	296	720199

a. γ–radiolysis of solutions; competition kinetics.
(?) Value is low because the product HCl competed with the CCl_4 for e^-_{solv} (710009).

References to Sheet No. R/3

640279 Adams, G.E.; Sedgwick, R.D., TRANS. FARADAY SOC. 60: 865–72 (1964).
670004 Basson, R.A.; van der Linde, H.J., J. CHEM. SOC. PT. A (1): 28–32 (1967).
670173 Basson, R.A., J. CHEM. SOC. PT. A (7): 1179–82 (1967).
698025 Jha, K.N.; Freeman, G.R., J. CHEM. PHYS. 51(7): 2846–50 (1969).
700064 Rzad, S.J.; Fendler, J.H., J. CHEM. PHYS. 52(10): 5395–403 (1970).
710009 Akhtar, S.M.S.; Freeman, G.R., J. PHYS. CHEM. 75(18): 2756–62 (1971).
720199 Jha, K.N.; Freeman, G.R., J. CHEM. PHYS. 57(4): 1408–14 (1972).

DATA SHEET R/4. *Ethanol liquid. Aromatic anions* + A or AH^+

Reaction	$k(dm^3/mol \cdot s)$	T(K)	Reference
biphenylide$^-$ + $C_2H_5OH \rightarrow C_{12}H_{11} + C_2H_5O^-$	2.6×10^4	296	640084
biphenylide$^-$ + $C_2H_5OH_2^+ \rightarrow C_{12}H_{11} + C_2H_5OH$	3.3×10^{10}	296	640084
anthracide$^-$ + $C_2H_5OH \rightarrow C_{14}H_{11} + C_2H_5O^-$	2.3×10^4	296	640084
anthracide$^-$ + $C_2H_5OH_2^+ \rightarrow C_{14}H_{11} + C_2H_5OH$	3.7×10^{10}	296	640084
p–terphenylide$^-$ + $C_2H_5OH \rightarrow C_{18}H_{15} + C_2H_5O^-$	2×10^2	296	640084
p–terphenylide$^-$ + $C_2H_5OH_2^+ \rightarrow C_{18}H_{15} + C_2H_5OH$	1.9×10^{10}	296	640084

Reference to Sheet No. R/4

640084 Arai, S.; Dorfman, L.M., J. CHEM. PHYS. 41: 2190–4 (1964).

DATA SHEET R/5. *Ethanol liquid.* $RO + RO^-$

Reaction	$k(dm^3/mol \cdot s)$	T(K)	Method	Reference
$CH_3\dot{C}HOH + C_2H_5O^- \underset{r}{\overset{f}{\rightleftharpoons}} CH_3CHO^- + C_2H_5OH$	$k_f < 10^3$ $k_r \leq 20$	room	pulse rad.	700647
$C_2H_5O\cdot + C_2H_5O^- \rightarrow CH_3CHO^- + C_2H_5OH$	$> 8 \times 10^7$	room	pulse rad.	700647
$CH_3\dot{C}HOH + OH^- \underset{r}{\overset{f}{\rightleftharpoons}} CH_3CHO^- + H_2O$	$k_f \cong 10^9$ $k_r \cong 10^5$ $pK_a = 11.6^a$	room	pulse rad. *aqueous*	660074

a. $K_a = [CH_3CHO^-][H^+]/[CH_3\dot{C}HOH]$

References to Sheet No. R/5

660074 Asmus, K.–D.; Henglein, A.; Wigger, A.; Beck, G., BER. BUNSENGES. PHYS. CHEM. 70: 756–8 (1966).
700647 Fletcher, J.W.; Richards, P.J.; Seddon, W.A., CAN. J. CHEM. 48: 3765–8 (1970).

DATA SHEET R/6. *Ethanol liquid.* $C_2H_5OH_2^+ + B$

Miscellaneous Reactions

(1,2) $2C_2H_5OH \underset{2}{\overset{1}{\rightleftharpoons}} C_2H_5OH_2^+ + C_2H_5O^-$, $pK_i = 19.12$, $k_1 = 1.01 \times 10^{-11} dm^3/mol \cdot s$, $k_2 = 3.85 \times 10^{10} dm^3/mol \cdot s$,
$\Delta G_1 = 29.4$ kcal/mol, $\Delta H_1 \cong 11.5$ kcal/mol, $\Delta S_1 = -60$ cal/deg·mol, T = 298 K (679116)
(3) $C_2H_5OH_2^+ + H_2O \rightleftharpoons C_2H_5OH + H_3O^+$, $K = [C_2H_5OH_2^+][H_2O]/[H_3O^+] = 0.15\ dm^3/mol$, $\Delta H = -5.0$ kcal/mol, 298 K (410001)
(4) $HNO_3 + C_2H_5OH \rightleftharpoons C_2H_5OH_2^+ + NO_3^-$, $pK = 3.57$, 298 K (410001)

	Acetal formation	$k(dm^3/mol \cdot s)$	E (kcal/mol)	T(K)	*Reference*
(5)	$CH_3CHO + C_2H_5OH_2^+ (+ C_2H_5OH) \rightarrow CH_3CH(OC_2H_5)_2 + H_3O^+$	2.4	22.6	298	340007
		1.4	15.5	298	410001

References to Sheet No. R/6

340007 Deyrup, A.J., J. AM. CHEM. SOC. 56: 60–4 (1934).
410001 Bell, R.P.; Norris, A.D., J. CHEM. SOC.: 118–20 (1941).
679116 Briere, G.; Gaspard, F., J. CHIM. PHYS. 64: 1071–84 (1967).
700172 Fletcher, J.W.; Richards, P.J.; Seddon, W.A., CAN. J. CHEM. 48: 1645–50 (1970).

DATA SHEET R*l*7. *Ethanol liquid.* $CH_3\dot{C}HOH + CH_3\dot{C}HOH$

(I) $2CH_3\dot{C}HOH \rightarrow CH_3CHO + C_2H_5OH$
(II) $2CH_3\dot{C}HOH \rightarrow (CH_3CHOH)_2$

k_I/k_{II}	T(K)	Method	Reference
0.9	room	γ–rad.	680575
0.8	room	γ–rad.	700172
0.9*	room	Derived from the scavengable yields of acetaldehyde and butanediol, using preferred yields from Sheets FP*l*2 and PP*l*2.	

