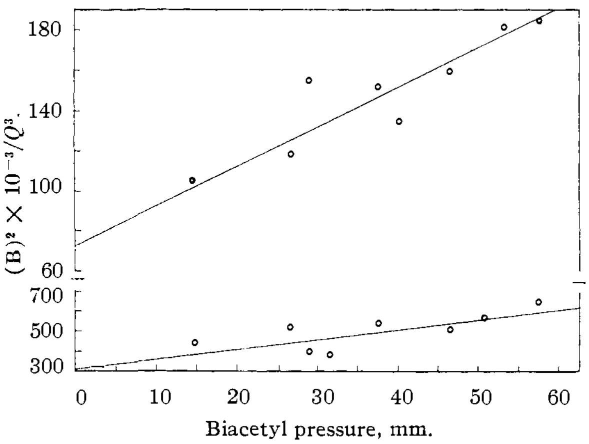

Fig. 3.—Plots of the biacetyl pressure squared times 10^{-3} divided by the phosphorescence yield *versus* the biacetyl pressure. Biacetyl pressure in mm. Temperature is 40°. Upper plot, incident radiation is 3130 Å. from BTH lamp; lower plot, 3020 Å. from BTH lamp.

Figure 2 shows plots of $(B)/Q_3$ *vs.* (B) at 3340 Å. and 3655 Å. The ratio of slope to intercept at 3655 Å. is 2.4×10^3 liters/mole, in satisfactory agreement with the value found in Fig. 1 cited in the previous paragraph.

The intercepts show that $(k_{2B} + k_{3B})$ is about 19 times as large at 3340 Å. as at 3655 Å. At 3655 Å. $(k_{2B} + k_{3B}) << k_5(B)$ at sufficiently high pressures and the data in Table I show phosphorescence yields to become about the same as at 4047 and 4358 Å. at the highest pressures studied.

At 3020 and 3130 Å., the values of $(B)/Q_3$ diminish with increase in pressure (not shown). Since these two wave lengths lie beyond a minimum in the absorption curve of biacetyl, there is every reason to believe that a second upper singlet state is produced. To account for the data in this part of the spectrum some steps must be added as

$$B + h\nu = B_n^{II} \tag{19}$$

$$B_n^{II} = D \tag{20}$$

$$B_n^{11} + B = B_0^{II} + B \tag{21}$$

$$B_0^{II}\,(+B) = B_n^{1}(+B) \tag{22}$$

where the superscript II refers to the second upper singlet state. By assumption of the steady state one derives the expression

$$\frac{(B)^2}{Q_3} = \frac{(k_{8B} + k_{9B})(k_{2B} + k_{3B})(k_{6B} + k_{7B} + k_{11B})(k_{20} + k_{21}(B))}{k_{5B}k_{7B}k_{8B}k_{21}}$$

Figure 3 shows plots of $(B)^2/Q_3$ *vs.* (B) which are straight lines within experimental error. This gives support to but not proof of the mechanism.

The wave length 3340 Å. lies just about at the minimum between two absorption regions. It is difficult to say which upper level is involved at this wave length. Possibly there are two overlapping absorptions.

Thus it is possible to give a reasonably complete picture of emission and photochemical behavior of biacetyl and within the limits of the data, which are less extensive and more difficult to obtain, also for acetone.

Acknowledgment.—The author wishes to extend his sincere thanks to Professor W. A. Noyes, Jr., for many helpful suggestions and criticisms.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF ROCHESTER]

Radiolysis of CH_3COOCH_3 and CH_3COOCD_3 by Cobalt-60 γ-Rays[1]

BY P. AUSLOOS AND C. N. TRUMBORE

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Results of studies on the radiolysis of liquid and gaseous CH_3COOCH_3 and CH_3COOCD_3 by cobalt-60 γ-radiation are reported. Yields of the volatile radiation decomposition products have been studied as a function of temperature, dose and the presence of added radical scavengers. A comparison of the isotopic hydrogen, methane, ethane and dimethyl ether species present in these products provides information about possible primary processes, hot radical effects and radical disproportionation and recombination reactions within the liquid "cage." Recombination of methyl radicals originating from the same parent molecule as well as abstraction reactions between radicals in the same cage are postulated to explain the non-statistical yields of CH_3CD_3 and the high yields of CH_3D and CH_3OCD_3 in the liquid phase.

