in turn, stems from the inaccuracy in the X-ray crystal density.

Under the assumption that $T_{\mathrm{m}}^{\mathrm{i}}$ represents the melting temperature of crystalline rubber when subject to no elastic deformation, the latent entropy for the latter hypothetical process may be obtained merely by dividing $\Delta H_{(c \to a)}$ by $T_{\mathrm{m}}^{\mathrm{i}}$. We thus find

$T_{\mathrm{m}}^{\mathrm{i}}$ = 302°K.
ΔH_{u} = 1280 ± 150 cal. per mole of C_5H_8
ΔS_{u} = 4.2 ± 0.4 cal. deg.$^{-1}$ per mole C_5H_8

These results compare favorably with those previously obtained by Roberts and Mandelkern[17] from the depression of the melting point of vulcanized rubber by diluents, namely

$T_{\mathrm{m}}^{\mathrm{i}}$ = 301°K.
ΔH_{u} = 1040 ± 60 cal. mole^{-1}
ΔS_{u} = 3.5 ± 0.2 cal. deg.$^{-1}$ mole^{-1}

We conclude that the transformation of highly orientated racked rubber, cross-linked by γ-radiation, to the amorphous state can be satisfactorily treated as a phase change. In particular, the dependence of the equilibrium stress on the temperature is in complete accord with the requirements of thermodynamic equilibrium between phases.

The authors are indebted to Drs. Mandelkern and Roberts for providing the samples used in this investigation and to Dr. Mandelkern for detailed suggestions and criticisms with reference to the interpretation of the results and the preparation of the manuscript.

PITTSBURGH 13, PA.

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[17] D. E. Roberts and L. Mandelkern, THIS JOURNAL, **77**, 781 (1955).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY AND THE DIVISION OF PHYSICAL SCIENCES, UNIVERSITY OF CALIFORNIA, RIVERSIDE]

Vapor-phase Photochemistry of *trans*-Methyl Propenyl Ketone[1,2]

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The vapor-phase photolysis of pure *trans*-methyl propenyl ketone (*trans*-3-penten-2-one) was studied over a wide range of temperatures, pressures and wave lengths. This α,β-unsaturated ketone is unusually stable toward photo-dissociation into radicals. At 25° from 3130 to 2380 Å. and at 3130 Å. and temperatures up to 275°, a photo-rearrangement of the *trans* to the *cis* isomer is the only significant reaction. At 2380 Å. and above 125°, reactions leading to non-condensable products become important. Φ_{CO} exceeds unity at 275° and pressures below 10 mm. Other non-condensable products are 2-butene, methane, propene and ethane in decreasing order of abundance. At 200 and 275°, the reciprocals of the quantum yields of CO, C_4H_8, C_3H_6 and CH_4 are directly proportional to pressure but independent of intensity. The ratios C_4H_8/CO, C_3H_6/CO and CH_4/CO are independent of pressure. Methyl isobutyl ketone is apparently a condensable product. A mechanism is proposed in which the primary process is formation of a photo-excited molecule.

The effects of structure on photochemical decompositions have been noted in ketones having successively larger alkyl substituents, with cyclic ketones and with ketones with cyclic side chains.[3,4] It seemed worthwhile to extend these studies of structure and photochemical reactivity to ketones with unsaturated aliphatic side chains and, in particular, to the conjugated system exhibited by *trans*-methyl propenyl ketone (*trans*-3-penten-2-one).

Experimental

The *trans* form of methyl propenyl ketone was prepared by the action of dimethylcadmium on crotonoyl chloride.[5-7] The product was purified by distillation through a Piros–Glover spinning band column at a reflux ratio of 20:1, and the fraction boiling at 121.1° was retained. Its refractive index was $n^{20}\mathrm{D}$ 1.4357 compared to $n^{20}\mathrm{D}$ 1.4350 in the I. C. T. The sample was distilled *in vacuo* into a reservoir where it was stored over Drierite at −80°.