	$(k_I + k_{II})$, $dm^3/mol\cdot s$	T(K)	Method	Reference
	$1.7 \times 10^6\ \epsilon_{297nm} \cong 4.1 \times 10^8$ [a] (5×10^8)[b]	296	pulse rad.	620140 (700647)
	$2.3 \times 10^6\ \epsilon_{300nm} \cong 1.1 \times 10^9$	room	pulse rad. + N_2O	690419
	1.0×10^9	room	unclear	700172
	7×10^8 [*b]	room	pulse rad.	700647
Aqueous	7×10^8	296	pulse rad., 0.8 *N* H_2SO_4 $\epsilon_{297} = 240 dm^3/mol\cdot cm$	630045
Aqueous	9×10^8	293	pulse rad., 0.1 *N* H_2SO_4 $\epsilon_{240} = 500 dm^3/mol\cdot cm$	670269
Aqueous	1.0×10^9	296	intermittent rad., $C_2H_5OH + H_2O_2$ chain	670094

* Preferred value.

a. Assuming $\epsilon_{297nm} = 240 dm^3/mol\cdot cm$, as in water.

b. Using $\epsilon_{255nm} = 870 dm^3/mol\cdot cm$ and $\epsilon_{297nm} = 290 dm^3/mol\cdot cm$.

References to Sheet No. R*l*7

620140 Taub, I.A.; Dorfman, L.M., J. AM. CHEM. SOC. 84: 4053–9 (1962).
630045 Dorfman, L.M.; Taub, I.A., J. AMER. CHEM. SOC. 85: 2370–4 (1963).
670094 Seddon, W.A.; Allen, A.O., J. PHYS. CHEM. 71: 1914–8 (1967).
670269 Cullis, C.F.; Francis, J.M.; Raef, Y.; Swallow, A.J., PROC. ROY. SOC. (LONDON) SER. A 300: 443–54 (1967).
680575 Basson, R.A., J. CHEM. SOC. PT. A (8): 1989–92 (1968).
690419 Simic, M.; Neta, P.; Hayon, E., J. PHYS. CHEM. 73(11): 3794–800 (1969).
700172 Fletcher, J.W.; Richards, P.J.; Seddon, W.A., CAN. J. CHEM. 48(11): 1645–50 (1970).
700647 Fletcher, J.W.; Richards, P.J.; Seddon, W.A., CAN. J. CHEM. 48(23): 3765–8 (1970).

DATA SHEET R/8. *Ethanol liquid.* H, C_2H_5OH, *Solute*

(I) $H + C_2H_5OH \rightarrow H_2 + R\cdot$
(II) $H + \text{Solute} \rightarrow HS\cdot$
(III) $H + \text{Solute} \rightarrow H_2 + R\cdot$
(IV) $H + RCl \rightarrow HCl + R\cdot$

Solute	*k* ratio	$k_I(dm^3/mol\cdot s)$[a]	T(K)	Method	Reference
	II/I				
p–benzoquinone	1450[a]		291	γ–rad., H_2 yield	590020
$(CH_3)_2CO$	77[a]	6.2×10^6 [a,b]	room	γ–rad., H_2 yield	670004
C_6H_6	24		room	γ–rad(+ H_2SO_4), H_2 yield	690651
	III/I				
n–C_6H_{14}	0.84[c]	5.9×10^6 [d]	308	Phot. of t–C_4H_9SD and C_6H_5SD	707158
	0.20	2.5×10^7 [d]	313	Phot. of tritiated $C_3H_7SH(T)$	707158
	IV/I				
$ClCH_2COOH$	132[a]		293	γ–rad., H_2 yield	670173
$ClCH_2COOH$	28[a]		201	γ–rad., H_2 yield	670173
Acidic aqueous ethanol		2×10^7	room	γ–rad.	670103
		2.5×10^7 [e]	298	γ–rad., H_2 and HD yields	710017
		2.6×10^7 [f]	288	e^- rad., esr	710003

a. This value should be accepted with reserve, because it is difficult to make clear distinction between the reactions of hydrogen atoms and those of electrons. The reactions attributed to hydrogen atoms in 670004 might have been spur reactions of electrons. The hydrogen atom rate constants reported by Hardwick (620067, etc.) should be re–examined for the same reason.
b. Assuming $k(H + (CH_3)_2CO) = 4.8 \times 10^8$ (620067).
c. Pryor, *et al*, prefer this value (707158).
d. Assuming $k(H + n\text{–}C_6H_{14}) = 4.9 \times 10^6$ (620067).
e. Relative to $k(H + C_6H_5COOH \rightarrow C_6H_6COOH) = 1.0 \times 10^9$ in solution containing $10^{-3}M$ C_6H_5COOH and $0.1M$ $HClO_4$(690001).
f. Relative to $k(H + C_6H_5COOH) = 8.5 \times 10^8$ in solution containing $10^{-3}M$ C_6H_5COOH and $0.1M$ $HClO_4$.

References to Sheet No. R/8

590020 Adams, G.E.; Baxendale, J.H.; Sedgwick, R.D., J. PHYS. CHEM. 63: 854–8 (1959).
620067 Hardwick, T.J., J. PHYS. CHEM. 66: 117–25 (1962).
670004 Basson, R.A.; van der Linde, H.J., J. CHEM. SOC. PT. A. (1): 28–32 (1967).
670103 Anbar, M.; Neta, P., INT. J. APPL. RAD. ISOTOPES 18: 493–23 (1967).
670173 Basson, R.A., J. CHEM. SOC. PT. A. (7): 1179–82 (1967).
690001 Neta, P.; Dorfman, L.M., J. PHYS. CHEM. 73: 413–7 (1969).
690651 Holcman, J.; Karolczak, S.; Kroh, J.; Mayer, J.; Mienska, M., INT. J. RADIAT. PHYS. CHEM. 1(4): 457–64 (1969).
707158 Pryor, W.A.; Stanley, J.P.; Griffith, M.G., SCIENCE 169: 181–2 (1970).
710003 Neta, P.; Fessenden, R.W.; Schuler, R.H., J. PHYS. CHEM. 75: 1654–66 (1971).
710017 Neta, P.; Holden, G.R.; Schuler, R.H., J. PHYS. CHEM. 75: 449–54 (1971).

