at an energy input rate of 1.6×10^{15} e.v. per g. sec. ($\approx 10^5$ rep. per hr.), [M] = 1 atm., and at 25°. For this estimation

$$k_{12} = 3.4 \times 10^{12} \exp(-6800/RT) \text{ cm.}^3 \text{ mole}^{-1} \text{ sec.}^{-1}$$

was used.[18] Concentrations of other radicals are probably of the same order of magnitude or less. Hence, at the experimental conditions employed in our work, the rate of reaction 12 is approximately 10^4 and 10^7 times faster than the rate of reactions 13 and 14, respectively, even if a steric factor of 1 is assumed for the latter processes.[19] Thus, the aforementioned approximation that all radicals undergo hydrogen abstraction reactions seems reasonable. Using this approximation and the nitric oxide inhibition data, G-values for various free radicals are calculated

M \ Radical	H	CH₃	C₂H₅
CH₄	2.8	*a*	. .
C₂H₆	2.8	0.3	*a*
C₃H₈	3.4	0.5	0.6

a Not able to estimate with the present method.

Due to the probable uncertainty arising from the contribution of radical recombination in chain lengthening processes, G-values for the radicals having a larger carbon number than the reactant are not estimated.

Meisels, Hamill and Williams[6] reported an ion pair yield of 1 for H in the radiolysis of argon + methane system, using both an isotopic exchange and a radical scavenger method (propylene).

(18) M. R. Berlie and D. J. LeRoy, *Disc. Faraday Soc.*, **14**, 50 (1953).

(19) Collision theory is used for this estimation.

Since energy required[20] to produce an ion pair in methane by α-particle irradiation is 31 e.v., their estimation corresponds to a $G(H) = 2.8$, in agreement with our result of 3.2.

Iodine probably is better than nitric oxide to identify individual free radicals[21]; but its use to estimate radical G-values is not advisable. Iodine does not inhibit the formation of hydrogen in methane radiolysis.[6] Since 41% of the hydrogen formed arises from radical processes, the above observation suggests that iodine cannot inhibit the type of reaction 7. Hence, the iodine method gives ambiguous energy yields for hydrogen atom and for those radicals produced by the interaction of hydrogen atom with the reactants. Hydrogen iodide accelerates the formation of hydrogen in methane radiolysis,[6] and its use involves similar uncertainties. Ethylene and propylene produce hydrocarbons such as methane, ethane and propane by reacting with hydrogen atoms and hydrocarbon free radicals produced by γ-irradiation.[22] For this reason, their use is also not advisable. Therefore, it appears that nitric oxide is one of the few radical scavengers which is satisfactory to estimate the energy yield of radicals, as well as the contributions of free radical reactions to the over-all radiolysis of gaseous hydrocarbons.

(20) W. P. Jesse and J. Sadanokis, *Phys. Rev.*, **97**, 1668 (1955).

(21) L. H. Gevantman and R. R. Williams, Jr., *J. Phys. Chem.*, **56** 569 (1952).

(22) This result will be published later.

PONCA CITY, OKLAHOMA

The Photolysis of Acetone in Some Fluorinated Solvents[1]

BY D. B. PETERSON AND GILBERT J. MAINS

Acetone, acetone-d_6 and a 1:1 mixture of acetone and acetone-d_6 have been photolyzed in liquid perfluorodimethylcyclobutane and in a liquid fluorinated cyclic ether. The distribution of isotopically substituted methanes and ethanes in the gaseous products is in agreement with a free radical mechanism. The variation of the ratio of the rate of methane production to the square root of the ethane production rate with acetone concentration is linear as suggested by the free radical mechanism. The ratio of the specific rate constant for hydrogen abstraction to the square root of the specific rate constant for ethane production is in agreement with vapor phase studies when diffusion is taken into account. Because the difference in the quantum yields of gaseous products in the fluorinated solvents cannot be attributed to "caging" effects, a difference in the yield of methyl radicals from the primary process due to quenching of the excited electronic state of acetone by these solvents is suggested as a possible explanation.

Introduction

Photochemical studies have been made of pure liquid acetone[2-5] and of solutions of acetone in various solvents.[2-6] In the early studies[2,3,6]

(1) Based on a thesis submitted by D. B. Peterson in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Carnegie Institute of Technology.

(2) E. J. Bowen and E. L. A. De la Praudiere, *J. Chem. Soc.*, 1503 (1934).

(3) E. J. Bowen and A. T. Horton, *ibid.*, 1685 (1936).

(4) P. E. Frankenburgh and W. A. Noyes, Jr., THIS JOURNAL, **75**, 2847 (1953).

