[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS, CALIFORNIA]

The Photochemical Decomposition of Acetone in Aqueous Solutions of Allyl Alcohol at 2537 Å.[1]

BY DAVID H. VOLMAN AND LYNWOOD W. SWANSON

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The photochemical decomposition of acetone at 2537 Å. has been studied in aqueous solutions with and without added allyl alcohol in the temperature range from 2 to 73°. The quantum yields of the gaseous products, methane, ethane and carbon monoxide, were determined. The results are consistent with a free radical mechanism in which methane is formed both by abstraction of hydrogen atoms from acetone by methyl radicals and by disproportionation between methyl and acetyl radicals. The temperature dependence of diffusion of methyl radicals was considered and shown to be important in the calculation of activation energy differences for abstraction and combination.

Introduction

Recent studies in this Laboratory have been directed at obtaining information about primary processes for photochemical reactions in aqueous solutions by the use of allyl alcohol as scavenger.[2] In our first work, on hydrogen peroxide, the photochemistry in water already had been extensively studied. The object of the present work was to extend the scavenger studies to an aqueous system which had received little attention.

The photochemistry of acetone in the gas phase has been studied extensively.[3] Considerable investigation of the photodecomposition in liquid acetone[4] and in non-aqueous solvents also has been made, the recent and comprehensive work being that of Peterson and Mains in fluorinated solvents.[5] In aqueous solutions, however, only preliminary and fragmentary experiments have been carried out. These experiments have established that acetic acid and methane are formed and that the quantum yields are low compared to those found in the gas phase.[6]

Experimental

Apparatus.—The reaction cell was a cylindrical quartz tube, 20 mm. in diameter and 34 cm. long. The cell was contained in a quartz jacket through which thermostated water passed. The irradiation zone was confined to a 24 cm. length of the cell by shields. A quartz stirrer, mounted at each end of the cell by Teflon bearings, was activated by an induction method which eliminated all external connections.[7] The entire assembly was contained within a helical mercury resonance arc housed in Vycor to limit the effective transmitted light to 2537 Å.

Solutions to be irradiated were degassed by several freeze-pump-thaw cycles and then introduced into the previously evacuated reaction cell. After irradiation the contents of the reaction cell were allowed to flow into an evacuated flask held in a Dry Ice bath. Non-condensable products were removed by freeze-thaw-pump cycles and separated according to volatility into three fractions by a train of traps including a Ward still.[8] The gases were transferred to a gas buret by a diffusion pump in series with a Toepler pump. The gases were identified by use of a mass spectrometer. The first fraction, removed at −215°, contained methane and carbon monoxide; the second fraction, removed at −183°, contained only ethane; the last fraction, removed at −160°, contained carbon dioxide and small amounts of propane.

TABLE I

PHOTOLYSIS OF AQUEOUS ACETONE AT 2537 Å.

Acetone $M \times 10^3$	$I \times 10^7$, E/cc./min.	Quantum yields × 10^2					
		CH_4	CO	C_2H_6	C_3H_8	CO_2	CH_3-CO_2H
2°							
53.8	3.38	1.9	0.08	0.38	0.05	0.2	1.1
53.8	8.9	1.4	.05	.40	.02	.2	..
53.8	15.5	1.0	.08	.52	.02	.2	0.4
53.8	21.1	1.5	.1	.84	.03	.1	0.1
26.8°							
5.38	2.77	3.3	0.25	4.6			..
5.38	2.77	3.3	..	4.3			9.9
10.8	2.78	3.6	.22	2.9			5.2
10.8	2.78	3.7	.22	2.8			..
33.7	2.74	5.3	.24	1.1			2.0
33.7	2.74	4.8	.19	1.0			..
53.8	2.95	4.4	.14	0.7			..
53.8	2.78	4.5	.11	.5			2.1
49°							
5.38	3.03	6.5	0.85	7.2	0.3	1.9	1.7
10.8	3.53	7.5	.57	5.0	.2	1.3	4.4
33.7	3.18	12.8	.62	3.5	.09	1.4	..
33.7	3.03	13.8	.67	3.4	.09	1.8	5.0
53.8	3.50	14.5	.43	1.6	.01	2.1	4.0
53.8	2.91	18.1	.60	2.2	.004	1.2	2.2
53.8	2.68	19.7	.68	2.4	...	2.7	6.0
73°							
5.38	2.55	13.3	5.1	13.0	1.1	5.7	6.5
5.38	2.55	12.2	3.8	11.8	1.5	7.2	..
10.8	2.55	15.0	4.2	9.8	0.6	2.2	7.8
10.8	2.55	14.2	3.0	8.3	.4	2.5	..
33.7	2.78	21.8	3.3	5.0	.1	2.1	13.0
33.7	2.78	20.0	2.8	4.0	.1	2.2	..
53.8	2.87	23.0	3.0	3.4	.1	1.1	8.4
53.8	3.71	27.5	3.2	5.2	.1	8.4	4.9
53.8	4.20	21.3	2.9	3.6	.1	5.9	9.6
53.8	5.50	19.7	3.0	3.8	.1	1.9	6.1
53.8	11.2	13.7	1.8	3.6	.1	3.5	4.8
53.8	21.6	12.9	1.5	4.4	.1	2.4	4.5
53.8	32.7	11.1	1.1	3.8	.1	1.5	7.3