Introduction

The vapor and liquid phase γ-radiolysis of CH_3COOCD_3 has been investigated in connection with recent photolysis and radiolysis studies of esters and ketones carried out in this Laboratory.[2] It was expected that a study of the partially deuterated methyl acetate would give more precise information about radical recombination and disproportionation reactions occurring in the electron track, spur or solvent cage arising from absorption of high energy electromagnetic radiation.

Vapor phase experiments were carried out to obtain some information on possible ion–molecule processes and on the influence of the solvent cage.

Scavengers have been added in both the vapor and liquid phase in order to ascertain the importance of hot radical reactions as well as to separate cage effects from thermal processes.

The vapor phase photolysis of CH_3COOCD_3 recently has been investigated over a wide temperature range,[3,4] and some of the conclusions drawn

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[1] This research was in part supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18 (600) 1528. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] P. Ausloos and J. Paulson, THIS JOURNAL, **80**, 5117 (1958).

[3] M. H. J. Wijnen, *J. Chem. Phys.*, **28**, 271 (1958).

[4] M. H. J. Wijnen, *ibid.*, **28**, 939 (1958).

TABLE I

VAPOR PHASE RADIOLYSIS OF CH_3COOCD_3

Pressure, 15 cm.; temp., 60°; rates, ml./min. ($\times 10^5$) at STP

Time, min.	Iodine, mm.	H_2	HD	D_2	CH_4	CH_3D	CD_3H	CD_4	Ethane	CO	CO_2
2830	..	0.420	0.80	0.235	1.37	0.11	0.495	0.028	0.20	2.01	0.85
2600	4.5	0.17	0.06	0.205	0.007	0.009	0.0075	0.01	0.03	1.57	0.76

from these investigations will be of use in the interpretation of the data presented in the work.

Experimental

Irradiations.—Liquid samples were irradiated in flat-bottomed 10-ml. Pyrex volumetric flasks fitted with a vacuum line attachment, which was sealed after introduction of the sample, and a break seal. One ml. of thoroughly degassed liquid was distilled from a storage bulb into a calibrated volume (1 ml. at STP) and from there into the irradiation cell. The latter contained the necessary evacuated solute when scavengers were to be added for a particular run. Except for the −195° run the cells were always put in the same position with respect to the radiation source. In the −80° run the cell described above was surrounded with powdered Dry Ice. A Dewar flask containing liquid nitrogen surrounded the −195° sample. Back-scatter of radiation into the cell due to the Dry Ice and liquid nitrogen was assumed to be negligible.

Samples were irradiated about three inches from a 400 Curie cobalt-60 source described elsewhere.[5] Support and reproducible positioning of the samples were provided by a Lucite plate 7.5 cm. wide, 8.5 cm. long and 0.6 cm. thick. Determination of the dose rate was accomplished through the use of the Fricke ferrous sulfate dosimeter, assuming a value of 15.45 for $G(Fe^{+3})$.[6] After correction for differences in electron density, the dose rate was found to be 0.819×10^{17} e.v./g./min. for the run carried out in the Dewar and 2.57×10^{17} e.v./g./min. for all other experiments.

The vapor phase experiments were carried out in a cylindrical Pyrex cell (6 cm. diameter, 15 cm. length) which was closed off by a break seal. The volume of gas irradiated was large in order to prevent a high percentage total decomposition of methyl acetate and in order to have large enough quantities of products to analyze. No absolute G-values were determined for these runs.

Materials.—Methyl-d_3 acetate was obtained from the Merck Co. and contained large quantities of an unidentified volatile compound which could be separated from the acetate by trap to trap distillations at −80°. Analysis by vapor-liquid partition chromatography after this treatment showed no impurities other than a trace of methanol. A mass spectrometric investigation of the compound gave a value of 67 for the peak height ratio 77/76. The 78 peak could be attributed entirely to the C^{13} isotope. From this it may be concluded that the material consisted of at least 98.5% $C_3H_3D_3O_2$. The fact that the 62 peak ($COOCD_3^+$) was 68 times the 66 peak height indicates that only the methoxy group contained the deuterium atoms.