Data Sheet **R*l*9**. *Ethanol liquid.* $CH_3+C_2H_5OH$

(I) $CH_3+CH_3CH_2OH \rightarrow CH_4+R\cdot$
(II) $\rightarrow CH_4+CH_3CHOH$
(III) $\rightarrow CH_4+CH_3CH_2O\cdot$
(IV) $\rightarrow CH_4+\cdot CH_2CH_2OH$
(V) CH_3 + benzoquinone $\rightarrow C_7H_7O_2\cdot$

k(relative)	T(K)	Method	Reference
$k_V/k_I=4{,}500$	291	γ−rad.	590020
$k_{II}/k_{III}=2.2^a$	301	γ−rad. (+1,3−pentadiene)	650027
$k_{II}/k_{IV}=6.2^b$	301	γ−rad. (+1,3−pentadiene)	650027

a. Based on scavengable CH_4; 1.8 based on unscavengable CH_4.[c]
b. Based on scavengable CH_4; 3.2 based on unscavengable CH_4.[c]
c. Unscavengable CH_4 is not a product of thermal CH_3 radicals.

References to Sheet No. R*l*9

590020 Adams, G. E.; Baxendale, J. H.; Sedgwick, R. D., J. PHYS. CHEM. 63: 854–8 (1959).
650027 Myron, J. J. J.; Freeman, G. R., CAN. J. CHEM. 43: 1484–92 (1965).

Data Sheet **R*l*10**. *Ethanol liquid. Miscellaneous reactions*

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(1) $C_2H_5OH \rightarrow [C_2H_5OH^+ + e^-]$
(2) $C_2H_5OH \rightarrow [CH_3CHOH^+ + H + e^-]$
(3) $[e^-] \rightarrow [e^-_{solv}]$
(4) $[C_2H_5OH^+ + C_2H_5OH] \rightarrow [C_2H_5O + C_2H_5OH_2^+]$
(5) $[CH_3CHOH^+ + C_2H_5OH] \rightarrow [CH_3CHO + C_2H_5OH_2^+]$
(6) $[C_2H_5OH_2^+ + e^-_{solv}] \rightarrow [C_2H_5OH + H]$
(7) $[C_2H_5OH_2^+ + e^-_{solv}] \rightarrow C_2H_5OH_2^+ + e^-_{solv}$ (free ions)

The square brackets indicate that the enclosed species are in a spur. Reactions (1)–(7) are discussed in 680047 and 700239, which also include other references.

(8) $e^- + C_6H_6 \rightarrow C_6H_6^-$
(9) $C_6H_6^- + C_2H_5OH \rightarrow C_6H_7\cdot + C_2H_5O^-$
(10) $C_2H_5OH^+ + Cl^-_{solv} \rightarrow C_2H_5OH + Cl$

(8) and (10) are assumed to occur prior to solvation of the newly generated e^- and $C_2H_5OH^+$. The concentration of C_6H_6 or Cl^-_{solv} required for (8) or (10) to intercept (3) or (4) is ~1*M* (700248).

References to Sheet No. R*l*10

680047 Russell, J. C.; Freeman, G. R., J. PHYS. CHEM. 72: 816–21 (1968).
700239 Freeman, G. R., ACTIONS CHIM. BIOL. RADIATIONS 14: 73–134 (1970).
700248 Khorana, S.; Hamill, W. H., J. PHYS. CHEM. 74: 2885–8 (1970).

DATA SHEET **R*s*1**. *Ethanol solid.* e^-_{solv}

Reaction[a]	log A(s^{-1})	E(kcal/mol)	k_1(s^{-1})	$t_{1/2}$	T(K)	Method	Reference
(1) $e^-_{solv} \rightarrow C_2H_5O^-_{solv} + H$	8	5	1 x 10^{-6}	~ 8 days	77	γ-rad.; H_2 yields, compare $t_{1/2} \cong 3\mu s$ (298K)	670023
	5.3	3.7			89–97	alkali metal + C_2H_5OH, esr	675117
			1 x 10^{-3}		107	optical, λ_{max} = 540 nm	700097

a. This reaction can be written in several different ways. It seems preferable to write it as a unimolecular decomposition of the solvated electron complex (1), rather than as a bimolecular reaction with an ethanol molecule (2) (700239).

$$e^-_{solv} + C_2H_5OH \rightarrow C_2H_5O^- + H \quad (2)$$

The reaction is driven by the difference between the solvation energies of e^- and ($C_2H_5O^-$ + H), so several ethanol molecules take part in the formation of the transition state. A third form (3) of the decomposition was proposed for mechanistic reasons that might not have been valid, so it should be treated with reserve.

$$e^-_{solv} + 2C_2H_5OH \rightarrow CH_3\dot{C}HOH + C_2H_5O^- + H_2 (3)$$

References to Sheet No. R*s*1

670023 Fletcher, J.W.; Freeman, G.R., CAN. J. CHEM. 45: 635–40 (1967).
675117 Bennett, J.E.; Mile, B.; Thomas, A., J. CHEM. SOC. PT. A: 1399–403 (1967).
700097 Habersbergerova, A.; Josimovic, Lj.; Teply, J., TRANS. FARADAY SOC. 66: 669–78 (1970).
700239 Freeman, G.R., ACTIONS CHIM. BIOL. RADIATIONS 14: 73–134 (1970).

