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

The Photochemical Decomposition of Acetone in the Presence of Deutero-biacetyl

BY DONALD S. HERR,[1] MAX S. MATHESON[1] AND W. D. WALTERS

A number of investigators have shown that the quantum yield for the near ultraviolet photochemical decomposition of acetone is considerably smaller than unity at temperatures below 60°.[2,3,4] This low quantum efficiency cannot be due to fluorescence because the observed fluorescence is reported as less than 3% of the absorbed light.[2] Moreover, the efficiency of the primary process

$$CH_3COCH_3 + h\nu = CH_3 + CH_3CO \qquad (1)$$

is in the neighborhood of one.[5] Therefore, to account for the low quantum yield, a radical recombination reaction[4,5]

$$CH_3 + CH_3CO = CH_3COCH_3 \qquad (2)$$

and also the reaction[6]

$$CH_3 + CH_3COCOCH_3 = CH_3COCH_3 + CH_3CO \quad (3)$$

have been suggested as processes for regenerating acetone. In order to determine the importance of this latter reaction, deutero-biacetyl has been added to acetone and the mixture irradiated. If reaction (3) does account for the low quantum yield obtained even at small percentages of decomposition where the biacetyl concentration is very small, then on addition of 1 mm. or more of deutero-biacetyl, most of the methyl radicals from the photolysis of acetone should react with the deutero-biacetyl. Under these conditions it might be expected that deutero-ethane should eventually be formed and that the amounts of ethane and carbon monoxide might not be the same as those in the photolysis of pure acetone. A more detailed consideration of these points will be given after the experimental results have been presented.

Experimental

Preparation of Deutero-biacetyl.—The deutero-biacetyl was prepared by an exchange reaction of biacetyl with heavy water. The biacetyl employed in this work was obtained from the Eastman Kodak Company, dried, and purified by repeated vacuum fractionation.[7] The deuterium oxide (99.6% D), obtained from Norway, was subjected to two vacuum distillations before use. A solution of biacetyl (~9%) was prepared using deuterium oxide (~99%) which was about 1 normal with respect to DCl. After an exchange time of three days at 56°, the biacetyl was separated in an apparatus similar to the one used to separate acetone from aqueous solutions.[8] After the biacetyl solution had been placed in the apparatus, the major portion of the acid was neutralized with calcium carbonate. The air which was drawn through the biacetyl solution was then passed over anhydrous calcium chloride and the biacetyl removed by condensation in a trap cooled with dry-ice. Approximately 85% of the original amount of biacetyl could be recovered in this manner. Moreover, experiments with light biacetyl indicated that not more than 1.5% was lost during the exchange process and that no detectable change in the biacetyl, according to measurements of refractive index, had occurred during the separation. The sample was then subjected to another period of exchange with deuterium oxide and again separated as above. In order to remove any dissolved gases, the deutero-biacetyl was distilled four or five times under high vacuum. One of the samples of deutero-biacetyl (88% D) was used without further drying, but the other (93% D) was dried further by the use of anhydrous copper sulfate. Control experiments with light biacetyl indicated that, under the experimental conditions employed, drying by copper sulfate did not cause any deterioration of the biacetyl.

To analyze for the deuterium content of the heavy biacetyl, a small sample was carefully burned in a stream of oxygen over heated platinum foil in an apparatus similar to that described by Geib.[9] The deuterium content of the water from the combustion of the biacetyl was determined by the same method as that used for the water from the combustion of ethane.

Apparatus and Technique.—Acetone containing approximately 1% of deutero-biacetyl was irradiated with a high pressure arc. In the earlier experiments with deutero-biacetyl (88% D) direct radiation from the mercury arc was used. In the later experiments to reduce to a minimum any direct decomposition of deutero-biacetyl a cobalt nickel sulfate filter together with a Red Purple Corex A glass was used to remove all lines of wave lengths longer than 3400 Å. The light source was adjusted to give the same incident intensity in every run, according to measurements made using a photronic cell. The acetone and deutero-biacetyl were frozen down directly in the cylindrical quartz cell (2.5 by 20 cm.) and then allowed to stand to ensure proper mixing. The temperature of the reaction vessel was varied by surrounding it with an electrically heated jacket, which was manually controlled to within one degree during a run. After irradiation the fixed gases were separated into carbon monoxide and ethane with liquid nitrogen and pentane mush baths according to the method

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[1] Fellows of the Sherman Clarke Fund for Chemical Research, University of Rochester.