(5) R. Pieck and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1304 (1955).

gaseous products were not detected. Subsequent investigations[4,5] revealed that carbon monoxide, methane and ethane are produced, but at quantum yields considerably lower than are observed in the vapor phase photolysis.

The interpretation of the results of the photolysis of pure liquid acetone is complicated by the rather poor analytical precision inherent to systems with low quantum efficiencies and by the inhomogeneous nature of the light absorption. Previous photo-

(6) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1521 (1938).

chemical studies of acetone solutions usually have involved hydrocarbon solvents. Such solvents are not truly inert because they are capable of undergoing addition reactions with excited acetone molecules.[5] Some photochemical studies of acetone have been made in carbon tetrachloride[2-4] but this solvent cannot be considered inert. Studies conducted by the authors indicate that acetone photosensitizes the decomposition of carbon tetrachloride giving rise to considerable yields of hydrogen chloride. The photosensitized decomposition of carbon tetrachloride by acetone also has been postulated to occur in the vapor phase.[7]

The purpose of the present study was to investigate the photolysis of dilute solutions of acetone in some perfluorinated solvents. Such solvents should be inert toward both acetone and the radicals produced by photochemical dissociation. Moreover, at low acetone concentrations the distribution of excited acetone molecules and subsequent dissociation fragments should be essentially uniform throughout the reaction vessel.

Experimental

The solvents were perfluorodimethylcyclobutane, C_6F_{12}, and Fluorochemical 0–75, a fluorinated cyclic ether with the empirical formula $C_8F_{16}O$, obtained from the Minnesota Mining and Manufacturing Company. The perfluorodimethylcyclobutane was used without further purification. An ultraviolet spectrum indicated that this solvent was essentially transparent from the visible out to about 2200 Å. The Fluorochemical 0–75 was purified byr efluxing it with concentrated sulfuric acid, washing with H_2O, passing it through a silica gel column and finally distilling. The fraction boiling at 101° was collected for use. An ultraviolet spectrum indicated that Fluorochemical 0–75 so purified was optically transparent out to 2200 Å.

Fisher Certified acetone (b.p. 56.1–56.4°) was purified by a procedure based on the method of Shipsey and Werner.[8] The purified acetone was distilled under vacuum into ampoules with glass break seals and stored in the dark until needed. Acetone-d_6, obtained from the New England Nuclear Corporation, was used without further purification. A mass spectrum of the acetone-d_6 sample indicated an isotopic purity of about 97%. Baker resublimed iodine was purified by further resublimation.

Two light sources were employed. For studies at wave lengths greater than 2800 Å. a BH-6 high pressure mercury lamp was employed in conjunction with Corning 9863 and 9700 glass filters. The light beam was collimated with a three inch diameter quartz lens with a six inch focal length. The reaction vessel used with this source was a quartz cylinder with a three inch plane circular quartz windows and had a volume of 165 cc. Prior to making a run the vessel was evacuated and flamed out; the solvent was then distilled into the vessel and degassed by distilling it back and forth between the reaction vessel and a solvent trap. The condensing vessel was cooled in a solid CO_2–acetone bath and the system was evacuated continuously during the degassing operation. Acetone then was introduced into the reaction vessel by rupturing the break seal on an ampoule previously attached to the system, and, after a final check for non-condensable gases, the reaction vessel was isolated from the line and allowed to reach room temperature. The solution was stirred magnetically. The neck of the reaction vessel was shielded with black tape to prevent possible photolysis of acetone vapor. After irradiation, the gaseous products were removed by distilling the solution from the reaction vessel into the solvent trap and, after each distillation, the gaseous products were pumped out and collected with a Toepler pump. A small line trap between the Toepler pump and the solvent trap was cooled in an isopentane

slush bath to condense out acetone vapor. The gaseous products were analyzed by vapor chromatography. The degassed solution was tested chemically for biacetyl by a procedure based upon the method of Prill and Hammer.[9]

The principal light source employed in this work was a Hanovia UA-15 lamp. The meter-long, medium pressure, lamp was coiled into a helix three inches in diameter and five inches long. The reaction cell, which had a volume of 58 cc. and which consisted of an inner quartz tube with a 27 mm. bore surrounded by a 54 mm. bore quartz jacket through which filter solution could be circulated, was reproducibly located within the coils of the lamp on the axis of the helix. Since the filter solution was circulated from a reservoir immersed in a constant temperature bath, it served to control the temperature of the photolyte as well as to filter the incident radiation. The methods of degassing samples prior to photolysis and of collecting and analyzing the gaseous products were essentially the same as those described for the studies with the BH-6 lamp.