The first fraction usually was analyzed by converting carbon monoxide to carbon dioxide by the reaction with cupric oxide in a cell at 290° incorporated into the gas train.

Solution Products.—In addition to an acid, which has been previously identified as acetic acid,[6] methyl ethyl ketone and small amounts of biacetyl and acetaldehyde were found in the photolysis products by extracting the irradiated solution with ether, distilling the ether and analyzing the residue by gas chromatography using a dinonyl phthalate column. However, neither a positive test for acetaldehyde with fuch-

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[1] Sponsored by the Office of Ordnance Research, U. S. Army.

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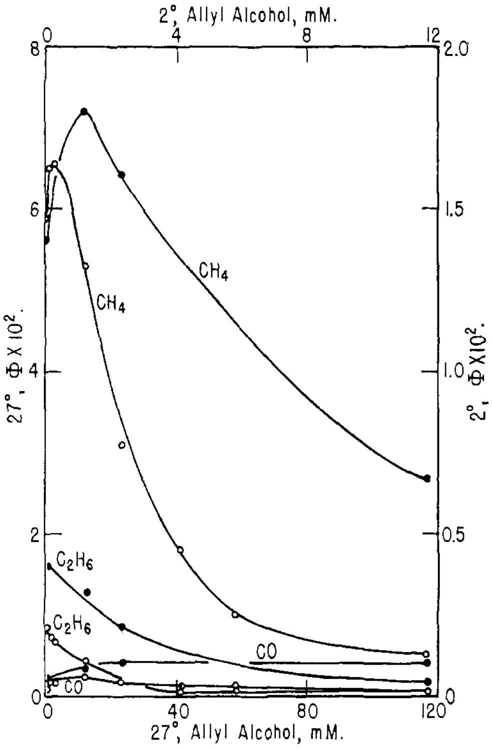

Fig. 1.—Quantum yields with added allyl alcohol: acetone, 0.054 *M;* solid circles, 2°; open circles, 27°; intensities: 2°, 8.94×10^{-7}; 27°, 3.7×10^{-7} Einst. $cc.^{-1}$ $min.^{-1}$.

sin-aldehyde reagent nor spectral evidence for biacetyl could be obtained. An irradiated solution treated with ferric chloride reagent gave a red color indicating an enolic substance possibly acetylacetone. Negative tests were obtained for peroxides. The acid yields were measured by titrating with standard base.

Actinometry.—Quantum yields were determined by the principle of equivalent optical densities[2,9] using monochloroacetic acid as the actinometer solution.

Results

Aqueous Acetone Photolysis.—The results obtained for solutions of acetone in water at various temperatures, intensities and concentrations are given in Table I. The decomposition of acetone was less than 10%. Results for carbon dioxide and acetic acid were erratic and seemed to depend on factors such as irradiation time and the length of time solutions were allowed to stand before analysis.

Aqueous Acetone–Allyl Alcohol Photolysis.—The results obtained for solutions of acetone and allyl alcohol in water are given in Figs. 1 and 2. The acetone concentration was fixed at 0.0538 *M* for all of these experiments. For all experiments at each fixed temperature, the intensity of absorbed light was kept constant. However, the intensity was not the same at the different temperatures used.

Discussion

Mechanism.—Pieck and Steacie[4] have shown that methyl radicals do not abstract hydrogen atoms from water when acetone is photolyzed in water solution. If abstraction of H-atom from water is not an important reaction, the photochemistry of acetone in water solution should not differ appreciably from the photochemistry in the gas phase except for general solution considerations and some specific interactions with water. However, the high concentrations possible in solution make reactions of free radicals with acetone a more important consideration.