Diphenylpicrylhydrazyl (DPPH) was obtained from Aldrich Chemical Co. and was kept under vacuum before being introduced into the cell.

Non-deuterated methyl acetate was obtained from Eastman Kodak Co. (White Label) and purified by distillation with rejection of a large head and tail fraction.

Analysis.—After irradiation, the cell was attached to an analysis system consisting of two traps, a modified Ward still and a Toepler pump. The hydrogen, carbon monoxide, methane fraction was removed at liquid nitrogen temperature and split into two fractions. The first fraction was analyzed mass spectrometrically in order to determine the H_2, HD, D_2 distribution, while the second fraction was analyzed by means of a hot cupric oxide furnace. Carbon dioxide and water were held back while the methane fraction was taken off and analyzed in the mass spectrometer. The contribution to the 1 and 2 peaks was determined and subsequently subtracted from the hydrogen spectrum obtained from the first fraction. The C_2 fraction was taken off at −175° and also analyzed mass spectrometrically. The carbon dioxide fraction was removed at −140°. On one occasion dimethyl ether was distilled quantitatively at −120°. This fraction, which also contained formaldehyde, was analyzed with the mass spectrometer.

Results

Vapor Phase.—Table I presents the rates of formation of the major volatile products formed in the radiolysis of CH_3COOCD_3 at 60° and 15 cm. pressure. In the second experiment iodine was present at a pressure of 4.3 mm.

In the absence of iodine the ratios $G(CH_4)/G(CH_3D)$ and $G(CD_3H)/G(CD_4)$ are, respectively, 12.4 and 17.7. In the presence of iodine, however, the total methane yield is reduced by 90% and the relative yields of the isotopic methanes produced are of the same order of magnitude.

HD is the major component of the hydrogen fraction in the absence of a scavenger and is most strongly reduced by iodine. $G(H_2)$ is suppressed by more than 50% while $G(D_2)$ is only slightly affected.

While the ethane fraction was too small to be analyzed with any accuracy, it is noted that iodine reduced the total ethane fraction to a trace amount.

Liquid Phase.—The results given in Table II can be summarized in part.

Effect of Temperature. a.—The G-values (yields in molecules/100 e.v. energy absorbed) for all products increase with increasing temperature from −80 to 52°. An analogous temperature effect has been reported in the helium ion radiolysis of isopropyl acetate.[7]

b.—Increasing the temperature from −80 to 52° increases the G-ratios of CH_4/CH_3D and CD_3H/OD_4, respectively, from 1 to 3.05 and from 2.6 to 6.25.

c.—The ratios H_2/D_2 and HD/D_2 increase slightly with increase in temperature.

Effect of Scavengers.—Comparison of the room temperature yields indicates that scavengers: (a) reduce the ratio $G(CH_4)/G(CH_3D)$ and $G(CD_3H/)G(CD_4)$ to values much below unity without affecting $G(CH_3D)$ and $C(CD_4)$ appreciably; (b) reduce the $G(H_2)/G(D_2)$ and $G(HD)/G(D_2)$ ratios; (c) do not appreciably affect $G(CO)$ and $G(CO_2)$ and; (d) increase the ratio $G(CH_3CD_3)/[G(C_2D_6)G(C_2H_6)]^{1/2}$.

Effect of Dose.—An increase by a factor of three in the total dose absorbed in the sample reduces the G-values for CH_4 and CD_3H appreciably without affecting the yields of the other products significantly.

Other Products. a.—D_2CO was observed as a major product both in the presence and absence of scavengers but was not determined quantitatively.

b.—Dimethyl ether was measured in the 27° high dose run. The G-value was found to be 0.17 ± 0.02. Mass spectrometer analysis gave a

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(5) J. G. Stang, Jr., G. Strickland, *et al.*, *Nucleonics*, **12**, 62 (1948).