Potassium ferrioxalate was employed as an actinometer.[10] Using potassium ferrioxalate solutions the intensity of the BH-6 lamp, filtered by Corning 9863 and 9700 glass filters, was found to be 4.8×10^{15} quanta cc.$^{-1}$ in the region 2800–3300[10] Å. The intensity of the coiled UA-15 lamp, filtered by one centimeter of 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene iodide,[11] was found to be 1.5×10^{16} quanta cc.$^{-1}$ sec.$^{-1}$. Using this filter solution the acetone solutions absorbed essentially monochromatic 2537 Å. radiation. The energy absorbed by the acetone solutions was estimated by a Beer–Lambert law calculation and because of the assumptions involved in such calculations, the absolute quantum yields probably are uncertain by a factor of two. The relative quantum yields are subject to somewhat less uncertainty ($\pm 5\%$).

Results

Acetone Photolysis in Perfluorodimethylcyclobutane.—To establish that the solvent was completely perfluorinated, a dilute solution of acetone-d_6 in perfluorodimethylcyclobutane was photolyzed and the isotopic methanes were collected and subjected to mass spectrometric analysis. The absence of CD_3H in excess of that expected from acetone-d_5 impurity indicated that the solvent was essentially free of reactive hydrogen.

A series of five runs was made in which the effect of acetone concentration on the yield and composition of gaseous products was determined. These experiments were made using the UA-15 lamp filtered to yield essentially monochromatic 2537 Å. radiation in the region 2000–3030 Å. Only the gaseous products were collected and analyzed. Chemical tests for biacetyl were negative, and these results were substantiated by the failure to observe its green fluorescence. (As prepared solutions of biacetyl in the solvent exhibited fluorescence at low concentrations and as such solutions were subjected to the same evacuation techniques as used for acetone, it may be concluded that biacetyl was absent in the acetone experiments.) The results of these experiments are summarized in Table I.

The results of the photolysis of a 1:1 mixture of acetone and acetone-d_6 in perfluorodimethylcyclobutane are included in Table I. The isotopic distribution of methanes and ethanes was determined by analysis of the mass spectrum of the gaseous products. The isotopic distribution of methanes was found to be: CH_4, 50.9%; CH_3D,

(7) R. J. Cvetanovic, F. A. Raal and E. W. R. Steacie, *Can. J. Chem.*, **31**, 171 (1953).

(8) K. Shipsey and E. A. Werner, *J. Chem. Soc.*, 1255 (1913).

(9) E. A. Prill and B. W. Hammer, *Iowa State College J. Sci.*, **12**, 385 (1938).

(10) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. (London)*, **A235**, 518 (1956).

(11) M. Kasha, *J. Opt. Soc. Am.*, **38**, 429 (1948).

TABLE I

YIELDS OF GASEOUS PRODUCTS AT VARIOUS
ACETONE CONCENTRATIONS[a]

Acetone, moles/l.	Irradn., min.	Total gas, cc. STP.	% CH₄	% CO	% C₂H₆	(Rate methane)[b] (Rate ethane)^{1/2}
0.023	180	0.68	20.8	28.1	51.1	1.57×10^6
.035	130	.47	32.2	25.3	42.5	2.60×10^6
.058[c]	120	.90	43.6	21.3	35.1	5.09×10^6
.083	105	.82	50.2	17.4	32.4	6.84×10^6
.112	90	1.19	57.2	19.0	23.8	1.18×10^7
.162	90	1.00	54.2	16.5	29.3	9.21×10^6

[a] All experiments in perfluorodimethylcyclobutane at 24.0° and 2537 Å. [b] Both rates have the units molecules/sec./cc. of solution. [c] This is total acetone concentration of a 1:1 mixture of acetone and acetone-d_6 in perfluorodimethylcyclobutane.

6.8%; CH_2D_2, 5.5%; CD_3H, 31.7%; CD_4, 5.5%; and the analysis of the ethanes was: C_2H_6, 40.4%; C_2H_5D, 0%; $C_2H_4D_2$, 16.6%; $C_2H_3D_3$, 30.3%; C_2HD_5, 2.0%; C_2D_6, 10.7%. The mass spectra were interpreted by reference to the methane patterns of Dibeler and Mohler[12] as corrected by Gordon and McNesby[16] and the ethane patterns of Schissler, Thompson and Turkevich.[13] Such interpretations are subject to considerable uncertainty because of variations in the patterns obtained with different spectrometers. The analysis of CD_4 and CD_3H should be quite accurate since their parent peaks at m/e ratios of 20 and 19 are unique. The analyses for the less deuterated methanes are complicated by spectral overlap and will be uncertain to the extent that the reference patterns are uncertain. Similarly, the analysis for ethane-d_6 should be quite accurate and the analysis for ethane-d_3 somewhat less accurate. The analysis of less deuterated ethanes is semi-quantitative because of the uncertainties in the spectral patterns