[2] Damon and Daniels, THIS JOURNAL, **55**, 2363 (1933).

[3] Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1456 (1934).

[4] Herr and Noyes, THIS JOURNAL, **62**, 2052 (1940).

[5] Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

[6] Taylor and Jungers, *Trans. Faraday Soc.*, **33**, 1353 (1938); Taylor and Rosenblum, *J. Chem. Phys.*, **6**, 119 (1938).

[7] Walters, THIS JOURNAL, **62**, 880 (1940).

[8] Reitz, *Z. physik. Chem.*, **A179**, 119 (1937).

[9] Geib, *ibid.*, **A180**, 211 (1937).

described by Manning.[10] It was observed that there was always a large excess of biacetyl left after exposure. Since the gas removed by the Toepler pump at liquid nitrogen temperature has been shown to be chiefly carbon monoxide,[4] this was designated as the carbon monoxide fraction. For a similar reason the fraction removed at the temperature of pentane mush (about −132°) has been designated as ethane. Practically no methane ($\leqslant 2\%$) is formed during the photolysis of acetone at room temperature.[4] However, a small amount of ethane as well as any methane, may be removed with the carbon monoxide fraction. Therefore in some runs, the carbon monoxide has been determined quantitatively by oxidation over copper oxide and any residual hydrocarbon combined with the ethane fraction from the pentane mush.

The ethane was then burned over a hot platinum wire in the presence of an excess of oxygen. All the carbon dioxide was removed by a series of distillations under high vacuum. The water, which was led over a large excess of previously distilled sodium, was completely converted to hydrogen by heating for a considerable time near the softening temperature of Pyrex.[11] This conversion had first been attempted over a hot tungsten wire, but with small samples this proved unsatisfactory. With the samples in the present study, namely, low deuterium content, equilibration over a hot nickel wire made no difference in the thermal conductivity of the gas obtained from the sodium treatment.

By means of a Toepler pump the gas was passed through two liquid air traps into a small thermal conductivity gage. The deuterium content was determined by a constant potential Wheatstone bridge apparatus similar to that described by Melville and Bolland.[12] Around the outside of the cell was placed a four-liter Dewar flask containing a water–ice mixture which was well stirred to ensure a uniform temperature. By this method with 75 mm. pressure in the micro-cell (rather than 50 mm.), the deuterium content of 0.05 cc. of gas (N. T. P.) can be determined to within ±0.5%.

The analysis system was calibrated with samples of water containing different percentages of deuterium oxide. A plot of the deuterium content against the change in resistance gave a curve with a negative deviation from the linear D_2–H_2 relationship in agreement with similar measurements made by Melville and Bolland using high pressures. The resistance of the cell increased 7.4% when hydrogen was replaced by deuterium. Measurements of unknowns were always accompanied by measurements of hydrogen and often by measurements of deuterium as well. Knowns and unknowns were of equal size.

Blank runs with deutero-biacetyl alone and with acetone alone were made for comparison purposes. The ethane fraction from the deutero-biacetyl alone was so small that the deuterium content could not be measured. In the course of the investigation no measurable difference in the behavior of the two samples of deutero-biacetyl was observed.

Results and Discussion

The results of experiments made at temperatures from 25 to 62° inclusive are shown in Table I. Under these conditions practically no deuterium, within the limits of experimental error,[13] was observed in the ethane fraction. The deuterium content represents atoms of deuterium compared with the total number of hydrogen and deuterium atoms. In the case of experiments at room temperature, for which the ethane to carbon monoxide ratios were measured, it is evident that the ratios for the runs with biacetyl added are very nearly the same as those for pure acetone. Likewise, when the time of exposure as well as the absorbed intensity is taken into consideration, the amount of ethane formed from acetone in the presence of biacetyl is in agreement with that obtained in the absence of biacetyl.

