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The Photolysis of Chloroacetone at 3130 Å.[1]

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The vapor phase photochemical decomposition of chloroacetone at wave length 3130 Å. has been studied over the temperature range 59 to 335°. The principal products identified mass spectrometrically are hydrogen chloride, acetone, acetonylacetone and symmetrical biacetylethylene. The quantum yields of hydrogen chloride and acetone increase, while those of the remaining two decrease with increasing temperature. At the higher temperatures, carbon monoxide, methane and methyl chloride are also formed. The effects of nitric oxide and of iodine on the photolysis have also been studied. In the presence of nitric oxide, the quantum yield of hydrogen chloride is increased slightly to a value close to unity while the yields of acetone and acetonylacetone become negligible and there is evidence that the nitroso compound, CH_3COCH_2NO, is formed. With iodine vapor present, iodoacetone is formed and acetonylacetone is again eliminated. The yield of hydrogen chloride is greatly reduced. The investigation indicates that the main primary process is $CH_3COCH_2Cl + h\gamma = CH_3COCH_2 + Cl$. The postulation of disproportionation as well as association of acetonyl radicals is necessary to explain the results. The activation energy for the abstraction of a hydrogen atom from chloroacetone by an acetonyl radical has been found to be 9 ± 1 kcal./mole assuming zero activation energy for the association of acetonyl radicals.

As far as is known, the photolysis of chloroacetone has not been studied previously. Its investigation was undertaken to determine to what extent the chlorine atom would cause the photolysis to differ from that of acetone, and to obtain information on the behavior of new radicals that might be formed.

Experimental

Eastman Kodak Company chloroacetone was dissolved in water and shaken repeatedly with small aliquots of ethyl ether. This procedure preferentially removes the main impurity, unsymmetrical dichloroacetone. The chloroacetone remaining in the water layer was extracted with ether and distilled at reduced pressure. The center fraction was dried over anhydrous calcium chloride and stored at Dry Ice temperature. Mass spectrometric analysis indicated better than 99.9% purity. The absorption spectrum of chloroacetone vapor in the near ultraviolet was measured on a Cary spectrophotometer and extends from 3300 to 2400 Å. with a maximum at 2900 Å.

Nitric oxide was prepared by the reduction of nitrite by iodide.[2] It was distilled in the vacuum apparatus from −183 to −196°, the center third being retained. Mass spectrometric analysis indicated that the only possible impurity was nitrogen. It was assumed that this would not influence the experiments. C.P. iodine was vacuum sublimed. A center fraction was retained and used. C.P. acetone was vacuum distilled with the retention of the center third. Mass spectrometric analysis showed no impurities.

The light source was an Hanovia Type A medium pressure mercury lamp. A fairly parallel and uniform light beam was achieved by use of a pair of quartz lenses with a combined focal length of 5 cm. The 3130 Å. filter combination was that described by Noyes and Leighton.[3] The potassium biphthalate solution was circulated to and from a three-liter reservoir. The transmission of the filter combination was measured on a Cary spectrophotometer and extends from 3100 to 3400 Å. with a maximum at 3130 Å. A cylindrical quartz cell with plane windows, 20 cm. in length, 3 cm. internal diameter, was used. In all experiments, the light beam filled the cell. An aluminum block housed the cell and was heated electrically. Variations of the light intensity were followed by a phototube (Beckman type 2342-1) mounted behind the cell and recorded on a sensitive milliammeter. The phototube, cell, block and connecting tubing were all enclosed in an air thermostat maintained at 60°. The reaction cell was connected by stopcocks to the chloroacetone supply and through a series of traps to the vacuum pumps and a Toepler pump. A Dry Ice trap virtually excluded mercury from the system. Pressures were measured with a calibrated click gage reproducible to better than 0.5 mm.

