from the flash lamp is rich in short wave lengths. Therefore it is possible that the reaction $NO_2 + h\nu = O + NO$ results in energy-rich, "hot," nitric oxide molecules. These then undergo the reaction

$$NO_2 + NO^* = N_2O + O_2 \qquad (5)$$

The results obtained to date with the time-of-flight mass spectrometer as an analytical device for fast reactions are largely preliminary and qualitative. They show, however, that the apparatus is a useful tool in kinetic research. Further refinements of it and the study of several reactions are continuing, therefore.

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CAMBRIDGE, MASS.

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Photolysis of Dimethyl Ketene Vapor

BY RICHARD A. HOLROYD[1] AND FRANCIS E. BLACET

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The photochemical behavior of dimethyl ketene vapor has been investigated with variations of wave length, pressure and temperature. Propylene and carbon monoxide were found to be the major products but under some conditions small yields of hydrogen, methane and hexene were detected. At 2537 Å. the quantum yield of CO was unity, within experimental error, under all conditions. The quantum yields of C_3H_6 increased (to a limiting value near unity) with either pressure of dimethyl ketene or pressure of added foreign gas. The existence of radical intermediates at this wave length was demonstrated by a tellurium mirror removal experiment. At 3660 Å. the quantum yields were pressure dependent, indicating the formation of a long-lived excited state. The results are interpreted in terms of a wave length dependent primary process.

The behavior of dimethyl ketene under the influence of ultraviolet light was studied as a potential source of isopropylidene radicals. The photolysis of dimethyl ketene had not been reported previous to this investigation. Some work has been reported which involves similar radical intermediates, however. The ethylidene radical has been reported to be an intermediate in the photolysis of methyl ketene[2]; indicating that the primary process is

$$CH_3CHCO + h\nu \longrightarrow CH_3CH + CO \qquad (1)$$

The rearrangement of ethylidene to ethylene appears to be quite rapid but reaction

$$CH_3CH + CH_3CHCO = C_4H_8 + CO \qquad (2)$$

also occurs. Other workers have postulated ethylidene as an intermediate in the pyrolysis of diazoethane[3a] and of ethane,[3b] and in the photolysis of diazoethane.[4,5]

The photolysis of ketene itself has been studied extensively[6] and methylene appears well established as an intermediate. On the basis of the work done on ketene and on methyl ketene, the photolysis of dimethyl ketene was expected to lead to dissociation into CO and isopropylidene

$$(CH_3)_2C{=}C{=}O + h\nu \longrightarrow CH_3\text{-}C\text{-}CH_3 + CO \qquad (I)$$

Thus it would be possible to study the kinetic behavior of this radical.

Experimental

Materials.—Dimethyl ketene was prepared by the pyrolysis of isobutyryl phthalimide in a modified "dimethyl ketene" lamp.[7] It was condensed at −196° and fractionated in a vacuum system to remove impurities, and stored at all times in a trap at −78° to prevent dimerization. A mass spectrogram (see Table IIb) proved the molecular weight to be 70 and also showed no large scale impurities were present. 99.8 per cent. of a sample brought in contact with water was absorbed. The product of this reaction was shown to be isobutyric acid by mass spectral analysis. As an additional check on purity, the ultraviolet spectrum of dimethyl ketene vapor was obtained and found to be similar to the spectrum of diethyl ketene.[8] No ultraviolet spectrum of dimethyl ketene had been reported for comparison. The results are shown in Fig. 1. The infrared spectrum of dimethyl ketene vapor was found to be similar to the published spectrum of ketene[9] as shown in Table I. The carbonyl absorption band at 1700 cm.$^{-1}$ which is typical of

TABLE I

THE INFRARED SPECTRAL BANDS OF KETENE AND DIMETHYL KETENE, CM.$^{-1}$

(s) denotes relatively strong absorption.

Dimethyl ketene	Ketene
	4230
3440	3510
3100	3265
2880(s)	3080(s)
	2540
2380	2290
2120(s)	2155(s)
1960	1967
1450	1402
1390(s)	1376(s)
1335	
1200	1215
	1136(s)
	1111
	1075
990	1048
720	

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[1] Postdoctoral fellow under a grant from the National Research Council Petroleum Research Fund.