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(7) A. S. Newton and P. O. Strom, *J. Phys. Chem.*, **62**, 21 (1958).

TABLE II

LIQUID PHASE RADIOLYSIS OF CH_3COOCD_3

Temp., °C.	−195	−80	27	27	52	27	27
Scavenger	. .	. .	. .	. .	. .	DPPH (1×10^{-2} *M*)	I_2 (2×10^{-2} *M*)
Time (min.)	2234	1534	990	2912	760	1040	976
G							
CO	0.212	1.45	1.65	1.69	1.91	1.63	1.69
CO_2	N. detd.	0.76	0.91	0.94	1.27	0.89	0.99
H_2	0.083	.202	.234	.238	0.275	.185	.179
HD	.083	.24	.26	.268	.34	.21	.184
D_2	.045	.12	.12	.124	.139	.12	.118
CH_4	.05	.399	.95	.63	1.39	.090	.072
CH_3D	.10	.389	.410	.40	0.457	.36	.325
CD_3H	.051	.156	.334	.240	.57	.044	.036
CD_4	.008	.060	.077	.076	.090	.07	.06
C_2H_6	N. detd.	.075	.106	.108	.128	.089	.073
CH_3CD_3	N. detd.	.177	.188	.193	.212	.174	.177
C_2D_6	N. detd.	.011	.014	.0144	.02	.0118	.009
$(CH_3CD_3)/[(C_2H_6 x C_2D_6)]^{1/2}$		6.1	4.85	4.9	4.32	5.4	6.75
$(CH_3D)/(CD_4)$	13.0	6.4	5.3	5.3	5.05	5.4	5.7
$(CH_4)/(CD_3H)$		2.55	2.85	2.62	2.47	2.05	2.0
$(C_2H_6)^{1/2}/(C_2D_6)^{1/2}$		2.52	2.73	2.75	2.62	2.75	2.79
$(CO + CO_2)/(CO_2)$		2.9	2.8	2.8	2.50	2.83	2.66

TABLE III

RADIOLYSIS OF CH_3COOCH_3

Temp., °C.	CH_3COOCH_3, cm.	I_2, cm.	Time, min.	H_2	CO	CO_2	CH_4	C_2H_6	CH_3OCH_3
						Rates, ml./min. ($\times 10^5$) at STP			
					Vapor phase				
27	21	. .	1347	2.14	2.68	1.10	1.76	0.43	0.034
65	21	0.6	1317	0.54	2.00	1.0	0.05	0.04	0.00
Temp., °C.		Scavenger, $M \times 10^2$	Time, min.	H_2	CO	CO_2	CH_4	C_2H_6	CH_3OCH_3
						G(molecules/100 e.v.)			
					Liquid phase				
−80		. .	264	0.639	1.24	0.8	0.94	0.34	0.16
27		. .	554	.76	1.64	.95	2.03	.34	.15
27 DPPH		1.0	208	.62	1.55	.96	0.58	.32	.15
27 I_2		1.0	447	.57	1.51	.90	0.50	.27	.14

value of about 7 for the ratio $G(CH_3OCD_3)/G(CD_3OCD_3)$.

c.—Methanol was a major product. A fraction distilled from a vapor–liquid partition chromatograph was analyzed with the aid of a mass spectrometer and could be ascribed entirely to CD_3OH. The starting material may have been CD_3OD, having been subsequently converted to CD_3OH by exchange in the chromatograph column.

d.—A trace of acetylene, mostly C_2H_2 and ethylene were observed among the products of both the vapor and liquid phase radiolysis.

Comparison with the Non-deuterated Compound.—Table III gives the *G*-values of the major volatile products formed in the vapor and liquid phase radiolysis of CH_3COOCH_3. The CO and CO_2 yields are essentially the same as those for the partially deuterated compound while the C_2H_6, CH_4 and H_2 yields are roughly 10 to 20% higher than the total equivalent yields in the radiolysis of CH_3COOCD_3. In the vapor phase, iodine reduces the ethane and dimethyl ether yields to negligible amounts. In the liquid phase, however, these products are only slightly affected.