For each run a small quantity of chloroacetone was removed from the storage bulb and degassed three times at −78°. It was allowed to fill the cell to the desired pressure. In the nitric oxide runs, the chloroacetone introduced was condensed with Dry Ice and the cell filled with the desired pressure of NO. In the iodine runs, the chloroacetone was condensed in a trap outside the cell. Iodine was admitted to the cell and its pressure measured. Finally, both the iodine and chloroacetone were condensed inside the cell with liquid nitrogen. In both the iodine and nitric oxide runs, mixing was achieved by diffusion over a two-hour period prior to the run. At the end of the nitric oxide runs, the excess NO was removed at −196° and discarded, and analysis for non-condensable products was not attempted. At the end of the iodine runs, the excess iodine was removed by reaction with mercury. All products were identified and analyzed in a modified Westinghouse, Type LV, mass spectrometer. Standardization was effected by introducing measured samples of pure compounds. Standard samples of CO, CH_4, CH_3Cl and HCl were measured in a micro-gas buret. In the case of acetone and acetonylacetone, a small quantity of the compound was condensed in an evacuated tube, weighed and expanded into a calibrated five-liter volume, to which was attached a smaller calibrated volume. After equilibrium, the smaller volume was closed and the amount of the compound contained in it (a known fraction of a known weight) introduced into the mass spectrometer.

From each run, the following fractions of products were analyzed separately.

(1) The material non-condensable at −196°.

(2) The fraction which volatilized at −78°. This consisted of most of the acetone and hydrogen chloride plus a little chloroacetone.

(3) Part of the fraction which volatilized at −50°. The undecomposed chloroacetone could be largely removed from the less volatile products by a two-hour fractionation at −50°. This portion was warmed to 0° and opened to a known volume. The vapor which filled this volume was analyzed. It consisted of chloroacetone plus most of any remaining acetone and hydrogen chloride.

(4) A repetition of (3), the known volume being filled a second time.

(5) The fraction remaining involatile at −50°. This contained the acetonylacetone. Experiments in which known amounts of acetonylacetone were added to chloroacetone indicated that some acetonylacetone was carried over with the chloroacetone at −50°. A correction in the yields of acetonylacetone to allow for this has been applied. Runs 14 and 15 are the only ones in which this correction amounts to more than 20%. For these two runs, the quantum yields of acetonylacetone must be considered only approximate.

In the determination of quantum yields, acetone was used as an internal actinometer. The quantum yield of carbon monoxide formation at 3130 Å. and 150° was assumed to be unity.[4]

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[1] This work was supported in part by the Office of Ordnance Research. The mass spectrometer employed was donated to the University of California, Los Angeles, by the Signal Oil and Gas Company of Los Angeles.

[2] H. L. Johnson and W. F. Giauque, THIS JOURNAL, **51**, 3194 (1929).

[3] W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941, p. 69.

[4] D. S. Herr and W. A. Noyes, Jr., THIS JOURNAL, **62**, 2052 (1940).

TABLE I

PHOTOLYSIS OF CHLOROACETONE AT 3130 Å.

Run no.	Temp., °C.	Time, min.	I_a,[a] quanta/sec. × 10^{-15}	(C),[b] mmoles/l.	Quantum yields, Φ HCl	Acetone	Acetonylacetone	CO	CH_4	CH_3Cl
2	59	9	10.9	2.27	0.72	0.12	..[c]	0.0	0.0	0.0
21	60	20	4.52	2.34	.86	.13	0.17	> .01	> .01	.0
10	150	20	7.16	1.69	.78	.08	.13	.027	.018	.0
19	150	20	4.66	1.78	.87	.15	.17	.022	.014	.0
11	204	20	6.01	1.84	.95	.22	.12	.072	.054	.003
13	252	20	6.05	1.74	1.02	.45	.09	.126	.089	.011
14	301	10	5.36	1.73	1.23	.63	.07	.149	.093	.025
15	335	15	5.10	1.58	1.49	.75	.04	.304	.184	.069

[a] Rate of light absorption. [b] Concentration of chloroacetone. [c] Not measured.