4. Spectroscopic Parameters

4.1. Optical Absorption Spectra

Optical absorption spectra of intermediates formed during the radiolysis of liquid ethanol have been measured using pulse techniques (620140, 650499, 660082, 690419, 700246, 700647, 710458, 720197). Spectra of e^-_{solv}, CH_3CHOH and $CH_3CHO^-_{solv}$ are shown in figures **S*l*,*s*1**, **S*l*2** and **S*l*3**. The $CH_3CHO^-_{solv}$ anion is obtained in good yield in strongly basic ethanol and in ethanol that contains acetaldehyde.

$$CH_3\dot{C}HOH + C_2H_5O^-_{solv} \rightarrow CH_3CHO^-_{solv} + C_2H_5OH \quad (1)$$
$$CH_3CHO + e^-_{solv} \rightarrow CH_3CHO^-_{solv} \quad (2)$$

$Cl_2^-{}_{solv}$ may form in solutions that contain a high concentration of Cl^-_{solv}. The suggested mechanism is (700246):

$$ROH^+ + Cl^-_{solv} \rightarrow ROH + Cl \quad (3)$$
$$Cl + Cl^-_{solv} \rightarrow Cl_2{}^-{}_{solv} \quad (4)$$

The absorption spectrum of $Cl_2{}^-{}_{solv}$ in ethanol is shown in figure **S*l*3**.

When solid pure ethanol is irradiated at 77 K to a dose of ~ 10^{19}eV/g it attains a deep blue color; at ~ 10^{20}eV/g it appears almost black. The color is due to the optical absorption of electrons trapped in the matrix. The optical absorption spectrum of the initially localized electrons shifts towards the blue as relaxation occurs in the solvating structure about the electron. The "solvation time" is about 3 ns in liquid ethanol at 166 K (710139) and about 5 μs in the glass at 77 K (720004).

The absorption spectrum of solvated electrons in solid ethanol at 77 K is compared with that in liquid ethanol at 298 K in figure **S*l*,*s*1**.

Characteristics of the optical spectra of e^-_{solv} and e^-_{trap} are listed in sheet nos. **S*l*1** and **S*s*1**. The energy of the absorption maximum E_{max} increases and the width of the spectrum at half height $W_{1/2}$ decreases with decreasing temperature and upon changing from the liquid to the glass phase.

The quantum efficiency of optical bleaching of irradiated ethanol at 78 K is dependent on the wavelength of the light used (fig. **S*s*2B**).

Characteristics of the optical spectra of $CH_3\dot{C}HOH$ and $CH_3CHO^-_{solv}$ are given in sheet no. **S*l*2**.

4.2. Electron Spin Resonance Absorption Spectra

ESR spectra of irradiated ethanol and e^-_{trap} at 77 K are shown in figure **S*s*3** (650517, 685130). Similar spectra are also reported in refs. 635001 and 700636.

The line width of the esr singlet of e^-_{trap} increases with increasing polarity of the matrix molecules (685130). This shift parallels the increasing energy of the optical absorption with increasing polarity of the organic matrix (685130).

The esr line width of e^-_{trap} in C_2H_5OD is only half that in C_2H_5OH (sheet no. **S*s*3**).

The esr spectra of $CH_3\dot{C}HOH$ and $\cdot CH_2CH_2OH$ in liquid ethanol are shown in figure **S*l*4**. They were obtained by photolysis of ethanol containing hydrogen peroxide (660074). The parameters are listed in sheet no. **S*l*3**.

Spectroscopic References

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DATA SHEET *Sl1*. *Properties derived from optical absorption spectra*: e^-_{solv}

State, T	liquid, 296 ± 3 K			
Reference	640113 650499 660082	710101	710769	720197
λ_{max}(nm)	700		700 ± 20[e]	688 ± 7[e]
E_{max}(eV)	1.77		1.77 ± 0.05	1.80 ± 0.02[e]
dE_{max}/dT (10^{-3}eV/deg)	− 3.4			− 3.2
$W_{1/2}$(eV)[a]	1.5			1.4
$dW_{1/2}/dT$ (10^{-3}eV/deg)	< 1			≤ 1
$G_{fi}\epsilon_{\lambda\,(max)}$[b]	15,000	15,200	16,000	16,000
$d(G_{fi}\epsilon_{\lambda\,(max)})/dT$	7	16		< 10
G_{fi}	1.0[c]			1.7
$\epsilon_{\lambda(max)}$ ($dm^3/mol \cdot cm$)	15,000[c]			9,400
f	0.87[c] (0.71[c,d])			0.4[d]

a. Peak width at half height.

b. Product of the free ion yield of solvated electrons and their molar absorbancy coefficient (decadic).

c. This value of G_{fi} appears to be too small (see sheet no. **PP*l*2**, so those of $\epsilon_{\lambda(max)}$ and f are probably too large.

d. Corrected for the internal field in the liquid (720197).

e. Independent of KOH concentration up to 2 *M*.

References to Sheet No. *Sl1*

640113 Taub, I.A.; Harter, D.A.; Sauer, M.C.Jr.; Dorfman, L.M., J. CHEM. PHYS. 41: 979–85 (1964).
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720197 Jha, K.N.; Bolton, G.L.; Freeman, G.R., J. PHYS. CHEM. 76(25): 3876–83 (1972).

Data Sheet S*s*1. *Properties derived from optical absorption spectra*: e^-_{trap}

State, T	Glassy solid, 77 ± 1 K						Glassy solid, 4 K
Reference	595002 610067	685130	700770	700636	720198	720145	720198
λ_{max}(nm)	512	543	531	530 ±	545	530	1500^c 495^e
E_{max}(eV)	2.42	2.28	2.33	2.3 ± 0.1^b	2.27		0.83^c 2.50^e
dE_{max}/dT (10^{-3}eV/deg)					− 3.0		d -3.2^e
$W_{1/2}$(eV)^a	1.0	1.0	1.1	1.2 ± 0.1^b	1.4		1.05^c 1.3^e
$dW_{1/2}/dT$ (10^{-3}eV/deg)					+ 1.7		$+1.5^e$
$G(e^-_{trap})$			2.5				
$\epsilon_{\lambda(max)}$ (dm^3/mol·cm)			10,000				

a. Peak width at half height.
b. The ± values indicate the extent of shift or scatter that can be caused by pre–annealing the glass before irradiation or by letting the irradiated sample sit in the dark for several hours at 77 K before measurement.
c. Electrons trapped in an unrelaxed matrix. The portion bleachable with 1700 nm light has E_{max} = 0.83 eV and $W_{1/2}$ = 0.5 eV and a narrow esr line (sheet no. S*s*2).
d. E_{max} shifts irreversibly towards higher energy when the sample is warmed towards 77 K. See figures S*s*4 and 5.
e. After warming to 77 K and re–cooling to 4 K. These electrons give a wide esr line, the same as at 77 K (sheet no. S*s*2).