Solid Phase.—The *G*-values of the products in the −195° experiment are considerably lower than those in the liquid phase runs. The ethane–CO_2 fraction was accidentally lost. The methane distribution differs considerably from the liquid phase runs.

Discussion

It is believed that most of the products of the radiolysis can be explained on the basis of known free radical processes. Therefore, possible ion–molecule reactions which might explain the same products will not be considered in this discussion. The discussion will be confined mainly to the CH_3COOCD_3 radiolysis results. It is expected that the same conclusions will be applicable to the CH_3COOCH_3 results.

Primary Events.—It cannot be decided from the results the extent to which dissociative processes which the molecule undergoes are to be attributed to a split of the excited molecule (formed either by direct excitation or by neutralization of the molecule–ion) or to a dissociation of the molecule–ion followed by a neutralization of the fragments. The processes given below consequently will have to be considered as being of an over-all character. The radicals produced in these processes may eventually decompose further as a result of the

$$\begin{array}{lll} CH_3COOCD_3 \longrightarrow & CH_3CO + OCD_3 & \text{(I)} \\ & CH_3 + CO_2 + CD_3 & \text{(II)} \\ & H + CH_2COOCD_3 & \text{(III)} \\ & D + CH_3COOCD_2 & \text{(IV)} \\ & CH_3CO + OCD + D_2 & \text{(V)} \end{array}$$

energy carried over from the primary split or from the neutralization process.

The high carbon monoxide yield in both the vapor and liquid phase radiolysis indicates that step I, followed by the decomposition of the acetyl radical, is the most probable primary process. The near independence of the carbon monoxide yield of scavenger addition shows that, at least to some extent, process I may be written

$$CH_3COOCD_3 \longrightarrow CH_3 + CO + OCD_3$$

Evidence for a dissociation of acetyl radicals as a result of energy carried over from the primary process also has been obtained in the photolysis of methyl acetate.[4]

The carbon dioxide yield is probably a good measure of the importance of process II, although it should be pointed out that this process may also proceed to some extent through an intermediate CH_3COO or $COOCD_3$ radical. Both radicals are known to be rather unstable.[8,9]

The reduction of the CO and CO_2 yields by addition of iodine to the vapor phase may also be explained by electron capture by iodine and/or the trapping CH_3CO, CH_3COO or $COOCD_3$ radicals. The relatively high D_2, CO and CO_2 yields indicate clearly, however, that I_2 acts mainly as a radical trap. In the liquid phase, an energy transfer involving I_2 or DPPH is apparently of minor importance in view of the fact that CO, CO_2, hydrogen, ethane and dimethyl ether are practically not affected by these scavengers. However, a DPPH concentration higher than 10^{-2} *M* reduces the yields of all products without appreciably affecting the relative distribution of these products. The latter effect is probably an energy transfer process.

The presence of H_2 in the vapor and liquid phase radiolysis, as well as the fact that the yield can be reduced to some extent by the addition of scavenger, is good evidence for the occurrence of III.

The fact that the D_2 yield is practically unaffected by scavengers in the liquid and vapor phase radiolysis, while HD is drastically reduced, can best be explained by the occurrence of step V. A process such as IV may also be of importance, although it is most likely that most D atoms originate from the decomposition of CD_3O or DCO formed in processes I and V, respectively. These D atoms may be expected to be thermal and to abstract an H atom from CH_3COOCD_3, in agreement with the pronounced reduction in HD when scavenger is present in the vapor phase. In the liquid phase HD can also be formed by disproportionation between H and CD_3O or DCO in or near the original γ-ray "spur" (an isolated region of ionization and/or excitation caused by the absorption of about 100–200 e.v. energy from a secondary electron).[10]

The H atoms formed in process III may be expected to have high translation energy and will consequently abstract both H and D atoms from the methyl acetate. The fact that in the vapor phase radiolysis in presence of iodine $G(H_2)/G(HD)$ is appreciably higher than unity may necessitate the postulation of an H_2 removal process.