[2] G. B. Kistiakowsky and B. H. Mahan, *J. Chem. Phys.*, **24**, 922 (1956).

[3] (a) F. O. Rice and A. L. Glasebrook, THIS JOURNAL, **56**, 741 (1934); (b) R. F. Barrow, T. G. Pearson and R. H. Purcell, *Trans. Faraday Soc.*, **35**, 880 (1939).

[4] D. H. Volman, F. E. Blacet, P. A. Leighton and R. K. Brinton, *J. Chem. Phys.*, **18**, 203 (1950).

[5] R. K. Brinton and D. H. Volman, *ibid.*, **19**, 1394 (1951).

[6] For references see A. N. Strachan and W. A. Noyes, Jr., THIS JOURNAL, **76**, 3258 (1954).

[7] "Organic Reactions," Vol. III, John Wiley and Sons, New York N. Y., 1946, p. 136.

[8] G. C. Lardy, *J. Chem. Phys.*, **21**, 353 (1924).

[9] National Bureau of Standards, Infrared Spectral Tables No. 699.

ketones was absent in both cases, thus eliminating ketones as possible contaminants. The vapor pressure of dimethyl ketene was found to be 1 mm. at −63° and 10 mm. at −37°.

Other Liquids.—**Acetone**: Braun acetone was distilled at a reflux ratio of 720/1 and further purified by vacuum fractionation. **Biacetyl**: Eastman Kodak White Label biacetyl was dried over calcium sulfate and distilled under 60 mm. nitrogen pressure and fractionated. **2,3-Dimethylbutene-2**: a sample of this material was obtained 99.9% pure from the National Bureau of Standards as standard sample No. 540 5S. Its mass spectrum is shown in Table IIa.

TABLE IIa

MASS SPECTRUM OF 2,3-DIMETHYL-BUTENE-2[a]

m/e	Intensity	m/e	Intensity
27	9.2	53	5.9
28	3.5	54	1.2
29	3.7	55	19.1
38	1.8	56	8.2
39	20.0	65	1.4
40	5.8	67	7.8
41	96.1	68	1.6
42	9.4	69	100.0
43	6.9	70	6.9
50	1.3	83	2.2
51	2.3	84	43.9 (p)
52	1.1	85	3.1

TABLE IIb

MASS SPECTRUM OF DIMETHYL KETENE[a]

m/e	Intensity	m/e	Intensity
15	2.4	41	73.6
25	1.4	42	16.0
26	4.6	43	8.1
27	13.5	53	1.8
28	12.1	55	2.0
36	2.1	68	3.9
37	6.4	69	1.7
38	8.6	70	100.0 (p)
39	37.9	71	4.5
40	26.0		

[a] Electron energy = 70 volts; accelerating potential = 400 volts; (only peaks with intensities greater than 1% of the parent have been included).

Gases.—**Carbon dioxide** was prepared by subliming Dry Ice and drying the evolved gas. It was degassed at −196° and found to be 99.9% pure. Oxygen was prepared by evaporating from a sample of liquid oxygen which had been condensed from cylinder oxygen. Hydrogen was taken from a cylinder and found to 99% pure.

Solids.—**Te**: Te metal was prepared by precipitation from an aqueous HCl solution of TeO_2 with SO_2 gas. **Tetramethylcyclobutanedione-1,3**: the absorption spectrum of this compound, the dimer of dimethyl ketene, showed two regions of absorption in the ultraviolet. One band showing some structure was found with peaks at 2830, 2960, 3030 and 3080 Å. The second band was broad with an absorption maximum at 3470 Å. The dimer was transparent, however, at both 2537 and 3660 Å. and since these were the two wave lengths utilized in this investigation, any dimer present as a contaminant would not cause a significant photochemical reaction.

Apparatus.—The light source was a Hanovia type A medium pressure Hg arc. For most of the experiments the 2537 Å. line was obtained by filtering the light with chlorine gas and $NiSO_4$ filters. Since dimethyl ketene does not absorb much beyond 4200 Å., the effective radiation was between 2200 and 2800 A. with a maximum at 2500 Å. For the determination of quantum yields, a quartz monochromator was used to isolate the 2537 Å. line. The 3660 A. line of the Hg arc was isolated with 9 mm. of a Corning 7–37 filter. Relative intensities were determined with a photocell. All products were analyzed on a modified model of a Westinghouse type LV mass spectrometer. For the determination of quantum yields, actinometers were used. The yield of CO from the photolysis of acetone was used as a measure of the light intensity at 2537 Å. The quantum yield of CO was assumed to be unity under these experimental conditions. The photolysis of biacetyl, for which the quantum yield of CO as a function of pressure and intensity has been determined,[10] was used as an actinometer at 3660 Å.