Acetone Photolysis in Fluorochemical 0-75.— The photolysis of a 0.012 M solution of acetone-d_6 in Fluorochemical 0-75 for 30 minutes yielded 0.81 cc. of gaseous products measured at STP. The gas was 80.2% methane and 19.8% carbon monoxide. An isotopic analysis of the methane by mass spectrometry yielded these data: CD_4, 0.2%; CD_3H, 85.4%; CH_2D_2 14.4%; CH_3D, 0%; CH_4, 0%. These results indicate that Fluorochemical 0-75 contains sufficient residual hydrogen to inhibit the formation of CD_4 and any ethane. Szwarc[14] has obtained anomalous results in the pyrolysis of acetyl peroxide in Fluorochemical 0-75 which he attributes to reactive hydrogen in the solvent.

The photolyses of acetone in Fluorochemical 0-75 were carried out at 2537 Å. using the UA-15 lamp and at wave lengths greater than 2800 Å. using the high pressure BH-6 lamp. The results of these experiments are summarized in Table II.

No significant wave length effect was observed. In both regions of the spectra the important products were carbon monoxide and methane. Only traces of ethane and biacetyl were observed. The green fluorescence of biacetyl was observed

(12) V. H. Dibeler and F. Mohler, J. Research Natl. Bur. Standards, 45, 441 (1950).

(13) D. O. Schissler, S. O. Thompson and J. Turkevich, Disc. Faraday Soc. 10, 46 (1951).

(14) M. Szwarc, THIS JOURNAL, 76, 5985 (1954).

TABLE II

YIELDS OF PRODUCTS IN FLUOROCHEMICAL 0-75 SOLVENT[a]

Acetone moles/l.	Wave length range, Å.	Irradn., min.	Total gas, cc. STP.	% CH₄	% CO	% C₂H₆	($n_B \times 10^7$)[b]
0.0075	2800–3300	30	0.43	77.0	23.0	...	..
.0135	2800–3300	30	1.10	78.0	22.0	...	9.34
.0440	2800–3300	30	1.42	81.6	18.4	...	6.90
.0988	2800–3300	30	2.12	83.8	16.2	...	3.20
.017	2537	1800	1.21	81.0	19.0	Trace	..
.013	2537	325	0.26	83.8	16.2	Trace	..
.092	2537	84	.17	82.7	15.8	1.5	..
.019	2537	901	.81	79.3	18.9	1.8	..
.016	2537	900	.56	84.5	14.4	1.1	..

[a] All experiments were carried out at 25°. [b] Moles of biacetyl times 10^7. Determination could not be made in all experiments.

after a few minutes irradiation in all the experiments reported in Table II. The appearance of the fluorescence served as an additional check on the extent to which the solvent was free from oxygen and, presumably, nitrogen.

Discussion

The quantum yields of gaseous products obtained by the photolysis of dilute solutions of acetone in perfluorodimethylcyclobutane and Fluorochemical 0-75 are of the same order of magnitude as those observed in the photolysis of liquid acetone.[15] These results are summarized in Table III.

The quantum yields of carbon monoxide and ethane are reduced drastically in passing from the vapor phase to the liquid phase. This is in qualitative accord with the predictions of the Franck–Rabinowitch "solvent cage effect" and, perhaps equally important, the predictions of the effect of deactivation of excited molecules by the solvent. It is noteworthy that a material balance has not been achieved in earlier investigations nor in this study. Attempts to identify liquid products by infrared spectroscopy and vapor chromatography have not been successful. While a complete elucidation of the acetone photolysis reactions in the liquid phase must await an analysis of liquid phase products, some conclusions can be reached based upon the gaseous products alone. Because of the difference in quantity and distribution of gaseous products arising from the photolysis of acetone in perfluorodimethylcyclobutane and Fluorochemical 0-75, these systems will be discussed separately.

The photolysis of acetone in perfluorodimethylcyclobutane would seem to proceed *via* an essentially free radical path. Within experimental errors, the isotopic distributions of methanes and ethanes in the gaseous products of the photolysis of 1:1 acetone-h_6 and acetone-d_6 solutions are in accord with a free radical mechanism. However, the ratio of CD_3H to CD_4 suggests that part of the methane may arise from some reaction other than methyl radical abstraction of hydrogen from an acetone molecule. The experimentally determined value of this ratio is about 5.80 (or 6.75 if CD_2H_2 is considered to arise by H atom abstraction) while the predicted value from the vapor phase data of McNesby and Gordon[16]

(15) D. S. Herr and W. A. Noyes, Jr., ibid., 62, 2052 (1940); L. Dorfman and W. A. Noyes, Jr., J. Chem. Phys., 16, 557 (1958).