References to Sheet No. S*s*1

595002 Alger, R.S.; Anderson, T.H.; Webb, L.A., J. CHEM. PHYS. 30: 695–706 (1959).
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720198 Hase, H.; Warashina, T.; Noda, M.; Namiki, A.; Higashimura, T., J. CHEM. PHYS. 57: 1039–45 (1972).

Data Sheet S*l*2. *Ethanol liquid. Properties derived from optical absorption spectra*: $CH_3\dot{C}HOH$, $CH_3CHO^-_{solv}$

	Species	T	λ_{max}(nm)	ϵ_λ (dm^3/mol·cm)	Reference
	$CH_3\dot{C}HOH$	room	< 230		690419
		room	~ 250	870_{255nm}	700647
		room		290_{297nm}	700647
	$CH_3CHO^-_{solv}$	room	< 270		690419
Aqueous	$CH_3\dot{C}HOH$	room	< 210	500_{255nm}	690419
				235_{297nm}	690419
Aqueous	$CH_3CHO^-_{solv}$	room	< 220	1300_{255nm}	690419
				890_{297nm}	690419

References to Sheet No. S*l*2

690419 Simic, M.; Neta, P.; Hayon, E., J. PHYS. CHEM. 73: 3794–800 (1969).
700647 Fletcher, J.W.; Richards, P.J.; Seddon, W.A., CAN. J. CHEM. 48: 3765–8 (1970).

DATA SHEET S*l*3. *Ethanol liquid. Properties derived from ESR spectra*: $CH_3\dot{C}HOH$, $\dot{C}H_2CH_2OH$

Species	g Factor[a]	ΔH (oersted)[b]	Reference
$CH_3\dot{C}HOH$	2.00323	0.2[c]	660840
$\dot{C}H_2CH_2OH$	2.00247		660840

a. Independent of temperature, 240 to 330 K.
b. Line–width
c. 0.17 at 240 K and 0.23 at 330 K.

$CH_3\dot{C}HOH$ Coupling Constants (oersted)

T(K)	a_α	a_β	a_{OH}
330	15.24	22.14	–
299	15.37	22.19	–
240	15.50	22.27	0.98
206			1.13

Reference to Sheet No. S*l*3

660840 Livingston, R.; Zeldes, H., J. CHEM. PHYS. 44: 1245–59 (1966).

DATA SHEET S*s*2. *Ethanol solid. Properties derived from ESR spectra*: e^-_{trap}

Solvent	T(K)	g factor	ΔH (oersted)[a]	Reference
C_2H_5OH	77	2.0010	14	650517
C_2H_5OH	77		12	685130
C_2H_5OH	4		5.5 ± 0.5[b]	720198
C_2H_5OH	4		13.5 ± 0.5[c]	720198
C_2H_5OD	77	2.0013	6	650517

a. Line–width between points of maximum slope of the absorption (between minimum and maximum of first derivative curve).
b. Electrons in unrelaxed matrix; optical E_{max} = 0.83 eV; see sheet no. S*l*,*s*1.
c. Electrons in relaxed matrix; optical E_{max} = 2.50 eV; see sheet no. S*l*,*s*1.

References to Sheet No. S*s*2

650517 Blandamer, M.J.; Shields, L.; Symons, M.C.R., J. CHEM. SOC.: 1127–31 (1965).
685130 Ekstrom, A.; Willard, J.E., J. PHYS. 72: 4599–603 (1968).
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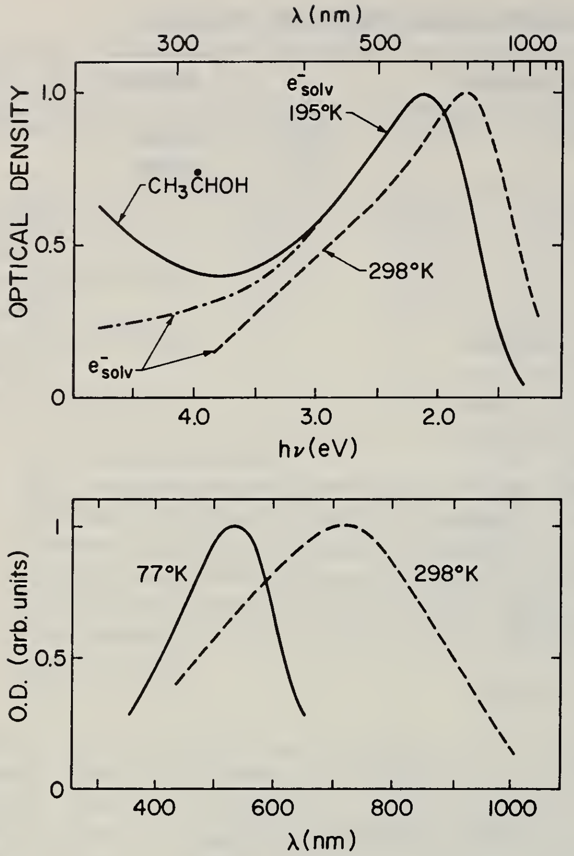

Figure Sl,s1. *Optical absorption spectra of e^-_{solv} in liquid ethanol at ~ 298 K* (650499) *and 195 K* (660082) *and in solid at 77 K* (685130). See also figure Ss2.