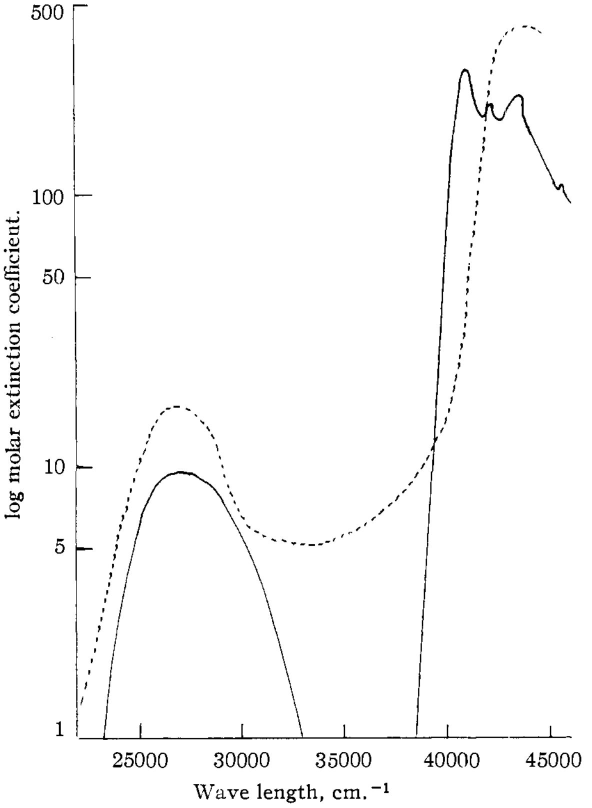

Fig. 1.—Ultraviolet absorption spectrum of dimethyl ketene and diethyl ketene: ———, dimethyl ketene vapor; ---------, diethyl ketene in hexane.

To test for the existence of radicals, a tellurium mirror removal experiment was tried. The apparatus was in all essential respects identical to that described by D. H. Volman.[4] Acetone was used to test for active mirrors and found to remove mirrors in 2 to 3 minutes using 2537 Å. radiation from a low pressure Hg resonance arc.

Results

The quantum yield of carbon monoxide under various experimental conditions is given in Table III.

TABLE III

QUANTUM YIELD OF CARBON MONOXIDE UNDER VARIOUS CONDITIONS AT 2537 Å.

Temp., °C.	Dimethyl ketene, moles/l. × 10^{+4}	I_a, Einsteins/sec. × 10^{10}	Φ_{CO}
30	46.6	4.11	1.06
30	26.7	3.22	0.94
36	1.34	0.479	1.11
176	46.6	3.84	1.15
			Av. 1.06 ± 0.06

There seems to be no significant trend in the quantum yield of carbon monoxide either with pressure, intensity or temperature over the range investigated.

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(10) G. F. Sheats and W. A. Noyes, Jr., THIS JOURNAL, **77**, 4532 (1955).

Photolysis of Dimethyl Ketene at 2537 Å.—Table IV shows the effect of varying the pressure of dimethyl ketene on hydrocarbon to carbon monoxide ratio. Since the quantum yield of CO is unity, the ratio propylene/CO may be equated to the quantum yield of propylene. At high pressures the yield of propylene is nearly unity at 30°. As the pressure is decreased below 10^{-3} mole/liter, the yield of propylene drops off rapidly and methane becomes a more important product. Variation of the intensity does not affect substantially the ratios of the products. Wall effects are not important at low pressures since the addition of large amounts of hydrogen has little effect on the ratios of products.

The effect of temperature is also shown in Table IV. The yield of propylene decreases with increasing temperature and methane is formed in larger yield, although even at the highest temperatures methane is still a relatively minor product. Hydrogen also is found in some runs at low pressures, but it is never more than 1% of the products.