TABLE II

EFFECT OF ADDED NO AND I_2 ON CHLOROACETONE PHOTOLYSIS

Run no.	Temp., °C.	Time, min.	I_a, quanta/sec. × 10^{-15}	P[a] (chloroacetone), mm.	P[a] (gas added), mm.	Quantum yields, Φ HCl	Acetone	Acetonylacetone	Biacetylethylene
20	150	20	4.59	49	3(NO)	1.15	0.0	0.0	Absent
19	150	20	4.66	47	0.0	0.87	.15	.17	Present
22	60	20	4.38	49	3(NO)	.99	.0	.0	Absent
21	60	20	4.52	48.5	0.0	.86	.13	.17	Present
23	61	20	4.29	47	3(I_2)	.15	..[b]	.0	Absent
25	82	30	3.21	50.5	10(I_2)	.13	..[b]	.0	Absent

[a] Pressure. [b] Not possible to measure.

Results

In Table I are shown the results of a series of runs conducted over the temperature range 59 to 335°. Appreciable thermal decomposition above 335° prevented the investigation from being carried to higher temperatures. No measurable quantity of ethane was detected in any of the runs. In fraction 5, in addition to acetonylacetone, a second compound always appeared with peaks at masses 69, 97 and 112. Symmetrical biacetylethylene was synthesized[5] and gave the same three peaks with their intensities in the same ratios as obtained for this compound. It was concluded, therefore, that biacetylethylene is a product of the photolysis. Unfortunately it did not prove possible to measure the yield of biacetylethylene quantitatively since the compound is insufficiently volatile for accurate analysis. However, the size of its mass spectra peaks would suggest that it is at least as important a product as acetonylacetone and that like the acetonylacetone its yield falls off at the higher temperatures. In addition, in fraction 5 smaller peaks at 131, 133, 146, 148 and 150 were observed. It seems reasonable to suppose that these are due to monochloro derivatives of acetonylacetone and biacetylethylene, but definite identification was not made.

In Table II are shown the results of photolysing chloroacetone in the presence of nitric oxide and of iodine. Dark runs not included in the table showed that there was no appreciable thermal reaction between chloroacetone and either nitric oxide or iodine under the conditions employed. In the nitric oxide runs, fraction 5 contained, in place of the missing acetonylacetone and biacetylethylene, two new compounds with peaks at 72 and 87 and at 54 and 96. Definite identification was not made, but it seems probable that the peaks are due to the compounds CH_3COCH_2NO and CH_3COCN. In addition, in fraction 2 larger peaks than could be accounted for were found at 44 and 27. This would suggest that carbon dioxide and hydrogen cyanide are also products of the reaction. In the iodine runs, fraction 5 contained sizeable amounts of a compound with peaks at 127, 141, 169 and 184, which is probably iodoacetone. Difficulties due to the formation of a complex between acetone and iodine made accurate analysis for acetone in these runs impossible. The indications were that acetone was still being formed in the presence of iodine.

Discussion

The Primary Process.—By analogy with acetone, it might be expected that the primary process would be either

$$CH_3COCH_2Cl + h\nu \longrightarrow CH_3CO + CH_2Cl \quad (1a)$$

$$\text{or } CH_3COCH_2Cl + h\nu \longrightarrow CH_3 + COCH_2Cl \quad (1b)$$

In Table I the total absence of or negligible quantities of methane, ethane, carbon monoxide and methyl chloride at the lower temperatures must mean that neither of these primary processes occurs to any extent. Instead, it seems that the absorbed energy is transmitted to the carbon–chlorine bond, which doubtless is weaker than either of the carbon–carbon bonds, and the main primary process becomes

$$CH_3COCH_2Cl + h\nu \longrightarrow CH_3COCH_2 + Cl \quad (1c)$$

The evidence for this reaction may be summarized as follows.