(16) J. R. McNesby and A. S. Gordon, THIS JOURNAL, 76, 1416 (1954).

TABLE III
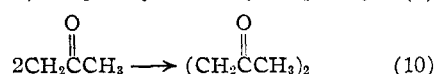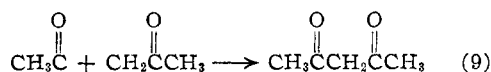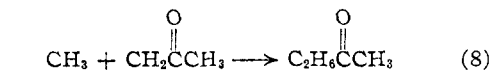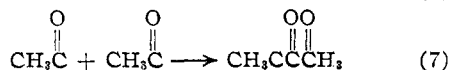QUANTUM YIELDS IN ACETONE PHOTOLYSIS[a]

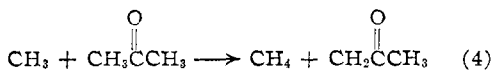| System	Ref.	Wave length, Å.	Φ_{CH_4}	Φ_{CO}	$\Phi_{C_2H_6}$
Acetone vapor[b]	15	2537	ca. 2×10^{-3}	0.25	0.35
Acetone liquid	5	2800–3300	2×10^{-3}	10^{-4}	10^{-4}
Acetone liquid	5	2537	2×10^{-3}	10^{-4}	10^{-4}
0.023 M acetone in perfluorodimethylcyclobutane		2537	10^{-3}	10^{-3}	2×10^{-3}
0.01 M acetone in 0–75[c]		2537	8×10^{-2}	2×10^{-2}	10^{-4}
0.01 M acetone in 0–75[c]		2800–3300	8×10^{-2}	2×10^{-2}	10^{-4}

[a] All liquid phase data at 25°. [b] Temperature is 25.5°. Data extrapolated to 0.023 M concentration of acetone vapor.
[c] The quantum yields are essentially independent of concentration in the region 10^{-2} M acetone in Fluorochemical 0–75.

is about 13.2. If CD$_4$ can arise from some process other than deuterium abstraction from acetone-d_6 in the liquid phase photolysis, the decreased ratio is understandable. It would be tempting to attribute the difference in these ratios of CD$_3$H to CD$_4$ in the liquid and vapor phase to the inapplicability of vapor phase rate constants to liquid phase studies. However, the solvent would be expected to exert the same effect on these two hydrogen abstraction reactions and, therefore, this explanation is rejected. It is interesting to note that Pieck and Steacie[5] found that the distribution of isotopic methanes arising from the photolysis of a 1:1 mixture of acetone-h_6 and acetone-d_6 in the liquid phase below 40° could not be accounted for exclusively by hydrogen abstraction reactions. These authors suggest the radical disproportionation reactions of methyl and acetyl radicals into methane and ketene (reaction 3 vide infra). Assuming a radical disproportionation explanation for the low CD$_3$H to CD$_4$ ratio in the liquid phase, between 6 and 10% of the methane must arise by disproportionation reactions at 25° and acetone-d_6 concentration of 0.029 M. This range of percentage of methane by disproportionation is in agreement with the results of Pieck and Steacie, who estimate 4% of the methane at 55° and 33% of the methane at −24° to arise from disproportionation. This agreement may be fortuitous since the disproportionation reaction in liquid acetone might be expected to be different from those in perfluorodimethylcyclobutane solutions if an appreciable fraction of these reactions were between geminate radicals. If the agreement is not fortuitous, it may be taken as evidence that the effects of a solvent cage are negligible in this system.

By analogy with vapor phase studies, this mechanism may be postulated to explain the photolysis of acetone in solution

$$CH_3\overset{O}{\overset{\|}{C}}CH_3 + h\nu \longrightarrow CH_3 + \overset{O}{\overset{\|}{C}}CH_3 \qquad (1)$$

$$CH_3 + \overset{O}{\overset{\|}{C}}CH_3 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_3 \qquad (2)$$

$$CH_3 + \overset{O}{\overset{\|}{C}}CH_3 \longrightarrow CH_4 + CH_2CO \qquad (3)$$

$$CH_3 + CH_3\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow CH_4 + CH_2\overset{O}{\overset{\|}{C}}CH_3 \qquad (4)$$

$$CH_3 + CH_3 \longrightarrow C_2H_6 \qquad (5)$$

$$CH_3\overset{O}{\overset{\|}{C}} \longrightarrow CH_3 + CO \qquad (6)$$

$$CH_3\overset{O}{\overset{\|}{C}} + CH_3\overset{O}{\overset{\|}{C}} \longrightarrow CH_3\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}CH_3 \qquad (7)$$

$$CH_3 + CH_2\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow C_2H_5\overset{O}{\overset{\|}{C}}CH_3 \qquad (8)$$