The D_2 and H_2 produced in the presence of scavengers in the vapor phase can also be explained by ion–molecule reactions of the type

$$R\cdot^+ + CH_3COOCD_3 \longrightarrow CH_3COOCDR^+ + D_2$$
$$R\cdot^+ + CH_3COOCD_3 \longrightarrow RCHCOOCD_3^+ + H_2$$

where $R\cdot^+ = CH_3\cdot^+$, $CH_3CO\cdot^+$ or $\cdot OCD_3^+$

A similar reaction has been proposed in the radiolysis of methane.[11]

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2$$

Secondary Reactions.—The elementary reactions (1) to (17) are considered to be the major steps leading to the formation of the measured products.

$$\begin{array}{llr} CH_3 + CH_3COOCD_3 \longrightarrow & CH_4 + CH_2COOCD_3 & (1) \\ & CH_3D + CH_3COOCD_2 & (2) \\ CD_3 + CH_3COOCD_3 \longrightarrow & CD_3H + CH_2COOCD_3 & (3) \\ & CD_4 + CH_3COOCD_2 & (4) \\ D + CH_3COOCD_3 \longrightarrow & HD + CH_2COOCD_3 & (5) \\ & D_2 + CH_3COOCD_2 & (6) \\ H + CH_3COOCD_3 \longrightarrow & H_2 + CH_2COOCD_3 & (7) \\ & HD + CH_3COOCD_2 & (8) \\ CH_3 + CH_3 \longrightarrow & C_2H_6 & (9) \\ CH_3 + CD_3 \longrightarrow & CH_3CD_3 & (10) \\ CD_3 + CD_3 \longrightarrow & C_2D_6 & (11) \\ CH_3 + CD_3O \longrightarrow & CH_3D + D_2CO & (12) \\ & CH_3OCD_3 & (13) \\ CD_3 + CD_3O \longrightarrow & CD_4 + CD_2O & (14) \\ & CD_3OCD_3 & (15) \\ H + CD_3O \longrightarrow & HD + D_2CO & (16) \\ D + CD_3O \longrightarrow & D_2 + D_2CO & (17) \end{array}$$

Reactions of Methyl Radicals with Methyl Acetate. a. Vapor Phase.—Due to the small steady-state radical concentration arising from the low γ-ray intensities in the vapor phase experiments, abstraction reactions 1–8 would be expected to prevail over the radical recombination and disproportionation steps 9–17.[9]

Recent vapor phase photolysis studies[4] indicate that H atom abstraction is strongly favored over a D atom abstraction from CH_3COOCD_3. For instance, it was found that at 153° k_1/k_2 was roughly equal to 20. The data of Table I are in good agreement with this observation. The high CH_4/CH_3D and CD_3H/CD_4 ratios in the absence of scavenger, as well as the strong reduction in methane yields caused by iodine, indicates that approximately 98% of the methane is formed by normal thermal abstraction of a hydrogen atom from

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(8) L. Jaffe, E. J. Prosen and M. Szwarc, *J. Chem. Phys.*, **27**, 416 (1957).

(9) P. Ausloos, *Can. J. Chem.*, **36**, 383 (1958).

(10) See J. L. Magee, *Ann. Rev. Nuclear Sci.*, 1953, or A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, **21**, 1080 (1953).

(11) (a) D. O. Schissler and D. P. Stevenson, *ibid.*, **24**, 926 (1956); (b) G. G. Meisels, W. H. Hamill and R. R. Williams, Jr., *ibid.*, **25**, 790 (1957).

methyl acetate. The methane distribution in the iodine experiment can be explained by hot radical processes.

b. **Liquid Phase.**—In the liquid phase experiments, the ratios CH_4/CH_3D and CD_3H/CD_4 are considerably lower than those found in the vapor phase run.[12] The G-values for CH_4 and CD_3H production are reduced by about 90% upon addition of scavengers at 27°. A somewhat similar observation has been made in a recent study on the radiolysis of CH_3COCH_3–CD_3COCD_3 mixtures.[1] In this system the CD_3H and CH_4 yields in the presence of scavengers can be attributed largely to hot radical abstraction reactions. Scavenger experiments show that only a small fraction of the CH_3D and CD_4 yields is due to a normal thermal abstraction process. It will be pointed out later that an appreciable fraction of the CH_3D and CD_4 can be accounted for by hot radical processes and disproportionation reactions in the γ-ray "track."