(a) Acetone and hydrogen chloride can be readily accounted for as two of the main products (Table I), assuming hydrogen abstraction on the part of both the acetonyl radicals and the chlorine atoms.

(b) Acetonylacetone as a product is explained by the recombination of two acetonyl radicals.

(c) Nitric oxide suppresses the formation of both acetone and acetonylacetone (Table II) and the

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[5] M. W. Goldberg and P. Müller, *Helv. Chim. Acta*, **21**, 1699 (1938).

formation of a compound with peaks at 72 and 87 is good evidence that it does so by reaction with acetonyl radicals to form CH_3COCH_2NO. The rearrangement of this nitroso compound to the oxime and the elimination of water forming CH_3COCN would account for the 54 and 69 peaks observed at the same time. The failure of the nitric oxide to suppress in addition the formation of hydrogen chloride must mean that the reaction $NO + Cl \rightarrow NOCl$ is slow. This idea is consistent with the lack of evidence for the reaction in the literature and by its absence as a back reaction in the photolysis of nitrosyl chloride.[6] The probable explanation is that third body restrictions apply.

(d) Acetonyl radicals would be expected to react with iodine, and the fact that acetonylacetone is no longer a product in the presence of iodine (Table II) and that iodoacetone is formed in its place is excellent evidence that this does occur. The formation of hydrogen chloride is also greatly reduced presumably by a similar reaction of I_2 with chlorine atom. Unfortunately, analysis for ICl to confirm this was not possible.

The failure of the iodine to suppress the formation of hydrogen chloride completely and the fact that the reduced value of the quantum yield of HCl is hardly altered by tripling the iodine concentration (Table II) may indicate that a second primary process is occurring to a limited extent, namely

$$CH_3COCH_2Cl + h\nu \longrightarrow CH_3COCH + HCl \quad (1d)$$

However, it is also possible that this hydrogen chloride is formed by secondary reactions instead of by (1d), and the apparent formation of acetone in the presence of iodine is an indication that such secondary reactions are taking place. The iodine system is not entirely straightforward and only further work can permit definite conclusions to be drawn about the hydrogen chloride formation. Further evidence for (1d) might be found in the formation of biacetylethylene as a major product in the normal photolysis. This compound would result from the combination of two CH_3COCH radicals. However, as will be seen later, there are also other ways in which CH_3COCH can be formed besides (1d) and consequently the evidence for HCl formation in a primary process is not conclusive. If it does occur, it accounts at most for only 15% of the absorbed energy.

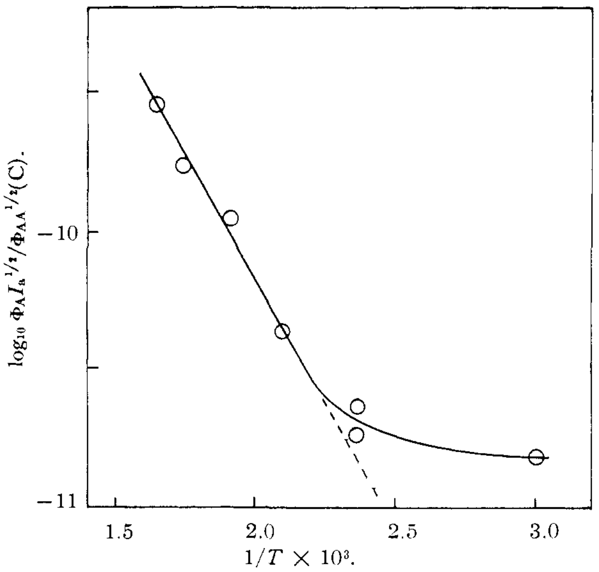

Fig. 1.—Plot of the logarithmic term *vs.* $1/T$ for chloroacetone photolysis. The straight line is consistent with an activation energy of 9 ± 1 kcal./mole.