Mallinckrodt "analytical grade" acetone was used as an actinometer. It was treated with Drierite, then distilled *in vacuo* into a storage reservoir. The quantum yield of carbon monoxide formation from the photolysis of acetone was assumed to be 1.00 at 125° and 50 mm. pressure.[8]

Photolyses were carried out in a cylindrical quartz reaction cell 200 mm. long and 30 mm. outside diameter. The cell volume was about 125 cc. A Hanovia "type A" Alpine Burner was mounted at the entrance slit of the quartz monochromator (Farrand Model 300 UV), and the light beam emerging from the monochromator was collimated by a 6" focal length quartz lens. The diameter of the light beam was adjusted so that the beam just filled the reaction cell. Relative light intensities were measured with an RCA 935 phototube in conjunction with an American Instrument Company microphotometer unit No. 10-210.

The quartz reaction cell was mounted in an aluminum block furnace inside an air-thermostated chamber. A trap, mercury manometer and the tubing and stopcocks leading to the reaction cell were also enclosed in the air-thermostat. The stopcocks connected the reaction cell to the methyl propenyl ketone supply, the actinometer supply and the sample collecting system. The furnace temperature was controlled with a Brown potentiometer, while the air-thermostat temperature was maintained at about 60° with a Fenwal thermoswitch.

Ward–LeRoy stills[9] were used to control the temperature, at which the photolysis products were collected. After each run, gases volatile at −110° were collected from the stills by means of a mercury diffusion pump in series with a

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[1] Abstracted in part from the Ph.D. thesis submitted to Northwestern University by R. S. Tolberg who held an Atomic Energy Commission Pre-doctoral Fellowship, 1951–1953. Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Cincinnati, Ohio, April 6, 1955.

[2] Communications should be addressed to J. N. Pitts, Jr., Division of Physical Sciences, University of California, Riverside, California.

[3] E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publishing Co., New York, N. Y., 1954.

[4] J. N. Pitts, Jr., *J. Chem. Ed.*, **34**, 112 (1957).

[5] The authors are indebted to Dr. John Patterson who prepared the sample used in these studies.

[6] H. C. Brown, THIS JOURNAL, **60**, 1325 (1938).

[7] J. Cason, *Chem. Revs.*, **40**, 15 (1947).

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

[9] D. J. LeRoy, *Can. Jour. Res.*, **B28**, 492 (1950).

Toepler pump. The gases were transferred to a Blacet-Leighton apparatus where carbon monoxide was removed by means of a silver oxide bead or a fused copper oxide-potassium hydroxide bead. The residual gases were analyzed for hydrocarbons on a Westinghouse type LV mass spectrometer.

The mass spectrum of the products showed the presence of butene. To determine which isomer was present, the butene was isolated from the remaining products with the aid of the Ward-LeRoy stills, the diffusion pump, and Toepler pump. Gases lighter than butene were removed with the LeRoy still at 150°, and butene was collected with the still temperature at 138°. The mass spectrum of this sample was compared with the mass spectra of standard samples of the butene isomers, and the unknown was identified as 2-butene. However, the percentage of the *cis* and *trans* isomers could not be determined with the mass spectrometer.

The condensable fractions from several runs were studied with either the mass spectrometer or a Beckman IR2T infrared spectrophotometer. The samples analyzed on the mass spectrometer were prepared by a rough separation of the condensables into three fractions. With the sample frozen in a Ward-LeRoy still, the temperature of the still was raised to −80°, and any volatile components were frozen into a trap at −190°. A second fraction was taken at −70°, and the remainder was frozen into a third trap on the manifold. Mass peaks from 166 to 27 were determined manually for these samples.

Results

Methyl propenyl ketone is remarkably stable toward photo-dissociation into gaseous products when irradiated with ultraviolet light. At room temperature, no decomposition was apparent with 3130 or 2380 Å. radiation. The full intensity of the mercury arc, however, led to gaseous products and to the condensation of a red-brown polymer on the quartz window.

The amount of decomposition increased with increasing temperature and with decreasing wave length. At 275°, 3130 Å. and 18 mm. pressure, the quantum yield of carbon monoxide was about 0.1. At shorter wave lengths, Φ_{CO} increased rapidly until at 2380 Å., 275°, and the same pressure, Φ_{CO} was 0.8.