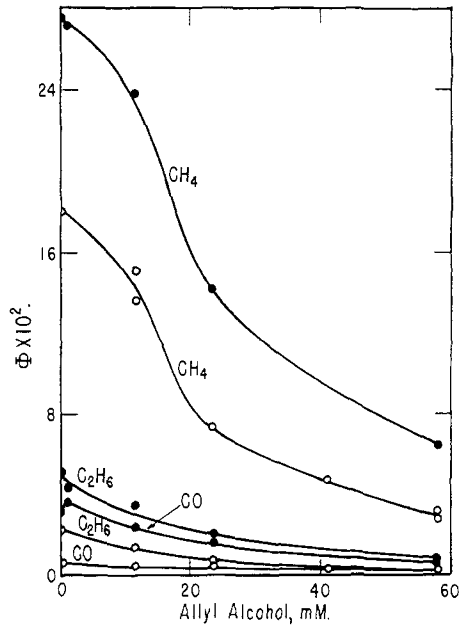

Fig. 2.—Quantum yields with added allyl alcohol; acetone, 0.054 *M;* solid circles, 73°; open circles, 49°; intensities: 49°, 2.9×10^{-7}; 73°, 3.7×10^{-7} Einst. $cc.^{-1}$ $min.^{-1}$.

Propane, although not generally considered in the gaseous photolysis, has previously been reported in small amounts.[10,11] Long[12] attributes this product to the reaction of ethyl radicals, formed by hydrogen atom abstraction from the product ethane, with methyl radicals.

The mechanism generally accepted for the formation of gaseous products in the gas phase photodecomposition is

$$(CH_3)_2CO + h\nu \longrightarrow CH_3 + CH_3CO \qquad k_1I_a \quad (1)$$

$$CH_3CO \longrightarrow CH_3 + CO \qquad k_2 \quad (2)$$

$$CH_3 + (CH_3)_2CO \longrightarrow CH_4 + CH_2COCH_3 \qquad k_3 \quad (3)$$

$$2CH_3 \longrightarrow C_2H_6 \qquad k_4 \quad (4)$$

The equations yield the expression

$$R_{CH_4}/R_{C_2H_6}{}^{1/2} = (k_3/k_4{}^{1/2})[(CH_3)_2CO] \qquad I$$

The data of Table I when used to test this equation gave a wide deviation from linearity for plots of $R_{CH_4}/R_{C_2H_6}{}^{1/2}$ as a function of acetone concentration. Pieck and Steacie[4] in experiments with liquid acetone have obtained good evidence for the disproportionation reaction

$$CH_3 + CH_3CO \longrightarrow CH_4 + CH_2CO \qquad k_5 \quad (5)$$

In water solution considerable acid is formed which is to be expected if ketene is formed as this would

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(11) L. Mandelcorn and E. W. R. Steacie, *Can. J. Chem.*, **32**, 79 (1954).

(12) L. A. Long, *J. Phys. Chem.*, **61**, 821 (1957).

lead to acetic acid by hydrolysis. Using also equation 5, the expression obtained is

$$\frac{R_{CH_4}}{R_{C_2H_6}{}^{1/2}\,R_{CO}} = \frac{k_3[(CH_3)_2CO]}{k_4{}^{1/2}\,R_{CO}} + \frac{k_5}{k_2k_4{}^{1/2}} \qquad (II)$$

The data of Table I were used to test this equation and the results are shown in Fig. 3. It may be observed that the primary data used for Fig. 3 were the experimentally determined rates of reaction which, however, also may be obtained from the data in Table I by multiplying the quantum yields by the absorbed intensity.

The slopes of the lines were used to evaluate $k_3/k_4{}^{1/2}$.

Temp., °C.	2	27	49	73
$(k_2/k_4{}^{1/2}) \times 10^{12}$ cc.$^{1/2}$ molecule$^{-1/2}$ sec.$^{-1/2}$	0.57	0.99	1.9	2.0

An Arrhenius plot of $k_3/k_4{}^{1/2}$ calculated as discussed is given in Fig. 4. An activation energy of 3.6 kcal. per mole was obtained.