Finally, the increasing amounts of carbon monoxide, methane and methyl chloride produced at the higher temperatures (Table I) might suggest that the primary processes (1a) and (1b) are beginning to occur at these temperatures. Although this possibility cannot be ruled out, it is more probable that the formation of these products is due to the decomposition of radicals, and that (1a) and (1b) are unimportant under all conditions.

The fact that Φ_{HCl} is near unity in the nitric oxide experiments indicates that the primary quantum yield, ϕ, of reaction (1c) also is 1.

Secondary Reactions.—The results provide evidence for the following secondary reactions

$$2CH_3COCH_2 \longrightarrow (CH_3COCH_2)_2 \quad (2)$$

$$CH_3COCH_2 + CH_3COCH_2Cl \longrightarrow CH_3COCH_3 + CH_3COCHCl \quad (3)$$

$$Cl + CH_3COCH_2Cl \longrightarrow HCl + CH_3COCHCl \quad (4)$$

$$CH_3COCH_2 + Cl \longrightarrow CH_3COCH_2Cl \quad (5)$$

$$2CH_3COCH_2 \longrightarrow CH_3COCH_3 + CH_3COCH \quad (6)$$

$$2CH_3COCH \longrightarrow CH_3COCH{=}CHCOCH_3 \quad (7)$$

Reaction (2) accounts for the formation of acetonylacetone. Other workers[7,8] have also reported evidence for this reaction. Reactions (3) and (4) are hydrogen abstraction reactions which account for acetone and hydrogen chloride in the products. The evidence for reaction (5) lies in the quantum yield of hydrogen chloride which is less than unity at the lower temperatures (Table I), but when nitric oxide is present and reacting with acetonyls, it approaches unity or slightly exceeds it (Table II). Furthermore, a reaction such as (5) would be expected to be more important the greater the concentration of radicals and hence the greater the light intensity. The quantum yield of hydrogen chloride should therefore be smaller at higher light intensities. Comparison of run 2 with run 21 and of 10 with 19 provides confirmation of this.

If reactions (2) and (3) are the only sources of acetonylacetone and of acetone, the following relationship is obtained from the rates of these reactions

$$\log_{10} \frac{\Phi_A I_a^{1/2}}{\Phi_{AA}^{1/2}(C)} = -\frac{E_3 - {}^1/_2 E_2}{2.30\ RT} + \log_{10} \frac{A_3}{A_2^{1/2}}$$

Φ_A and Φ_{AA} are the quantum yields of acetone and acetonylacetone, respectively, and (C) is the concentration of chloroacetone. $\text{Log}_{10}\, \Phi_A I_a^{1/2}/\Phi_{AA}(C)$ is plotted against $1/T$ in Fig. 1. The points are reasonably linear at the higher temperatures but depart from linearity at the two lowest temperatures. The simplest explanation is that reaction (3) is not the only source of acetone. A second acetone producing reaction important at the lower tempera-

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[6] G. B. Kistiakowsky, This Journal, **52**, 102 (1930).

[7] F. O. Rice, E. L. Rodowskas and W. R. Lewis, *ibid.*, **56**, 2497 (1934).

[8] J. R. McNesby, T. W. Davis and A. S. Gordon, *ibid.*, **76**, 823 (1954).