Although no decomposition was observed at room temperature, infrared analysis of the recovered ketone showed the presence of the *cis* isomer of methyl propenyl ketone as well as the original *trans* isomer. This *trans-cis* conversion was observed at room temperature following irradiation at either 3130 or 2380 Å. It is probably the main reaction, even at 275°, with 3130 Å. radiation but no quantitative measure of this conversion was obtained. A 12 hr. dark run at 275° and 14.5 mm. showed no *trans-cis* conversion and no significant decomposition.

Table I presents the results of the photolyses at 2380 Å. at a series of temperatures, pressures and intensities. The quantum yields of all products show pronounced temperature and pressure dependence. They increase as the temperature is raised and the pressure is lowered. For example, a decrease in the pressure of methyl propenyl ketone from 38 to 2.5 mm. results in the doubling of Φ_{CO}. At pressures less than 10 mm., the quantum yield of carbon monoxide exceeds unity.

The absorption spectra of acetone and methyl propenyl ketone differ sharply and the largest source of error in the *absolute* values of the quantum yields of products arises from the use of acetone as an actinometer. The magnitude of this error is difficult to estimate. The *relative* values of Φ_{CO} should be good to about ±5%. The errors in the butene and methane yields are also about ±5%, while for propene and ethane they are approximately ±10% and >10%, respectively.

Although the individual quantum yields showed a strong pressure dependence, the ratios of the quantum yields of 2-butene, methane and propene to Φ_{CO}, given in Table II were essentially constant over the entire pressure range from 38 to 2.5 mm. at 275° and 9.0 to 17.5 mm. at 200°. This indicated that collisional deactivation may have been responsible for the decrease in quantum yields with increasing pressure. To test this possibility, an inert gas, carbon dioxide, was added to the system in run 54. In comparing the results of this run with that on the pure ketone (run 52), it is evident that the added carbon dioxide depressed the individual quantum yields by about 25%, but the ratios of the quantum yields of either C_4H_8, CH_4 or C_3H_6 to Φ_{CO} were unchanged.

The effect of intensity on the product yields is demonstrated by runs 52, 51 and 57. A reduction in light intensity from 2.08×10^{14} to 1.03×10^{14} quanta absorbed per second, reduced the production of ethane by a factor of two but, within experimental error, had no effect on the other quantum yields. An over-all reduction by a factor of about six to $I_a = 0.36 \times 10^{14}$ gave, for a very long run, a value of about 1.2 for the quantum yield of carbon monoxide. This increase in Φ_{CO} may be real, although, at these very low light intensities and long runs the error in Φ_{CO} is at least ± 10%. Analyses were not obtained for the hydrocarbon products.

Mass spectrometric analysis of fractions of the condensate from run 48 showed the presence of a hexadiene and other compounds, presumably ketones, with masses up to 166. The structure of the hexadiene was not established other than the negative evidence that it was not the 1,5-hexadiene or the 2,3-dimethyl-1,4-butadiene. Certain peak ratios in the mass spectra agreed with those for 4-methyl-2-pentanone found in the A.P.I. Tables.

Because of the similarity of the structures of crotonaldehyde and methyl propenyl ketone, one photolysis of the aldehyde was carried out under the following conditions: 265°, 15 mm. pressure, $I_a = 2.6 \times 10^{14}$ quanta/sec. In addition to the hydrogen, methane and propylene reported previously,[10,11] small amounts of butene and ethane were found in the present study. The quantum yields were CO = 1.45, $C_3H_6 = 0.51$, $H_2 = 0.10$, 2-butene = 0.05, $CH_4 = 0.07$ and $C_2H_6 = 0.006$. The significance of these results and those of Blacet and co-workers is discussed briefly in connection with the proposed mechanism for methyl propenyl ketone photolysis.

Discussion

The stability of *trans*-methyl propenyl ketone toward photodissociation is in sharp contrast to the aliphatic ketones. For example, in the case of acetone, methyl ethyl ketone, diethyl ketone, di-*n*-propyl ketone, diisopropyl ketone and methyl *n*-

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(10) F. E. Blacet and J. G. Roof, THIS JOURNAL, **58**, 73 (1936).

(11) F. E. Blacet and J. E. LuValle, *ibid.*, **61**, 273 (1939).