$$CH_3\overset{O}{\overset{\|}{C}} + CH_2\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3 \qquad (9)$$

$$2CH_2\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow (CH_2\overset{O}{\overset{\|}{C}}CH_3)_2 \qquad (10)$$
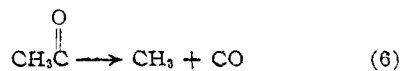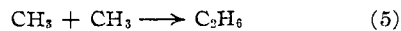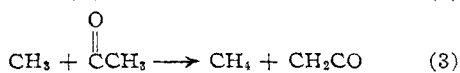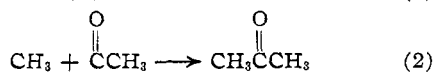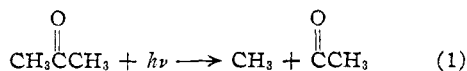
Experimental substantiation of some of the aspects of this mechanism can be obtained from the data of Table I. According to the mechanism the rate of production of methane and the rate of the production of ethane are given by the equations

$$R_{CH_4} = k_3(CH_3)(\overset{O}{\overset{\|}{C}}CH_3) + k_4(CH_3)(CH_3\overset{O}{\overset{\|}{C}}CH_3) \qquad (I)$$

$$R_{C_2H_6} = k_5(CH_3)^2 \qquad (II)$$

Assuming that the rate of radical disproportionation, reaction 3, is small compared to the rate of reaction 4, a graph of $R_{CH_4}/R_{C_2H_6}^{1/2}$ versus acetone concentration should be linear. (As noted previously, reaction 3 may account for 6–10% M at total methane production when the concentration of acetone-h_6 is 0.029 M at 25°. This percentage would be expected to decrease with increasing acetone concentration. The graph of $R_{CH_4}/R_{C_2H_6}^{1/2}$ versus acetone concentration would be expected to deviate from linearity markedly only at acetone concentrations below 0.005 M. We have not investigated the low concentration range.) The data of Table I are plotted in Fig. 1. While the data tend to scatter at higher acetone concentrations a reasonably straight line can be drawn through the points. The slope of this line gives the ratio $k_4/k_5^{1/2}$ directly as $1.2 \pm 0.1 \times 10^{-13}$ cc.$^{1/2}$ molecule$^{-1/2}$ sec.$^{-1/2}$. This result is in excellent agreement with those obtained by Pieck and Steacie.[5] The comparable ratio of rate constants for the vapor phase[17] is 6.8×10^{-15} cc.$^{1/2}$ molecule$^{-1/2}$ sec.$^{-1/2}$. Assuming that reaction 4 proceeds at the same rate in the liquid as in the vapor[18] the difference between these ratios of rate constants must then be attributed to a difference in the specific rate constant for reaction 5 in the liquid and vapor. Assuming further that the difference in the assumed specific rate constants for reaction 5 in the liquid and in the vapor arises from a difference in activation energy rather than from a difference in frequency factors, a difference in activation energy

(17) A. F. Trotman-Dickenson and E. W. R. Steacie, J. Chem. Phys., 18, 1097 (1950).

(18) Some justification for this assumption can be found in the quantum yields of methane in the vapor and in the solution given in Table III. See also Chapter VII, E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution," Oxford Press, London, 1947.
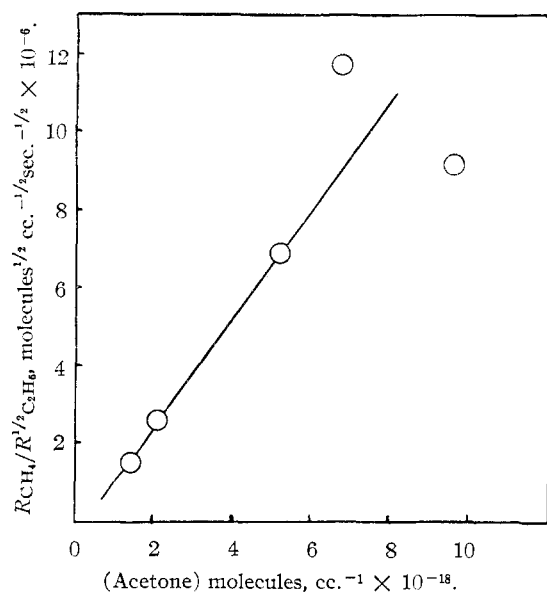
Fig. 1.—The photolysis of acetone in some fluorinated solvents.

is obtained: $E_5^{liq} - E_5^{vap} = 3.4 \pm 0.3$ kcal. mole. This difference in activation energy is of the same order of magnitude as the activation energy for the temperature dependence of viscosity of perfluorocarbons.[19] Since the activation energy of viscosity and diffusion are of the same order of magnitude these calculations seem reasonable. Additional experiments to determine the activation energies of reactions 4 and 5 are being undertaken and will be reported later.[20]