TABLE IV

RATIOS OF PRODUCTS AT 2537 Å. FOR PURE DIMETHYL KETENE

Temp., °C.	Dimethyl ketene, moles/l. $\times 10^4$	I_a, Einsteins/sec. $\times 10^9$	C_3H_6/CO	CH_4/CO
30	123.6	4.13	0.92	...
30	73.8	3.77	.94	...
30	47.1	4.12	.97	...
30	32.1	5.86	.90	0.007
30	9.6	3.85	1.00	.005
30	5.1	2.68	0.80	.008
30	1.6	2.29	.76	.010
30	1.34	0.053	.70	.010
30	0.41	1.03	.52	.012
30	0.17	0.25	.43	.015
30	0.064	0.11	.37	.014
79	9.6	5.23	.94	.010
132	9.9	6.79	.83	.014
175	1.0	2.77	.52	.017
175	0.59	2.23	.58	.021
175	0.21	....	.44	.023
204	9.4	8.39	.76	.018
230	11.2	20.5	.78	.017

At low pressures and all temperatures there is an obvious lack of material balance. If the quantum yield of CO is equated to the yield of dimethyl ketene disappearance, there are not enough hydrocarbon products to account for the amount of dimethyl ketene decomposed. Mass spectrometric analysis of the condensable products shows that one or many high molecular weight products are formed. These products have not been characterized, but a comparison of the spectrum with that of tetramethylethylene shows that this isomer of hexene is not produced in any significant amount. Examination of the photolysis cell following a series of photolyses revealed the presence of a polymeric deposit on the cell walls, qualitatively accounting for the missing products.

Table V shows the effect of various foreign gases on the photolysis under conditions of constant absorbed intensity and constant dimethyl ketene pressure. For pure dimethyl ketene at a concentration of 0.67×10^{-4} mole/liter, the quantum yield of propylene is 0.58 at 30°. The addition of an inert gas such as carbon dioxide causes an increase in this yield and when a sufficient amount of carbon dioxide has been added, the quantum yield of propylene is nearly unity.

TABLE V

2537 Å. RESULTS—EFFECT OF FOREIGN GASES—TEMP., 30°

Dimethyl ketene, moles/l. $\times 10^4$	Foreign gas, moles/l. $\times 10^4$	I_a, Einsteins/sec. $\times 10^9$	C_3H_6/CO
0.67	0	1.04	0.58
.62	16.3 (H_2)	1.34	.65
.67	17.6 (CO_2)	0.66	.72
.68	27.1 (CO_2)	1.07	.82
.65	53.2 (CO_2)	0.97	.95
.69	163 (CO_2)	.88	0.97
.60	18.7 (C_6H_{14})	.54	1.2

TABLE VI

QUANTUM YIELDS AT 3660 Å.

Temp., °C.	Dimethyl ketene, moles/l. $\times 10^4$	I_a, Einsteins/sec. $\times 10^9$	Φ_{CO}	$\Phi_{C_3H_6}$	$k_8/k_9 \times 10^{-}$
31	0.69	0.129	0.039	0.038	22
31	6.07	0.948	.0073	.0061	25
31	39.4	3.31	.0015	.0011	23
31	81.6	5.83	.00098	.00060	20
				Av.	22 ± 2
60	6.15	1.17	.0074	.0067	
90	5.93	1.15	.011	.010	

A series of experiments were performed to detect radical intermediates in the photodecomposition. First hydrogen was used as a scavenger for isopropylidene radicals.

$$CH_3\text{-}C\text{-}CH_3 + H_2 \longrightarrow CH_3\text{-}CH\text{-}CH_3 + H \quad (3)$$

The analogous reaction of hydrogen with methylene is known to occur.[11] In an experiment at 186° with a large excess of hydrogen present, no propane was formed. This indicated that no abstraction reactions such as (3) occurred under the experimental conditions.

Oxygen was tried as a scavenger for isopropylidene radicals. However, oxygen and dimethyl ketene react thermally to give acetone and carbon dioxide in a ratio of 0.85 to 1. The rate of this reaction is slow so that its contribution to the photooxidation may be calculated. When oxygen is added, the yield of propylene from the photolysis decreases slightly while the formation of acetone and carbon dioxide is enhanced. This suggests the occurrence of a reaction such as

$$CH_3\text{-}C\text{-}CH_3 + O_2 \longrightarrow CH_3\text{-}CO\text{-}CH_3 + O \quad (4)$$

However, because of the dark reaction, the results are in question.