Diffusion Effect.—Although this value is quite low compared to the gas phase value of 9.7,[13] it is in line with the value of about 5 kcal. which may be calculated from the data of Pieck and Steacie[4] for the photolysis in liquid acetone at 2537 Å. in the same temperature region. $k_3/k_4{}^{1/2}$ in solution is high compared to the gas phase value as pointed out by Peterson and Mains.[4] These authors attribute this to a lowering of k_4 since it is expected that the combination of two free radicals in solution would be diffusion controlled. For a diffusion controlled reaction the collision frequency may be expressed as

$$Z = aD$$

where a essentially is temperature independent and D is the diffusion coefficient.[14] For non-associated liquids, D is empirically found to vary exponentially with $1/T$ and the temperature coefficient can be represented in terms of an activation energy, E_D.[14,15]

For water and other associated liquids, this exponential relationship does not hold.[15] However, we are able to make a correction for diffusion. Theories of diffusion in liquids[16] from diverse points of view, Einstein and Eyring, relate diffusion and viscosity by equations of the form

$$D = bT/\eta$$

The temperature dependence of diffusion may then be determined from the temperature dependence of viscosity. We have found that a plot of the log of viscosity of water[17] against log T in the temperature region of our interest may be fairly well represented by a straight line from which the empirical relation[7] $\eta = c/T$ is obtained. The following values showing the constancy of ηT^7 are obtained for viscosity in poises. The diffusion coefficient may then be taken as $D = dT$.[8] The data of Longsworth[18] for the diffusion of various substances in water are in good agreement with this expression. This temperature dependence of diffusion may be taken into account by adding 4 log T, since the square root of k_4 is involved, to the values of log $k_3/k_4{}^{1/2}$. The corrected values are also shown in Fig. 4. The curve obtained is more nearly linear than the original and an activation energy of 6.0 kcal./mole for $(E_3-E_4)/2$ is obtained. Although this value is still low compared to the gas phase value, it is in good agreement with that obtained by Pieck and Steacie in liquid acetone.[4] Since the viscosity of acetone[19] varies exponentially with $1/T$ and an apparent activation energy of 1.66 kcal./mole is obtained, $E_D/2$ may be taken as about 0.8 kcal./mole for diffusion in liquid acetone. This value may be used to raise those found by Pieck and Steacie to about 6 kcal. at 2537 Å. and to about 9 kcal. for the data at 3130 A.

Temp., °C.	0	10	20	30	40	50	60	70
$\eta T^7 \times 10^{-17}$	2.0	1.9	1.9	1.9	1.9	2.0	2.1	2.2

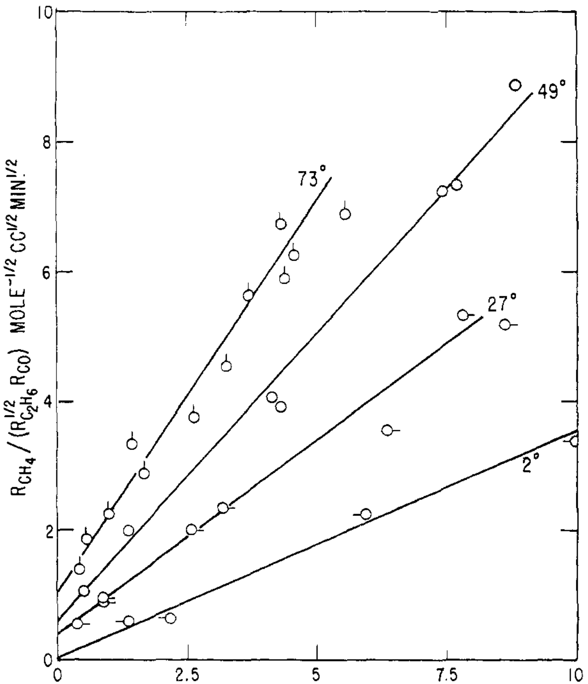

Fig. 3.—Plot according to equation II; ordinates have been multiplied by: 2°, 5 × 10^{-6}; 27°, 5 × 10^{-6}; 49°, 2 × 10^{-5}; 73°, 1 × 10^{-4}. Abcissas have been multiplied by: 2°, 5 × 10^{-5}; 27°, 5 × 10^{-5}; 49°, 2.5 × 10^{-4}; 73°, 1 × 10^{-3}.

The intercepts of Fig. 3 may be used to yield values of $k_5/k_2k_4{}^{1/2}$

Temp., °C.	2	27	49	73
$(k_5/k_2k_4{}^{1/2}) \times 10^6$ cc.$^{1/2}$ molecule$^{-1/2}$ sec.$^{1/2}$	0.2	0.8	0.3	0.1

Both (4) and (5) are radical-radical reactions and, therefore, are expected to be diffusion controlled.