TABLE I

PHOTOLYSIS OF MIXTURES OF ACETONE AND DEUTERO-BIACETYL AT TEMPERATURES UP TO 62°

P_A, mm.	P_{Ac_2}, mm.	Time, min.	Temp., °C.	Moles of ethane × 10^6	N_{Et}/N_{CO}	% D in ethane
191	1.3[a]	575	25	>10	..	0.4
221	2.1[a]	350	27	>10	..	.6
151	1.0	~300	25	>10	..	.2
178	1.3	300	25	9.64	..	.0
95	1.4	195	25	5.90	1.56	.0
0	1.4	180	25	0.17	..	...
135	1.6	180	25	6.17	1.58	.0
0	1.6	180	25	0.20	..	...
150	0	110	26	4.08	1.65	...
162	0	180	25	..	1.45[b]	...
107	0	272	25	..	1.67[b]	...
192	1.6	100	60	8.75	1.08	.2
0	1.6	120	60	0.20	..	...
187	1.5	120	62	8.70[c]	1.08[d]	.4

[a] In these runs deutero-biacetyl (88% D) was used. In the others, deutero-biacetyl (93% D). [b] From the data of Herr and Noyes at 3130 Å. [c] Represents the total hydrocarbon fraction removed by the Toepler pump at the melting point of pentane (about −132°) or below. [d] Ratio of the hydrocarbon fraction to the carbon monoxide determined by analysis.

The data can best be considered in connection with the various reactions already established or postulated for the photolysis of acetone

$$\begin{aligned}
CH_3COCH_3 + h\nu &= CH_3 + CH_3CO &\quad (1)\\
CH_3CO &= CH_3 + CO &\quad (4)\\
2CH_3 &= C_2H_6 &\quad (5)\\
2CH_3CO &= CH_3COCOCH_3 &\quad (6)\\
CH_3 + CH_3CO &= C_2H_6 + CO &\quad (7)\\
CH_3 + CH_3CO &= CH_3COCH_3 &\quad (2)\\
CH_3 + CH_3COCOCH_3 &= CH_3COCH_3 + CH_3CO &\quad (3)
\end{aligned}$$

For the purpose of discussion it will be assumed

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(10) Manning, THIS JOURNAL, **56**, 2589 (1934).

(11) Rollefson, *J. Chem. Phys.*, **2**, 144 (1934); Abel, Bratu and Redlich, *Z. physik. Chem.*, **A173**, 353 (1935).

(12) Melville and Bolland, *Proc. Roy. Soc.* (London), **A160**, 384 (1937); *Trans. Faraday Soc.*, **33**, 1316 (1937).

(13) The fact that slight positive amounts of deuterium were quite often obtained would seem to indicate that a very small amount of deutero-ethane is actually present.

that reaction (3) is the reaction chiefly responsible for the low quantum yield of acetone disappearance (~0.25 at 3130 Å. with a pressure of 120 mm.), and on this assumption certain predictions will be made. The fact that the experimental results do not agree with these predictions will indicate that reaction (3) is not important.

The low quantum yield has been measured at small percentages of decomposition (~0.1%) where of necessity the pressure of biacetyl formed during the decomposition must be small.[4] However, in the present investigation the biacetyl pressure was probably 10^2 times as great as in the normal decomposition under the above mentioned conditions. If reaction (3) is rapid enough to account for the regeneration of approximately 75% of the acetone under normal conditions, then in the presence of added biacetyl nearly all of the methyl radicals should be used up and be replaced by acetyl radicals.