As a final test for radicals, the Paneth mirror removal technique was used. Dimethyl ketene in a flow system at a pressure of about 1 mm. was found to remove tellurium mirrors when photolyzed with 2537 Å. radiation. The length of time necessary to remove a mirror was somewhat longer for dimethyl ketene than for acetone. This experiment supports the existence of radicals as intermediates in the photolysis.

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[11] H. Gesser and E. W. R. Steacie, *Can. J. Chem.*, **34**, 113 (1956).

Photolysis of Dimethyl Ketene at 3660 Å.—The photochemical behavior of dimethyl ketene is markedly wave length dependent. At 3660 Å. the quantum yields are low and pressure dependent. As shown in Table VI, carbon monoxide and propylene are still the major products and the yield of both decreases as the pressure increases. Methane and hydrogen are not products at this wave length, but the mass spectral data show that a hexene is produced particularly at higher pressures. Because of the low quantum yields, necessitating lengthy photolyses, few runs were done at 3660 Å.

Discussion

The results of this investigation are similar in many respects to the photochemical behavior of both ketene[6] and methyl ketene.[1] The primary process in ketene at short wave lengths is direct dissociation into CO and methylene. The behavior of methyl ketene is similar in that rupture of the carbon–carbon double bond probably occurs and the intermediate, ethylidene, isomerizes to ethylene. If the primary process in dimethyl ketene is

$$(CH_3)_2{=}C{=}C{=}O + h\nu \longrightarrow CH_3\text{-}C\text{-}CH_3 + CO \quad \text{(I)}$$

the isopropylidene radical may be expected to isomerize similarly to propylene. Because of the wave length effect, the results at 2537 and 3660 Å. will be discussed separately.

2537 Å.—Absorption of light of this wave length leads to direct dissociation into isopropylidene and CO as in (I). The validity of this is supported by the following observations: (1) the mirror removal experiments indicate that radicals are present in the photolysis and the possibility of a direct intramolecular rearrangement into propylene and CO is excluded. (2) The lack of variation of Φ_{CO} with dimethyl ketene concentration and with the concentration of added foreign gases such as CO_2 demonstrate that the primary process does not involve an excited dimethyl ketene molecule. (3) The variation of the yield of propylene with pressure points to a reaction other than intramolecular rearrangement for the formation of propylene.

Although a complete mechanism cannot be given at this time, a set of reactions may be suggested which qualitatively explain the results. Propylene is formed by isomerization of isopropylidene.

$$CH_3\text{-}C\text{-}CH_3 \longrightarrow C_3H_6^* \quad (5)$$

Since tetramethylethylene is not a product, reaction 5 must be fast compared to the dimerization of isopropylidene. Reaction 5 is probably exothermic by the same amount as the isomerization of ethylidene to ethylene, that is, by about 65 kcal./mole.[2] Therefore, one expects propylene to be formed with some excitation energy, necessitating stabilization by collision.

$$C_3H_6^* + M \longrightarrow C_3H_6 + M \quad (6)$$

$C_3H_6^*$ may also decompose at low pressures providing there is sufficient energy available.

$$C_3H_6^* \longrightarrow D \quad (7)$$

Studies of the pyrolysis of propylene have suggested activation energies as low as 57.1 kcal./mole,[12] and as high as 72 kcal./mole[13] for the decomposition. Products of the pyrolysis include methane, hydrogen, ethane, ethylene and higher hydrocarbons.

It is reasonable to assume that $C_3H_6^*$ may decompose if it is not quickly deactivated by collision. This is consistent with the increase in the methane yield at low pressures and the effect of inert gases such as CO_2 on the propylene yield. The data for dimethyl ketene alone at 30° may be used to estimate k_7/k_6 which is found to be $\sim 5 \times 10^{-5}$ mole/liter. If the isopropylidene radical also contains excess energy from the primary process, then propylene will be formed with energy in excess of the assumed 65 kcal./mole.