A fairly crude estimate of the relative CH_3/CD_3 yields can be obtained by considering the ratio $CO + CO_2/CO_2$, given in Table II. The CH_4/CD_3H ratios in the absence of scavengers are in fair agreement with this value. Subtraction of hot radical contribution will affect these ratios only slightly.

The increase of $G(CH_4)/G(CH_3D)$ and $G(CD_3H)/G(CD_4)$ with an increase in temperature is in agreement with the suggestion made before that the thermal radicals CH_3CO, $COOCD_3$ and/or CH_3COO decompose more readily at higher temperatures. However, competition between abstraction and recombination of methyl radicals with the larger radicals such as CH_3COOCD_2 and CH_2COOCD_3, would also lead to the same trend and it may be expected that both effects contribute.

The methane results in the two 27° runs in the absence of scavengers show clearly that the CH_4 and CD_3H yields decrease with increasing fractional decomposition of the parent molecule. The other methane yields as well as the yields of all other measured products are constant with increasing dose. This may be considered as good evidence for the assumption that only the thermal methyl radicals which escaped from the track are affected by further irradiation. This depletion of methanes can be explained by an addition of the methyl radicals to unsaturated radiolysis products. Methyl radicals in or near the "spur" should not be affected by these relatively small scavenger concentrations.

Reactions in the "Spur" Region. a. Methyl Radical Recombination.—Since the energy absorbed per mole would be roughly the same in both phases, and because in the liquid phase radical–radical reactions are diffusion controlled,[13] normal homogeneous radical recombination and disproportionation reactions involving methyl and methoxy radicals ought to be of minor importance as compared with abstraction reactions from methyl acetate. In the liquid phase radiolysis studies, however, a fairly high percentage of the radicals may be expected to recombine or disproportionate throughout a region in or near the liquid "cage" in which the radicals are originally formed. When scavengers are present, essentially all radical processes occurring outside the immediate vicinity of the γ-ray "spur" will be suppressed. Thus, all products (other than scavenger addition products) formed under these conditions can be attributed to hot radical abstraction reactions or recombination and disproportionation reactions occurring in or near the γ-ray "spur."

Table II indicates, for example, that ethane formation is only slightly reduced by iodine or DPPH in the liquid phase. This would indicate that ethane formation occurs close to the site of methyl radical formation.

If there were a random statistical distribution of CH_3 and CD_3 radicals whose recombination in the bulk of the liquid was responsible for ethane formation, a value of about two for $G(CH_3CD_3)/[G(C_2H_6) \times G(C_2D_6)]^{1/2}$ would be expected. One finds significantly higher values for this ratio, as seen in Table II, values which change with the addition of scavenger and with temperature.

These results can be explained by assuming that recombination of radicals originating from the same molecule takes place as well as recombination with radicals originating from adjacent molecules. This would necessarily lead to a higher CH_3CD_3 yield than might be expected from a consideration of the relative radical concentrations.

This interpretation is substantiated by results from the study of mixtures of light and heavy acetone already mentioned.[1] In this study one might expect from the arguments listed above a value for $G(CH_3CD_3)/[G(C_2D_6)]^{1/2}$ which is *lower* than the equilibrium value of approximately two. A value of 0.93 is deduced from the data, indicating that recombination of radicals from the same molecule also occurs in ketones.

Alternative explanations such as intramolecular rearrangements or ion–molecule reactions may be excluded in view of the fact that ethane was a negligible product in the vapor phase radiolysis in the presence of scavengers.

The increase of $G(CH_3CD_3)/[G(C_2H_6)G(C_2D_6)]^{1/2}$ with decreasing temperature can be explained by a reduced mixing of the radicals between neighboring liquid cages within the spur due to the lowering of diffusion rates. The fact that scavengers increase $G(CH_3CD_3)/[G(C_2H_6)G(C_2D_6)]^{1/2}$ indicates that radicals diffusing from one liquid cage to another may be trapped by the scavenger.