A detailed discussion of the effect of this reaction is rendered difficult because the relative importance of some of the subsequent reactions, such as (4) and (7), has not been definitely established. However, in the normal decomposition, since the ethane production exceeds that of carbon monoxide, a large part of the ethane must be formed through reaction (5), regardless of the importance[5] of reaction (7). With added biacetyl, replacement of methyl radicals by acetyl should result, therefore, in a considerable decrease in the amount of ethane. The effect upon the formation of carbon monoxide cannot be predicted with certainty, but it would seem to be exceedingly fortuitous if the amount of carbon monoxide is not altered when acetyl radicals are produced from methyl radicals. Nevertheless, the ethane to carbon monoxide ratio should be smaller, because, although it might be possible that the carbon monoxide formation is reduced, the ethane formation should be decreased to a greater extent.

Moreover, since deutero-acetyl radicals are replacing methyl radicals according to the equation

$$CH_3 + CD_3COCOCD_3 = CH_3COCD_3 + CD_3CO \qquad (3')$$

it would be expected that any ethane formed would contain an appreciable amount of deuterium, irrespective of whether reaction

$$CD_3CO = CD_3 + CO \qquad (4')$$

occurs, followed by a recombination of methyl radicals, or a reaction

$$CH_3 + CD_3CO = CH_3CD_3 + CO \qquad (7')$$

takes place.

Since no significant amounts of deuterium were found in the ethane and since in the presence of biacetyl the ethane to carbon monoxide ratios (likewise the quantum yields of ethane and carbon monoxide formation) agree with those for the acetone alone, it would appear that reaction (3) is not the one responsible for the low quantum yield in the photolysis of acetone.

In addition to the above experiments, a few runs were made at room temperature in which light, instead of heavy, biacetyl was used. Samples of acetone at pressures of 100–150 mm. with and without 1.0 mm. of biacetal were irradiated with light of wave length 3000–4000 Å., obtained from a zinc spark by the use of a red purple Corex A filter. The quantum yield of carbon monoxide formation was found to be the same (within an experimental error of 10%) in the presence or absence of biacetyl.

TABLE II

PHOTOLYSIS OF MIXTURES OF ACETONE AND DEUTERO-BIACETYL AT HIGHER TEMPERATURES

P_A, mm.	P_{Ac_2}, mm.	Time, min.	Temp., °C.	Moles of ethane × 10^6	% D in ethane
201	1.8	75	80	11.17	6.9
0	1.8	75	80	0.37	..
98	3.2[a]	60	99	3.71	12.9
0	3.2[a]	60	99	0.22	..
200	1.4	45	98	7.43[b]	7.2
0	1.4	45	98	0.18	..
194	1.6	45	98	5.90	11.3
0	1.6	45	98	0.23	..

[a] Deutero-biacetyl (88% D) and an unfiltered mercury arc. In all other runs deutero-biacetyl (93% D). [b] Represents total hydrocarbon fraction removable by Toepler pump at the melting point of pentane (−132°) or below.

The data from the experiments at higher temperatures are given in Table II. At these temperatures, particularly near 100°, in the normal photochemical decomposition of acetone the quantum yields of carbon monoxide formation, ethane formation, and acetone disappearance are practically identical and very close to one. This indicates that the reactions which form biacetyl or regenerate acetone are not important compared to reactions producing ethane and carbon monoxide. An explanation can be found either in the instability of the acetyl radicals, or in the occurrence of reaction (7) in preference to reaction (2). Since the concentration of biacetyl is extremely small at these temperatures, reaction (3) would not take place to any appreciable extent in the ordinary decomposition. With added biacetyl, however, it is possible for methyl radicals to attack a biacetyl molecule. That some such reaction does take place is indicated by the deuterium content of the ethane fraction.

It is to be noted that some of the deuterium in the ethane fraction comes from the direct decomposition of deutero-biacetyl. In fact, the ethane formed in the blank runs with deutero-biacetyl amounts to 3–4% of that found in the decomposition of acetone. If any radicals other than methyl which are formed in the photochemical decomposition of biacetyl are unstable at these elevated temperatures, or if they react readily to form ethane by some reaction similar to (7) it might be assumed that the quantum yield is near one and that the deutero-ethane in the blank would represent the amount of deutero-ethane due to the direct decomposition of deutero-biacetyl in the presence of acetone. But, for equal incident intensities, the absorption of light by the acetone present will reduce the intensity (within the cell) in the absorption region common to both acetone and biacetyl, so that the amount of direct decomposition will be less, perhaps as much as 40%, in the presence of acetone.