If the decomposition of propylene involves monovalent radicals, these will add to dimethyl ketene forming high molecular weight products and polymers. Such radical addition reactions are well known. Ketene itself reacts with methyl radicals to form acetonyl[11] and Bell and Blacet have shown that methyl radicals add to the carbonyl group in biacetyl.[14]

3660 Å.—The results at this wave length cannot be interpreted in terms of the mechanism proposed for shorter wave lengths. It is necessary to invoke an entirely different primary process to explain the results. The quantum yields for propylene and CO are well below unity and decrease with increasing dimethyl ketene concentration. This suggests that the absorption of light leads to an excited state which may be quenched by collision similar to the primary process in ketene at this wave length.[6] The following mechanism is proposed

$$(CH_3)_2{=}C{=}C{=}O + h\nu \longrightarrow (CH_3)_2{=}C{=}C{=}O^* \quad \text{(II)}$$

$$(CH_3)_2{=}C{=}C{=}O^* + (CH_3)_2{=}C{=}C{=}O \longrightarrow 2(CH_3)_2{=}C{=}C{=}O \quad (8)$$

$$(CH_3)_2{=}C{=}C{=}O^* \longrightarrow CH_3\text{-}C\text{-}CH_3 + CO \quad (9)$$

$$CH_3\text{-}C\text{-}CH_3 + (CH_3)_2{=}C{=}C{=}O \longrightarrow CO + \text{hexene} \quad (10)$$

$$(CH_3)_2{=}C{=}C{=}O^* \longrightarrow (CH_3)_2{=}C{=}C{=}O \quad (11)$$

Since the ratio of propylene to carbon monoxide is never unity except at low concentrations, equation 9 cannot be an intramolecular rearrangement but instead must form isopropylidene. The identification of hexene in the products necessitates reaction 10. The isopropylidene radical reacts as in (10) but also isomerizes *via* reactions 5 and 6. Because of the lower value of the Einstein at 3660 Å., this radical will contain less excess energy which probably accounts for the lack of observation of decomposition products of propylene.

If reaction 10 is neglected, the mechanism predicts that

$$1/\Phi_{C_3H_6} = 1 + k_{11}/k_9 + k_8(\text{DMK})/k_9$$

If a plot of $1/\Phi_{C_3H_6}$ as a function of the dimethyl ketene concentration is made, the best straight line through the points has an intercept of about 11 and a slope of 22×10^4. Therefore $k_8/k_9 = 22 \pm 2 \times 10^4$ liters/mole and $k_{11}/k_9 = 10$.

The primary process for ketene at this wave

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[12] K. U. Ingold and F. J. Stubbs, *J. Chem. Soc.*, 1749 (1951).

[13] M. Szwarc, *J. Chem. Phys.*, **17**, 284 (1949).

[14] W. E. Bell and F. E. Blacet, THIS JOURNAL, **76**, 5332 (1954).

length is similar and the reactions corresponding to reactions 8, 9 and 11 are 13, 14 and 15, respectively.

$$CH_2CO + h\nu \longrightarrow CH_2CO^* \qquad (12)$$

$$CH_2CO + CH_2CO^* \longrightarrow 2CH_2CO \qquad (13)$$

$$CH_2CO^* \longrightarrow CH_2 + CO \qquad (14)$$

$$CH_2CO^* \longrightarrow CH_2CO \qquad (15)$$

The ratio k_{13}/k_{14} for ketene is 4.7 × 10^4 liters/mole.[6] The close agreement of the two ratios: k_{13}/k_{14} and k_8/k_9, is indicative of the similarity of the primary processes in ketene and dimethyl ketene. An internal conversion of CH_2CO^* to the ground state is important in ketene[15] and appears to be important in dimethyl ketene. The value of k_{11}/k_9 compares well with the value of k_{15}/k_{14} which is of the order of 26 at room temperature.

A calculation of the mean life of $(CH_3)_2{=}C{=}C{=}O^*$ from the integrated absorption coefficient gives $\tau = 2 \times 10^{-6}$ second, which is longer than the mean life for CH_2CO^* which is 0.3×10^{-6} second.[6] However, a longer lifetime would be expected for $(CH_3)_2{=}C{=}C{=}O^*$ because of the extra degrees of freedom in this molecule.

Conclusion

The results reported in this paper indicate a similarity in the photochemical behavior of the three ketenes investigated so far. The primary process is wave length dependent and similar in ketene and dimethyl ketene, but secondary reactions are different. Ketene, itself, is unique in that methylene cannot isomerize to a stable molecule as can ethylidene and isopropylidene. The rate of isomerization of isopropylidene is probably faster than the rate of isomerization of ethylidene since six hydrogens are available to shift; however, there is no evidence to verify this hypothesis.