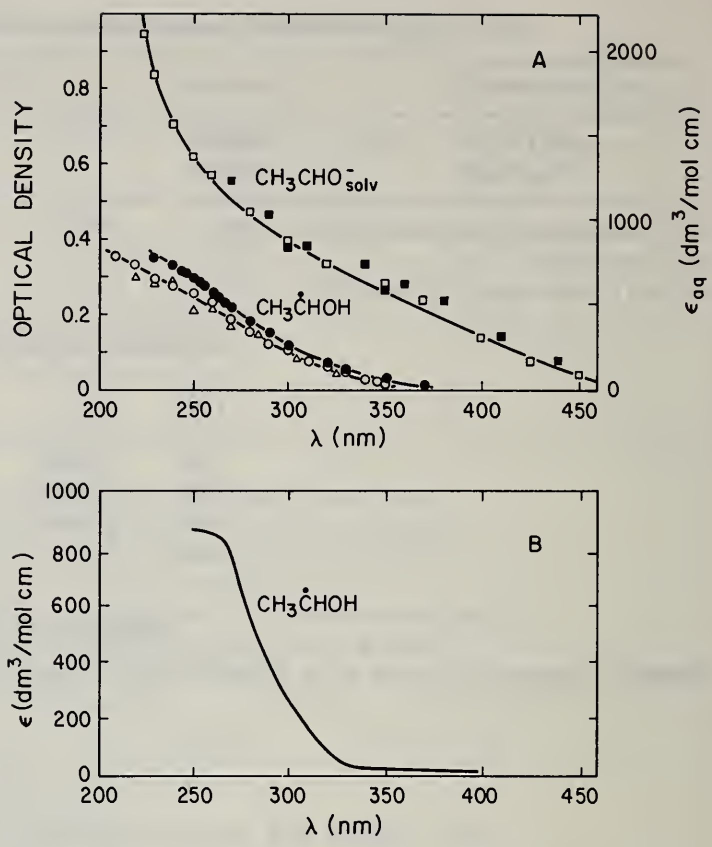

Figure Sl2. *Optical absorption spectra of CH_3CHOH and $CH_3CHO^-_{solv}$.*

A(690419): 1 atm N_2O added as electron scavenger; room temperature.
Liquid ethanol: pulse dose 1.7 x 10^{18}eV/g; ●, neutral; ■, NaOH added. *Aqueous 0.1M ethanol*: pulse dose 2.2 x 10^{18}eV/g; △, pH 1; ○, pH 6; □, pH 13; ϵ_{aq} applies only to the aqueous solutions.

B(700647): pure ethanol, room temperature, pulse dose ⩽ 6 x 10^{17}eV/g.

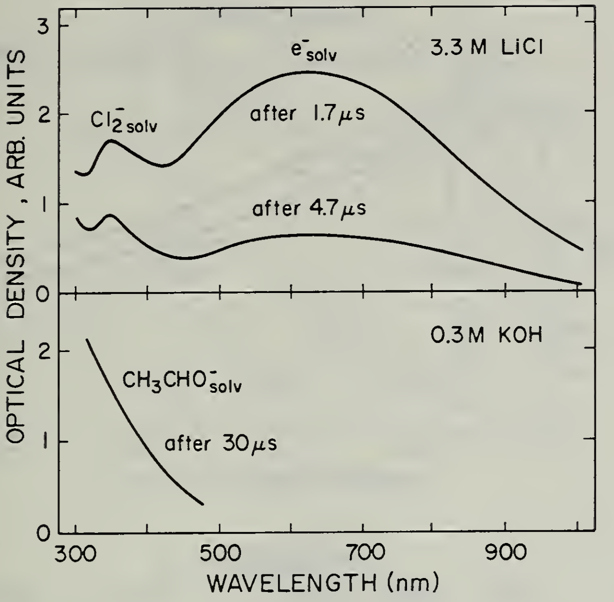

Figure S*l*3. *Optical absorption spectra of* e^-_{solv} *and* $Cl_2{}^-_{solv}$ *in 3.3 M LiCl and* $CH_3CHO^-_{solv}$ *in 0.3 M KOH.* Ethanol solvent. Room temperature. Pulse length ≅ 1μs; dose ≅ 10^{18}eV/g. (700246)

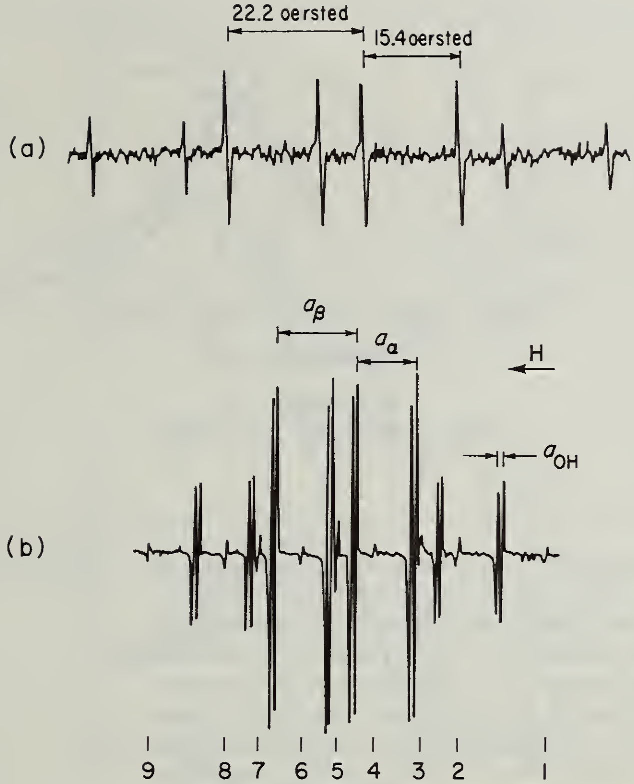

Figure S*l*4. *First derivatives of esr spectra of* $CH_3\dot{C}HOH$ *and* $\dot{C}H_2CH_2OH$ *in liquid ethanol* (660840).
(a) $CH_3\dot{C}HOH$ at 299 K.
(b) $CH_3\dot{C}HOH$ (strong lines) and $\dot{C}H_2CH_2OH$ (numbered lines) at 203 K.