tures but decreasing in importance as the temperature is raised would account for the curvature. Reaction (6) meets these requirements since similar disproportionation reactions have been shown to have small activation energies,[9,10] and in consequence to play their largest role at the lower temperatures. The acetone produced by this disproportionation of acetonyls would be expected to follow a similar trend with temperature to that of the acetonylacetone which is produced by their combination. At 60° the ratio of disproportionation to combination is given simply by Φ_A/Φ_{AA} since at this temperature the acetone from (3) is negligible. If it is assumed that this ratio whose value is 0.76 remains constant, the acetone due to (6) can be calculated for all other runs from Φ_{AA}. Subtraction of this acetone due to disproportionation from the total acetone enables the acetone due to abstraction to be obtained. A plot similar to that in Fig. 1 but using these corrected values of the acetone yield due to (3) gives $E_3 - {}^1/_2E_2 = 9.7$ kcal./mole. This compares with a value of 8.3 kcal./mole obtained from the linear portion of Fig. 1. Since some uncertainties exist as to the assumptions made in obtaining the first value, it seems best to ascribe a mean value of 9 ± 1 kcal./mole to $E_3 - {}^1/_2E_2$. If E_2 is small, 9 ± 1 kcal./mole will be the activation energy for reaction (3). The ratio of the steric factors $P_3/P_2^{1/2}$ proves to be $\sim 10^{-2}$. This is slightly higher than that found for similar pairs of reactions in other systems,[9-11] and may indicate that P_2 is less than unity, probably for steric reasons. The CH_3COCH radicals produced by (6), and by (1d) if it occurs, may combine by (7) and the fact that biacetylethylene is a major product is good evidence for this reaction.

The results do not afford much information as to the fate of the chloroacetonyl radicals produced in (3) and (4). For convenience only one of the two possible isomers has been written in the equations, but the fairly normal activation energy of 8 to 10 kcal. for (3) suggests that hydrogen abstraction may take place at both ends of the chloroacetone molecule and that both chloroacetonyl isomers may be formed. Once formed, it seems reasonable to suppose that these radicals react in ways similar to acetonyls, that they add to chlorine atoms and combine and disproportionate both with themselves and with acetonyls. The peaks found at 148 and 150 are evidence of their combination with acetonyls to form chloroacetonylacetone.

$$CH_3COCHCl + CH_2COCH_3 \longrightarrow CH_3COCHClCH_2COCH_3 \quad (8)$$

The peaks at 131, 133, 146 and 148 support disproportionation reactions such as (9) leading eventually by (10) to monochloro substituted biacetylethylene.

$$CH_3COCHCl + CH_2COCH_3 \longrightarrow CH_3COCCl + CH_3COCH_3 \quad (9)$$

$$CH_3COCCl + CHCOCH_3 \longrightarrow CH_3COCCl{=}CHCOCH_3 \quad (10)$$

Reaction (9), it will be seen, can also be a further source of acetone. This, however, will not seriously affect the calculation made previously of the acetone formed by abstraction, since the trends of acetone from two disproportionation reactions will be very much the same as if the acetone were all arising from one such reaction. It may explain, however, why the ratio of disproportionation to combination of 0.76 appears to be higher than in the case of other radicals[9,10] since the ratio may really represent the sum of two disproportionation reactions (6) and (9) compared with the one combination reaction (2).

Finally, chloroacetonyl radicals may decompose. Above 250° the quantum yield of hydrogen chloride rises above unity and a chain reaction must be taking place. The most obvious chain step is

$$CH_3COCHCl \longrightarrow CH_3COCH + Cl \quad (11)$$

In addition, the increasing amounts of CO, CH_4 and CH_3Cl at the higher temperatures are most likely due to decomposition of all or any of the radicals $CH_3COCHCl$, CH_3COCH_2 and CH_3COCH, followed by abstraction reactions. The total absence of ethane may be due to the presence of hydrogen chloride and to the reaction

$$CH_3 + HCl \longrightarrow CH_4 + Cl \quad (12)$$

followed by regeneration of HCl by abstraction. This has been suggested by other workers[12] to account for similar results.

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[9] C. R. Masson, THIS JOURNAL, **74**, 4731 (1952).

[10] K. O. Kutschke, M. H. J. Wignen and E. W. R. Steacie, *ibid.*, **74**, 714 (1952).

[11] A. F. Trotman-Dickenson, J. R. Birchard and E. W. R. Steacie, *J. Chem. Phys.*, **16**, 553 (1948).

[12] R. Cvetanovic and E. W. R. Steacie, *Can. J. Chem.*, **31**, 158, 171 (1953).