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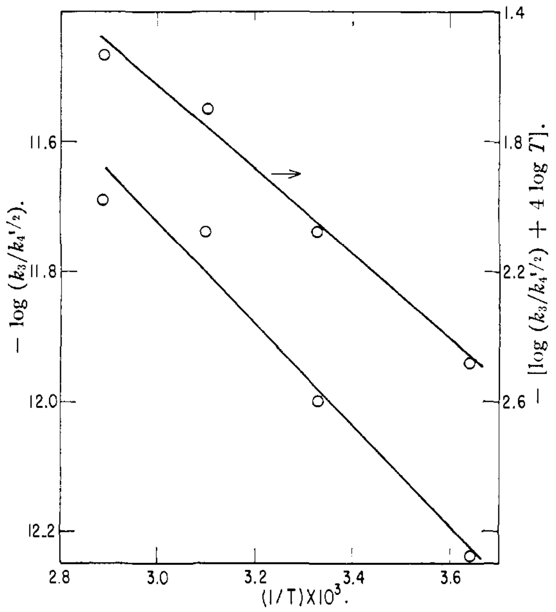

Fig. 4.—Arrhenius plot of rate constant ratios derived from slopes of Fig. 3; upper curve corrected for temperature dependence of diffusion.

An argument similar to the one we have already used suggests that 4 log T should be subtracted from the values of log $k_5/k_2k_4^{1/2}$ to account for the temperature dependence of diffusion. Although such a treatment tends to correct the apparently anomalous value at 2°, the adjusted values do not lead to a linear Arrhenius plot unless the 2° value is neglected. The validity of this calculation is dubious for such a complex combination of rate constants. However, it may be observed that if the 2° result is not used, an activation energy, $E = E_2 + E_4/2 - E_5$, of about 9 kcal./mole is obtained. Since E_2 is about 13 kcal./mole in the gas phase[20] and E_4 may be taken as zero and E_5 is probably in the range of 0-4 kcal./mole, this value is reasonable.

Effect of Allyl Alcohol.—The effect of allyl alcohol, particularly at 27° where the highest concentrations were used, shows that the formation of gaseous products probably proceeds completely by a free radical mechanism. The virtual elimination of methane at an allyl alcohol concentration of 0.1 M shows that simple hydrolysis of photo-excited acetone to yield acetic acid and methane, which had been assumed by early workers,[6] cannot account for methane formation.

An interesting result was the increase in quantum yield of methane and carbon monoxide at 2 and 27° for low alcohol concentrations. This does not occur at the higher temperatures. A possible explanation for this phenomenon is that methyl radicals in the solvent cage react with allyl alcohol much more rapidly than do acetyl radicals. This prevents recombination of acetyl and methyl to form acetone and allows acetyl radicals to escape the cage and actually obtain a higher concentration than in the absence of scavenger. This in turn favors the disproportionation reaction 5 which has relatively greater importance at low temperature because of the low activation energy usually associated with disproportionation reactions.

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[Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa]

The Starch–Iodine–Iodide Interaction. Part I. Spectrophotometric Investigations[1]

By John A. Thoma[2] and Dexter French

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Maltodextrins having six or more glucose units react with iodine–iodide solutions to form complexes which can be detected spectrophotometrically. Triiodide complexes exhibit absorption spectra essentially identical with the triiodide ion; hence triiodide complexes are not visually detectable. Dextrins with 9 or more glucose units give polyiodine complexes with enhancement of the absorption and shift to longer wave length, thus giving visible colors. Iodide ion was found to be necessary for the formation of blue starch–iodine complexes in aqueous solution. The apparent failure of amylose to form an iodide-free iodine complex suggests that amylose exists primarily as a random coil in aqueous solution.

Introduction

The effect of chain length on the stoichiometry and absorption spectrum of the starch–iodine complex is known only semiquantitatively.[3,4] This deficiency has resulted principally from a lack of individual pure or adequately characterized starch saccharides, in the chain length range where small changes in chain length give large changes in (a) the tendency to form complexes and (b) the types of complexes formed.

Recently, maltodextrin saccharides up to G_{18}[5] have been isolated by column chromatography on cellulose columns.[6] These individual compounds afforded an unparalleled opportunity to examine definitively the effect of chain length on the starch–iodine complex.

Experimental

Materials.—All inorganic reagents were commercial reagent grade and used without further purification.

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[2] Brookhaven National Laboratory, Upton, Long Island, New York. Union Carbide and Carbon Fellow 1957–1958.

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