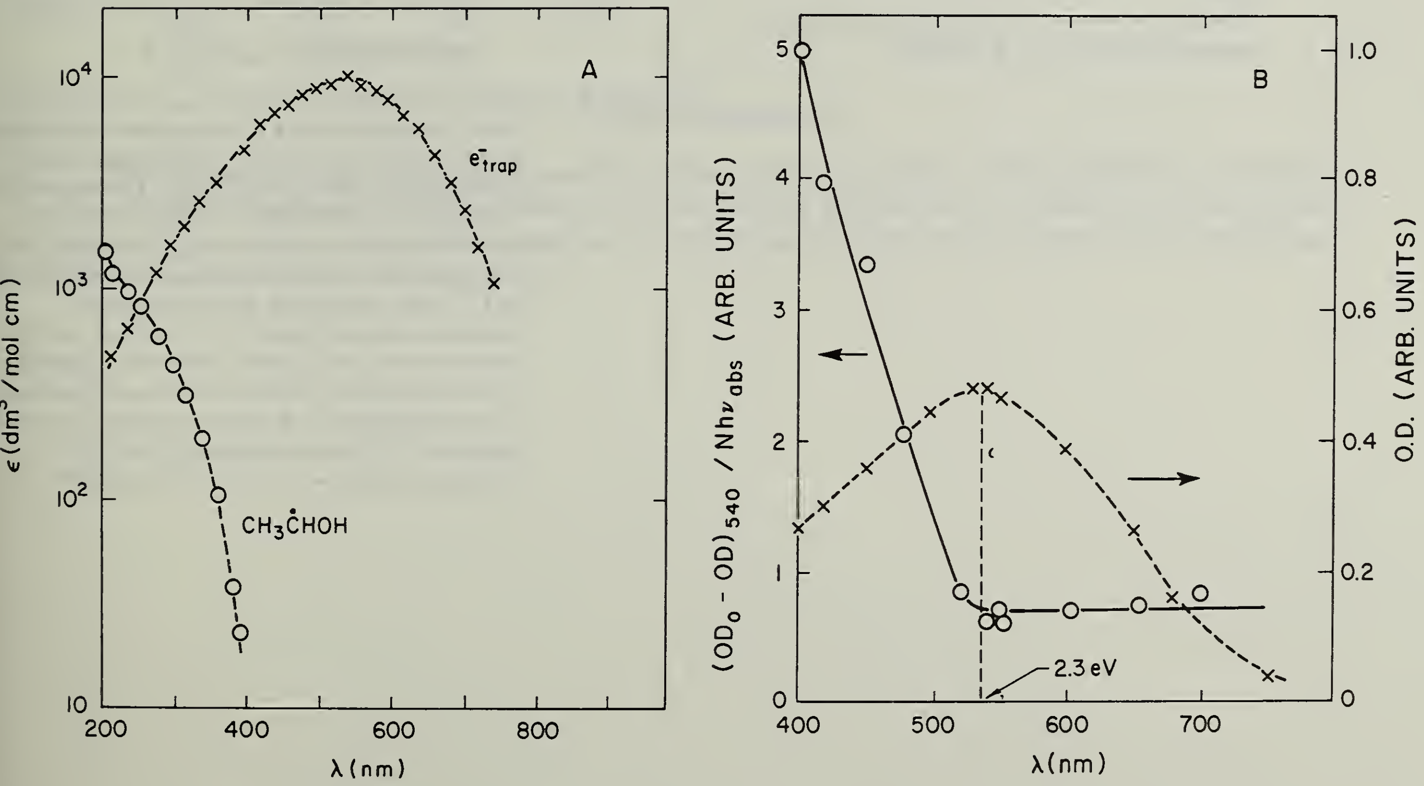

Figure S*s*2. *Optical properties of γ–irradiated ethanol at 78 K* (700770). Dose not stated.
A: Spectra of extinction coefficients of trapped electrons and $CH_3\dot{C}HOH$ radicals.
B: Spectrum of relative quantum efficiencies for bleaching.

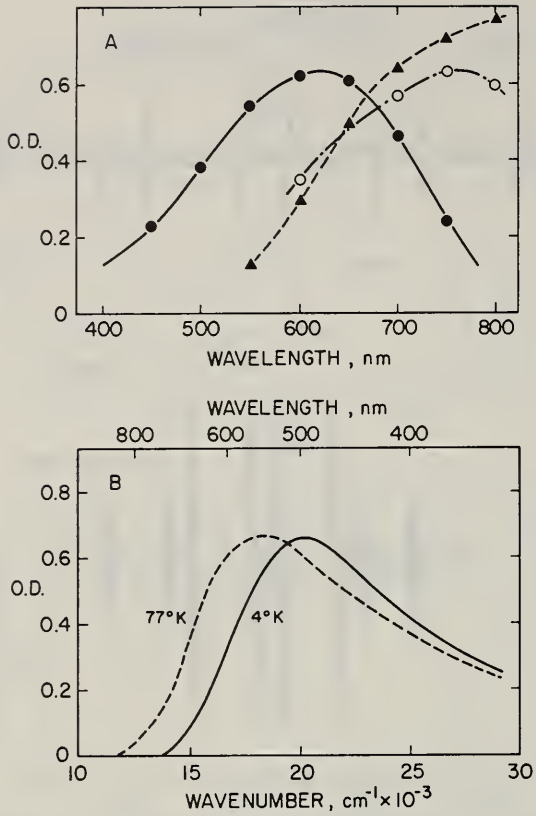

FIGURE Ss3. A: *Transient absorption of* e^-_{trap} *in ethanol glass at 77 K at ––– 0.1 μs, —·— 3 μs, and —— 7 μs after a 6 x* 10^{17} *eV/g, 1.1 μs pulse* (720004).

B: *Optical absorption spectra of* e^-_{trap} *in ethanol glass.*

The spectra were recorded at 77 and 4 K after gamma radiolysis at 77 K (720198).