To account for the deuterium content in excess of that expected from the blank, it can be assumed, provided that no sensitized decomposition occurs, that methyl radicals do react with biacetyl. If reaction (3′) occurs, deutero-ethane should result from the subsequent decomposition or reaction of the deutero-acetyl radicals. With the assumption that the acetyl radicals are unstable and that the disappearance of methyl radicals is a wall reaction, the methyl radical concentration can be calculated. On the basis of the diffusion equation for a cylindrical vessel and an accommodation coefficient of 10^{-3} for the wall,[14] the average methyl radical concentration was found to be 1×10^{13} radicals per cc. On the other hand, if acetyl radicals are stable and reaction (7) is the important reaction for the disappearance of methyl and acetyl radicals, a similar concentration of methyl radicals would be obtained if reaction (7) involves either an activation energy of 5.6 kcal. or a steric factor of 5×10^{-4}, using a mean molecular diameter of 3.5 Å.

From the data at 98° the ethane formation can be calculated to be approximately 2.5×10^{-11} mole per cc. per sec. Assuming that in the presence of 1.5 mm. of biacetyl this ethane contains 8% D as a result of reaction (3′), for a mean molecular diameter of 4.0 Å. only one in every 5.9×10^7 collisions of a methyl radical and a biacetyl molecule will lead to reaction. If the steric factor were one, this would correspond to an Arrhenius factor, $e^{-E/RT}$, with $E = 13$ kcal. per mole.[15] Therefore, even if reaction (3′) is responsible for the deutero-ethane at the elevated temperatures, the above results also indicate that at room temperature under normal conditions where the biacetyl concentration is small this reaction is of negligible importance.

This conclusion was further substantiated by experiments in which lead tetramethyl was decomposed photochemically at room temperature in the presence of light biacetyl. Light corresponding to the four zinc lines centering around 2100 Å. was used since biacetyl is transparent in this region[16] while lead tetramethyl absorbs these wave lengths very strongly.[17] Although there was some reaction between methyl radicals and biacetyl, the rate was much too small to account for the regeneration of acetone. Reaction (2) therefore appears to be the probable cause of the low quantum yield.

When a methyl radical attacks a biacetyl molecule, reactions other than reaction (3) are possible. In fact, since removal of a hydrogen atom by a radical usually occurs in preference to the breaking of the carbon skeleton, the reaction

$$CH_3 + CD_3COCOCD_3 = CH_3D + CD_2COCOCD_3 \quad (8)$$

might be more likely than reaction (3′). If the radical formed by this process decomposes into a deutero-acetyl radical and ketene, it could account for the deuterium content in the ethane fraction at the higher temperatures. Moreover, if ketene is formed and is not rapidly polymerized, a small amount of it might get into the ethane fraction. Since the ultimate fate of the final products of reaction (8) is not known, a calculation of the activation energy from the observed data does not seem to be justified. However, a value not far different from the 13 kcal. calculated above might be expected.

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[14] Method similar to that of Kassel and Storch, THIS JOURNAL, **57**, 672 (1935). If one in 10^4 bimolecular collisions between methyl radicals (assuming $\sigma = 3.0$ Å.) in the gas phase leads to recombination, the disappearance of methyl radicals homogeneously will be about 10% as important as the wall reaction.

[15] A change in the methyl radical concentration by a factor of ten will affect the activation energy only to the extent of 1.7 kcal.

[16] Sponer, "Molekülspektren," Verlag Julius Springer, Berlin, 1935, Vol. 1, p. 117; Ells, THIS JOURNAL, **60**, 1864 (1938).

[17] Leighton and Mortensen, *ibid.*, **58**, 448 (1936); Duncan and Murray, *J. Chem. Phys.*, **2** 636 (1934).