The essentially uniform reduction of the quantum yields of carbon monoxide and ethane in passing from the vapor phase to the perfluorodimethylcyclo-butane solution may be attributed to a reduction in the concentrations of methyl and acetyl radicals due either to "cage effects" or to a reduction in the quantum yield of the primary step by solvent quenching. Solvent quenching would be expected to predominate in pure liquid acetone, and it is in this case that the quantum yields of carbon monoxide and ethane are the lowest. If "cage effects" were exclusively responsible for the reduction on the quantum yields of ethane and carbon monoxide, it would be expected that the liquid phase quantum yields would increase with decreasing molecular weight of the solvent. The opposite effect is observed. While it is difficult to conceive of saturated fluorocarbons quenching the photo-excited state of acetone, some such effect would seem to be operating. The quenching act need not leave the excited acetone molecule in the ground electronic state but only in a less-energetic state which does not result in gaseous products.

It is interesting to note that the spontaneous decomposition of an excited acetyl radical, viz.

$$(CH_3)\overset{\overset{\text{O}}{\|}}{C}{}^* \longrightarrow CH_3 + CO \qquad (11)$$
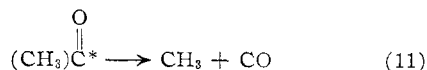
(19) C. Slesser and S. R. Schram, "Preparation, Properties, and Technology of Fluorine and Organic Fluoro Compounds," McGraw-Hill Book Co., New York, N. Y., 1951.

(20) R. Doepker and Gilbert J. Mains, to be published.

cannot be as important in the liquid phase as in the vapor. It is estimated that 22% of the primary decomposition results in the excited acetyl radicals in the vapor phase.[15] Since the quantum yield of carbon monoxide is reduced by a factor much smaller than 0.22, the availability of the solvent molecules as quenching partners for either excited acetone molecules and/or excited acetyl radicals probably accounts for the greatly reduced quantum yield of carbon monoxide.

Among the gaseous products from the photolysis of acetone in perfluorodimethylcyclobutane solvent, between four and five methyl groups appear for each carbonyl group. Since biacetyl is not detected among the products, the balance of the carbonyl groups must form liquid products by reactions such as (3) and (9). As previously mentioned, present analytical techniques are not successful for the analysis of such products.

The photolysis of acetone in fluorochemical 0-75 results in methane and carbon monoxide as the principal gaseous products. Traces of ethane are detected in very long runs. Biacetyl was detected in rather small quantities; approximately one mole of biacetyl was formed for every ten moles of carbon monoxide.

The observation of methane as the principal product is not surprising in view of the residual hydrogen content of the solvent. Since the photolysis of acetone-d_6 resulted almost exclusively in CD_3H, the residual hydrogen must be relatively reactive. Szwarc has concluded similarly that the residual hydrogen in Fluorochemical 0-75 is reactive.[14] It is significant that the quantum yield of methane in Fluorochemical 0-75 is about sixteen times greater than the quantum yield of all methyl groups observed in the gaseous products in perfluorodimethylcyclobutane. It would seem that this effect must be due to a difference in the efficiency of the primary process or to a difference in the extent to which geminate recombination occurs in the two solvents. The physical properties of the two solvents suggest that Fluorochemical 0-75 should "cage" radicals more efficiently than the lower molecular weight solvent, perfluorodimethyl-cyclobutane. This prediction is just opposite to the observed effect. An alternate explanation is that hydrogen abstraction from the "caging" molecules competes efficiently with geminate recombination. Since perfluorodimethylcyclobutane contains no reactive hydrogen, geminate recombination would occur without such competition.

The photolysis of solutions of acetone in Fluoro-chemical 0-75 in the presence of traces of iodine do not substantiate such an argument. At an iodine concentration of 2×10^{-4} M, photolysis for periods sufficiently long to have produced several cubic centimeters of gaseous products in the absence of iodine yielded only traces of carbon monoxide and no methane. At this concentration only one molecule in 42,000 is an iodine molecule and free radical scavenging would not be expected to compete with geminate recombination nor rapid hydrogen abstraction from a "caging" molecule. Nor can the total absence of methane be conveniently explained by the presence of the iodine–acetone complex since the ratio of acetone molecules to

iodine molecules was over two hundred in these experiments.