It may be pointed out that if the CH_3 and CD_3 diffuse at approximately the same rate, the ratio $(C_2H_6)^{1/2}/(C_2D_6)^{1/2}$ should be roughly equal to the $CO + CO_2/CO_2$ ratio. The last two columns of Table II show these two ratios of G-values for all the conditions investigated. There is good agreement both in the presence and absence of added scavenger.

b. **Disproportionation between Methyl and Methoxy Radicals.**—Other reactions which might be expected to occur in the track are processes such as 12–15. The ratios of the rate constants k_{12}/k_{13} and k_{14}/k_{15} recently have been found to be equal to 1.4 and 1.8, respectively.[4]

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(12) A liquid phase photolysis experiment at 27° gave values of close to 15 for these ratios, in good agreement with the vapor phase radiolysis results. P. Ausloos, unpublished results.

(13) P. Ausloos, *Can. J. Chem.*, 36, 400 (1958).

In view of the presence of dimethyl ether among the products, the high CH_3D and CD_4 yields may be explained largely by reactions 12 and 14. The comparatively small variation of the *G*-values of CH_3D and CD_4 with the addition of scavengers and with temperature indicates that these reactions take place close to the original gamma ray "spur." Hot radical effects may be responsible for a fraction of these yields and, in analogy with the CH_3COCH_3–CD_3COCD_3 investigations, it may be expected that the yields of these hot radical abstraction processes are not higher than the yields of CH_4 and CD_3H produced in the presence of scavengers. From this it follows that the CH_3D/CD_4 ratios given in Table II will only give a rough idea of the relative importance of reactions 12 and 14 and that in all likelihood the ratios are too low. The ratio of the yields of $CH_3OCD_3/CD_3OCD_3 = 7$ probably gives a much closer estimate of the relative importance of reactions 12 and 14, as well as 13 and 15. At any rate the results indicate clearly that reactions 12 and 13 occur with a probability which is about twice as high as may be expected from the relative CH_3/CD_3 concentrations as calculated from the $G(CO) + G(CO_2)/G(CO_2)$ ratios. In agreement with the ethane results it may be concluded that disproportionation and recombination occurs to a large extent between radicals originating from the same molecule, *i.e.*, within the liquid cage.

The ratio CH_3D/CD_4 follows the same trend with temperature and added scavengers as the previously discussed ethane relationship. The hot radical contribution may however affect this trend to some extent. At $-195°$ the CH_3D/CD_4 ratio is over twice the room temperature value indicating that, in the solid state, reactions between radicals originating from the same molecule will occur more readily than those originating from different molecules. Verification of this can be seen from the fact that the CD_3H yield is, percentage wise, the least reduced of the methane yields when going from the liquid phase to the solid phase.

Total Radical Yields.—Recently Bouby and Gilson[14] reported a value of 6.5 for the radical yield (G_R) in the γ-ray radiolysis of methyl acetate. This value was determined by colorimetric measurements of the disappearance of DPPH, assuming the DPPH traps all radicals. From the results given in this paper, it can be concluded that this value is, in all probability, too low and that it only represents those radicals which escaped from the spur or cage. It can be seen that from the results given in Table II and including the dimethyl ether yield that the total number of radicals originally formed within the liquid cage must be higher than the value reported above.

A minimum value of the number of radicals produced in the CH_3COOCH_3 radiolysis can be obtained from $2[G(CO) + G(CO_2) + G(H_2)] = 6.7$. It must be further pointed out that the actual value will be higher in view of the fact that: (a) the CH_3CO and CH_3CO_2 radicals have not been accounted for and (b) some of the H atoms may eventually have disappeared by addition to the ester. The fact that the hydrogen yields are only slightly affected by scavengers seems to indicate that most of the thermal hydrogen atoms which escape the track have not been accounted for[15] (or they are all predominantly hot in the liquid phase).

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(14) L. Bouby and N. Gilson, "International Congress of Radiation Research," University of Vermont, Burlington, Vermont, August 10–16, 1958.

(15) It has been reported recently that acetone is an efficient trap for H atoms produced in the radiolysis of 2-propanol; J. Strong and J. Burr, THIS JOURNAL, **81**, 775 (1959).

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