An inspection of Table I shows that the deuterium content of the ethane fraction in mixtures of acetone and deutero-biacetyl at room temperatures is less than the amount which might be anticipated from the direct decomposition of the deutero-biacetyl.[18] A plausible explanation of this fact can be found in the homogeneous recombination of methyl and acetyl radicals which is of importance at the lower temperatures but not at the higher. In the presence of acetone, which is also being photochemically decomposed, the concentrations of methyl and acetyl radicals are increased and diffusion to the walls hindered. Since no reaction, such as (3), occurs, there are relatively few deutero-radicals in the presence of a large number of light radicals. Under these conditions radicals containing deuterium (which probably lead to ethane formation at the walls in the case of biacetyl alone at low pressures) may be used up according to reaction (2), and consequently less deutero-ethane would be formed. Reaction (6) may take place to some extent homogeneously, and this may also be of some significance as the acetyl radical concentration is increased.

In connection with the photolysis of biacetyl at room temperature it has been reported previously,[19] and it was observed again in this investigation with deutero-biacetyl that the ratio of the carbon monoxide fraction to the ethane fraction exceeds two. Assuming that methyl and acetyl radicals are present in the photolysis of biacetyl, one of the possible causes of this result might also be the formation of acetone from methyl and acetyl radicals. In this case, the disappearance of some of the molecules of biacetyl would result in the formation of carbon monoxide, but no ethane. Moreover, at the higher temperatures reaction (8) will become increasingly important.

Summary

The near ultraviolet photochemical decomposition of acetone in the presence of about 1% deutero-biacetyl was investigated in the temperature range 25 to 99°. At room temperature practically no deuterium was found in the ethane formed, and no change either in the ethane to carbon monoxide ratio or in the quantum yield of ethane formation was observed when deutero-biacetyl was present. Likewise, the addition of light biacetyl did not alter the quantum yield of carbon monoxide formation.

At a temperature of 80° or above the ethane fraction contains appreciable amounts of deuterium, indicating that at higher temperatures methyl radicals probably attack the deutero-biacetyl molecules.

It was concluded that the reaction $CH_3 + CH_3COCOCH_3 = CH_3COCH_3 + CH_3CO$ is not of importance in accounting for the low quantum yield of the photolysis of acetone.

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[18] As already mentioned, the direct decomposition in the presence of acetone should be less than in the blank. Also, some light biacetyl is formed during the photolysis of acetone at room temperature. However, it is estimated that the average deuterium content of the biacetyl present during a run will be approximately 83%. On this basis about 1.5–2% D might be expected in the ethane.

[19] Kirkbride and Norrish, *Trans. Faraday Soc.*, **27**, 404 (1931).

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The Removal of Oxygen Impurity from Tank Nitrogen by Means of Cobaltous Oxide

BY H. ARMIN PAGEL AND ELDON D. FRANK

LeBlanc and Möbius[1] have shown that pure oxygen at atmospheric pressure and room temperature is rapidly absorbed by cobaltous oxide if the oxide is prepared in high vacuum at comparatively low decomposition temperatures. We have found that the oxygen impurity in tank nitrogen can be removed by passing the latter through a column of cobaltous oxide prepared according to the above conditions.

Preparation of the Oxide.—The Pyrex glass absorption tower, which was used in a vertical position, was made as follows. The bulb containing the cobaltous oxide was 18 cm. long by 2 cm. inside diameter. A 5-mm. inside diameter tube sealed to the lower end of the bulb extended downward about 6 cm. where it was bent at 90 degrees and connected to a three-way stopcock by means of heavy pressure tubing. A plug of Pyrex glass wool just below the seal served to hold the oxide in place. A section of tubing 8 cm. long by 8 mm. inside diameter was sealed to the upper end of the bulb. Twenty-five grams of Baker and Adamson reagent quality, cobaltous carbonate was then introduced through this opening after which a two-way stopcock was sealed on. (In order to recharge the tower it was then merely necessary to break the 8 mm. section to remove the contents. Any adhering oxide was dissolved

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[1] M. LeBlanc and E. Möbius, *Z. physik. Chem.*, **142**, 175 (1929).