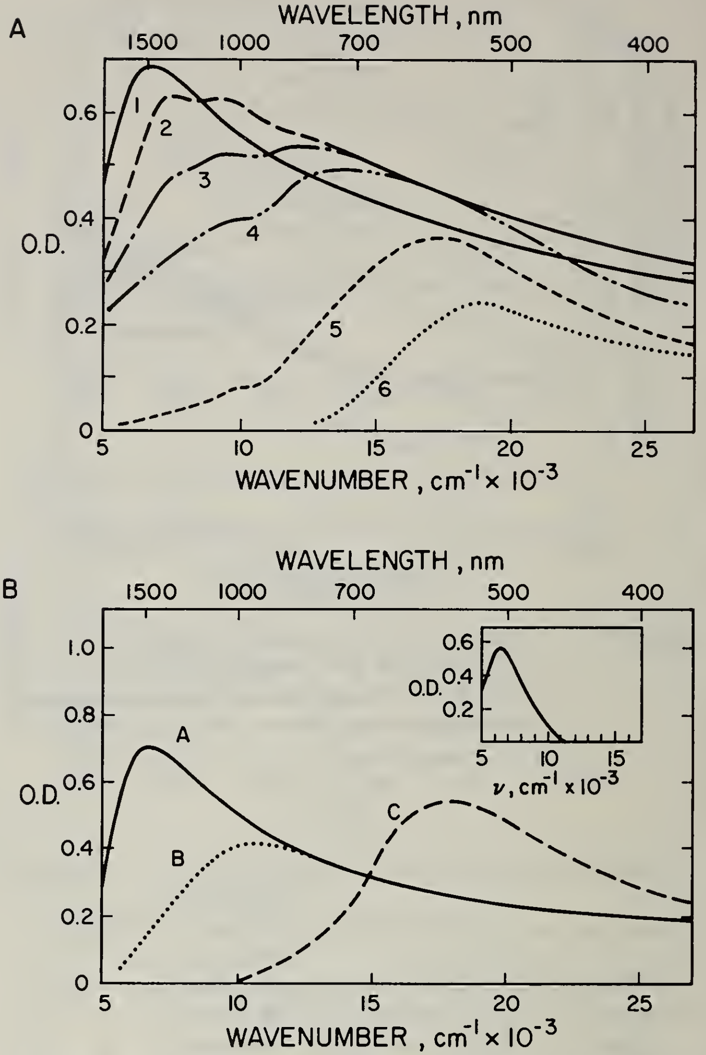

FIGURE Ss4. A: *Optical absorption spectra of* e^-_{trap} *in ethanol glass.* After the radiolysis at 4 K, the spectra were obtained at 4 (1), 10 (2), 19 (3), 30 (4), 42 (5), and 77 K (6). The total dose was 1.5 x 10^{19}eV/g. The rate of the temperature rise was about 1 deg/min (720198).

B: *Optical absorption spectra of* e^-_{trap} *in ethanol glass.* The spectrum A was obtained at 4 K after radiolysis at 4 K. The spectrum B was obtained after photobleaching with light of λ = 1700 nm at 4 K. Subtraction of the spectrum B from the spectrum A gives a spectrum shown in the insert. Spectrum C was obtained at 77 K when the sample was warmed rapidly to 77 K after irradiation at 4 K. The total gamma dose was 1.5 x 10^{19}eV/g (720198).

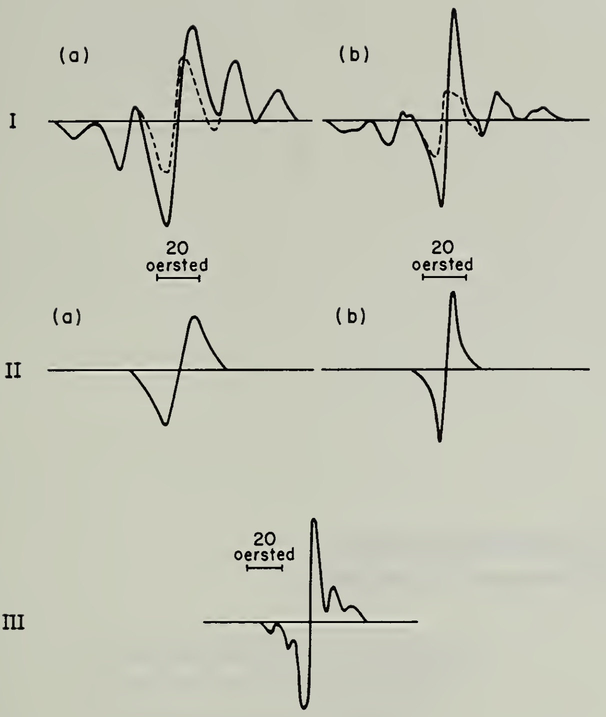

FIGURE Ss5. *First derivatives of esr spectra of γ–irradiated ethanol at 77 K.* Cavity frequency ~ 9.5 GHz.
I and II (650790) (a) C_2H_5OH, (b) C_2H_5OD
I —— before bleaching; – – – – after bleaching with visible light, leaving radicals trapped in the matrix.
II e^-_{trap}, by difference between the curves in I.
III (685130) before bleaching.

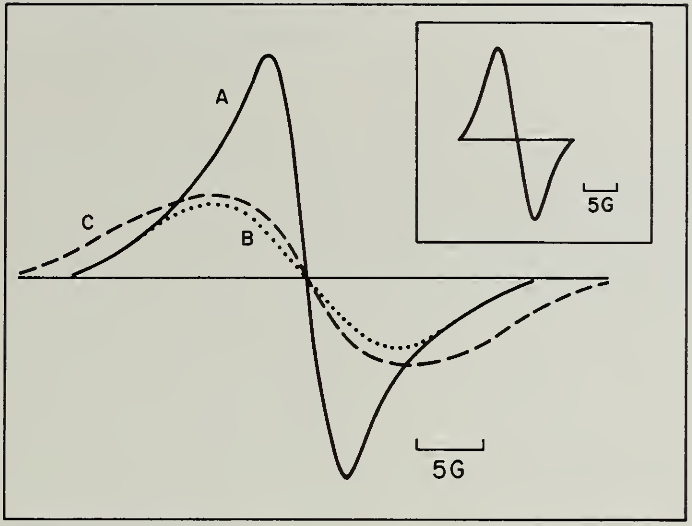

FIGURE Ss6. *ESR spectra of e^-_{trap} in ethanol glass.* The spectrum A was obtained at 4 K after radiolysis at 4 K. The spectrum B was obtained after photobleaching with light of λ > 1000 nm at 4 K. Subtraction of spectrum B from spectrum A gives a singlet spectrum shown in the insert. Spectrum C was measured at 4 K after the sample which was irradiated at 4 K was warmed rapidly to 77 K. The total dose was 1.1 x 10^{19}eV/g (720198).

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