Acknowledgment.—The authors are indebted to Mr. R. Vanselow for his assistance and helpful suggestions.

LOS ANGELES, CALIF.

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(15) G. B. Porter, THIS JOURNAL, **79**, 827 (1957).

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

The Photolysis of Trimethylamine[1]

BY H. GESSER, J. T. MULLHAUPT AND J. E. GRIFFITHS

RECEIVED APRIL 10, 1957

The photochemical decomposition of trimethylamine was investigated over the temperature range of −78 to 175°. The products were hydrogen, methane, ethane and a "liquid." At high temperatures the methane and ethane are primarily formed by the abstraction and recombination reactions of methyl radicals and the hydrogen is formed by a molecular reaction. At low temperatures both methane and hydrogen are probably formed by molecular elimination reactions.

Introduction

The photochemical decomposition of the amines have not been investigated in great detail. The photolysis of methylamine[2] seems complicated by the possibility of more than one primary process. The mechanism of the photolytic decomposition of dimethylamine and trimethylamine is even more uncertain. Bamford[3] had shown that the products of the photolysis of trimethylamine at 100° were hydrogen, methane, ethane and polymer. The mechanism he proposed to account for these products is

$$(CH_3)_3N + h\nu \longrightarrow (CH_3)_2N + CH_3 \qquad (1)$$

$$2(CH_3)_2N \longrightarrow (CH_3)_2NH + CH_3\dot{N}CH_2 \qquad (2)$$

$$(CH_3)_2NH + h\nu \longrightarrow (CH_3)_2N + H \qquad (3)$$

$$(CH_3)_2NH + H \longrightarrow (CH_3)_2N + H_2 \qquad (4)$$

$$(CH_3)_2NH + CH_3 \longrightarrow (CH_3)_2N + CH_4 \qquad (5)$$

$$H + CH_3 \longrightarrow CH_4 \qquad (6)$$

$$2CH_3 \longrightarrow C_2H_6 \qquad (7)$$

$$CH_3\dot{N}CH_2 \longrightarrow CH_3{-}N{=}CH_2 \longrightarrow \text{Polymer} \qquad (8)$$

This mechanism must be revised in view of the comparatively low value of 8.8 kcal.[4] for the activation

$$CH_3 + (CH_3)_3N \longrightarrow CH_4 + (CH_3)_2NCH_2 \qquad (9)$$

energy of the abstraction reaction in comparison to 7.2 kcal.[4] for reaction 5.

TABLE I

System A; Reaction time, 4.5 hr.

[TMA]	[C_5H_{10}]	Temp., °K.	R_{CH_4}	$R_{C_2H_6}$	R_{H_2}	$k_4/k_7{}^{1/2}$ (mol./cm.^{3}/sec.)$^{1/2}$ × 10^{13}
molecules/cm.^{3} × 10^{-18}			molecules/cm.^{3}/sec. × 10^{-12}			
1.61		299	0.58	1.51	0.96	3.9
1.62	1.44	298	0.50	1.46	0.72	
1.40		347	1.21	1.52	1.05	7.4
1.39	1.28	349	1.04	1.56	0.98	
1.22		398	1.99	1.79	1.55	12.2
1.22	1.22	400	2.45	1.43	1.20	
1.09		448	3.42	0.88	1.50	33.4
1.09	1.09	445	3.62	0.29	1.21	

It was believed that the mechanism could be tested by a study of the product yields in the presence of a hydrocarbon and at low temperatures where reactions requiring high activation energies would become unimportant. Cyclopentane was chosen as the hydrocarbon because its vapors did not interfere with the analysis of the products and because it has a low value for the activation energies of abstraction by hydrogen atoms, 7.7 kcal.[5] and methyl radicals, 8.5 kcal.[4]

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[1] This work was supported in part by a Naval Research Contract of the U. S. Navy and by the National Research Council of Canada.

[2] For review see W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941.

[3] C. H. Bamford, *J. Chem. Soc.*, 17 (1939).

[4] A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951).

[5] H. I. Schiff and E. W. R. Steacie, *Can. J. Chem.*, **29**, 1 (1951).