It would seem necessary to conclude that the difference in the quantum yields of gaseous products in Fluorochemical 0–75 and perfluorodimethyl-cyclobutane solvents is due mainly to a difference in the quenching efficiencies of the two solvents. Studies of the photolysis of acetone in mixtures of the two solvents have been made, but since the data do not fit any simple quenching mechanism, the results are inconclusive and will not be reported in further detail. The photolysis of acetone in completely fluorinated Fluorochemical 0–75 should be useful in establishing whether or not quenching is responsible for the difference in the quantum yields in these fluorinated solvents. We are presently engaged in carrying out these experiments.[20]

Tracer Experiments on the Oxidation of Oxalic Acid

BY RONALD M. MILBURN AND HENRY TAUBE

The exchange of oxygen between oxalic acid and the solvent water at 25° follows the rate law, Rate (g. atom l.$^{-1}$ min.$^{-1}$) = 7.4 × 10^{-3} ($H_2C_2O_4$) + 4.4 × 10^{-2} ($H_2C_2O_4$)(H^+). When oxalic acid is oxidized by Ce(IV) or hypochlorous acid, none of the oxygen in the CO_2 originates in the solvent or oxidizing agent. When H_2O_2 is the oxidizing agent, approximately $^2/_3$ atoms of oxygen for each CO_2 are derived from the oxidizing agent. No evidence was found for exchange between CO_2 and $C_2O_4^-$ induced by the oxidation of $C_2O_4^-$ by Mn(III).

Many kinetic measurements have been made on reactions in which oxalic acid or its ions in water reacts with oxidizing agents, but important problems of mechanism remain unsolved in many of the systems. Some of these can be resolved by oxygen-tracer experiments, which in principle can answer questions such as these: Is oxygen from the solvent incorporated into the CO_2 which is evolved? Is oxygen transferred to oxalate from the oxidizing agent on reaction? We are reporting the results of such oxygen-tracer experiments with selected oxidizing agents as the principal theme of this paper. Results on the related study, the exchange of oxygen between oxalate and water, are also reported, as well as those obtained in a search for evidence of a free radical intermediate in the oxidation of oxalate by Mn(III).

Part A. Oxygen Exchange between Oxalate and Water

Experimental

Solutions of oxalic acid of normal isotopic composition in normal water were prepared at three acidities. Each solution was mixed with O^{18}-enriched water at 25°, the temperature at which the exchange reaction took place. Samples were withdrawn at intervals, rapidly cooled to 0° and oxidized with acidic Ce(IV). The CO_2 produced was swept from the solution with a stream of N_2, dried and condensed for isotopic analysis. This method of isotopic assay anticipates the results which properly belong in the next section and are there reported. These results prove that Ce(IV) liberates CO_2 from oxalic acid in water without change in the isotopic composition of the oxygen. The small exchange that does take place can be attributed to direct exchange between CO_2 and solvent during the time the CO_2 stays in solution.

Results

The data, consisting of the isotopic composition of the CO_2 as a function of time, were treated in the usual way, plotting $2.3 \log (N_\infty - N_0)/(N_\infty - N_t)$ against t to determine the exchange specific rate k for an experiment (N's represent the atom fraction O^{18} at the times defined by the subscripts). Then for each experiment a value of R, the rate of exchange in g. atom of oxygen per liter per minute is calculated using the equation[1]

$$R = k \frac{4(H_2O)[\text{oxalic}]}{(H_2O) + 4[\text{oxalic}]}$$

The values R for the three sets of concentration conditions are summarized in Table I. Throughout, total stoichiometric concentrations are represented by formulas enclosed in brackets, actual concentrations allowing for the distribution among various equilibrium forms, by the formulas in parentheses.

TABLE I

THE RATE OF EXCHANGE OF OXYGEN BETWEEN OXALATE AND WATER

(Concentrations recorded are stoichiometric)

[$H_2C_2O_4$]	[$Na_2C_2O_4$]	[$HClO_4$]	Rate, g. atom l.$^{-1}$ min.$^{-1}$
0.100	...	1.00	4.6 × 10^{-3}
.100	...	..	4.2 × 10^{-4}
.050	0.050	..	1.98 × 10^{-5}

To interpret these rate data, the equilibrium compositions of the solutions must be calculated, taking into account the two equilibria

$$H_2C_2O_4 = H^+ + HC_2O_4^- \qquad K_1$$
$$HC_2O_4^- = H^+ + C_2O_4^- \qquad K_2$$
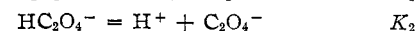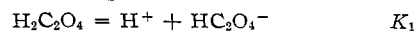
At the two higher acidities, only the first equilibrium is important. The values of K_1 for all of the conditions were calculated from the equation

$$\log K_1 = \log K_1^0 - \log \frac{\gamma_{H^+}\gamma_{HC_2O_4^-}}{\gamma_{H_2C_2O_4}}$$

(1) A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 11.