TABLE I

QUANTUM YIELDS FROM THE PHOTOLYSIS OF METHYL PROPENYL KETONE AT 2380 Å.

Run no.	Temp., °C.	Time, sec. × 10^{-4}	Pressure of MPK, mm.	I_a, (quanta abs./sec.) × 10^{-14}	Quantum yields				
					Carbon monoxide	2-Butene	Propene	Methane	Ethane
22	60	7.52	19.0	3.15	0.015	n.d.	n.d.	n.d.	n.d.
60	125	6.73	10.0	1.97	.14	0.025	0.016	0.015	0.004
33	200	1.21	9.0	2.53	.53	.13	.072	.064	.009
42	200	1.80	11.5	2.22	.43	.077	.040	.043	.003
41	200	2.16	12.5	2.33	.40	.074	.033	.038	.002
34	200	1.48	17.5	2.64	.27	.063	.034	.034	.003
53	275	0.90	2.5	1.65	1.23	.35	.15	.24	.016
50	275	1.44	5.0	1.93	1.15	.32	.13	.22	.010
52	275	1.09	10.5	2.08	0.96	.28	.10	.17	.007
48	275	4.06	28.5	2.35	0.64	.19	.073	.11	.001
49	275	1.44	38.0	2.36	0.57	.16	.071	.09	.001
54[a]	275	1.39	10.5	2.06	0.72	.20	.075	.13	.004
57	275	8.71	10.5	0.36	1.2	n.d.	n.d.	n.d.	n.d.
51	275	3.92	10.5	1.03	0.99	0.28	0.10	0.19	0.003

[a] 22.5 mm. pressure of carbon dioxide added. n.d.—not determined.

TABLE II

RATIOS OF QUANTUM YIELDS OF THE NON-CONDENSABLE PRODUCTS TO THE QUANTUM YIELDS OF CO AT 2380A.

Run no.	Temp., °C.	Pressure ketone, mm.	I_a, (quanta abs./sec.) × 10^{-14}	Ratios of quantum yields			
				C_4H_8/CO	C_3H_6/CO	CH_4/CO	C_2H_6/CO
60	125	10.0	1.97	0.18	0.11	0.11	0.028
33	200	9.0	2.53	.25	.14	.12	.017
42	200	11.5	2.22	.18	.093	.10	.007
41	200	12.5	2.33	.19	.083	.095	.005
34	200	17.5	2.64	.23	.13	.13	.011
			Av.	.21 ± 0.03	.11 ± 0.02	.11 ± 0.01	
53	275	2.5	1.65	.28	.12	.20	.013
50	275	5.0	1.93	.28	.11	.19	.009
52	275	10.5	2.08	.29	.10	.18	.007
48	275	28.5	2.35	.30	.11	.17	.002
49	275	38.0	2.36	.28	.12	.16	.002
			Av.	.29 ± 0.01	.11 ± 0.01	.18 ± 0.01	
54[a]	275	10.5	2.06	.28	.10	.18	.006
51[b]	275	10.5	1.03	.27	.10	.19	.003

[a] 22.5 mm. of CO_2 added. [b] Lower intensity run.

butyl ketone, the sum of the primary quantum yields of dissociation are at least 0.5 at 3130 Å. and 120°.[3,4] Under similar conditions the quantum yield of carbon monoxide is less than 0.01 for the α,β-unsaturated ketone. At room temperature and wave lengths from 3130 to 2380 Å. the *trans-cis* conversion is the only reaction of significance. The analogous compound, crotonaldehyde, is far more stable than the aliphatic aldehydes over this wave length range, and there is little doubt that in each case the C═C bond in conjugation with the carbonyl group is responsible.

The photochemistry of *trans*-methyl propenyl ketone differs in another important respect from that of the aliphatic ketones. Addition reactions to the olefinic bond are important, and the ketone itself acts as a free radical "trap." Methyl radicals apparently have low energies of activation for such addition reactions. Mandelcorn and Steacie[12] report a value of 2.5 kcal./mole for the addition of methyl radicals to butadiene, compared to 6.0 ± 1.0 kcal. for methyl addition to propene. They also found that the rate of addition of the C_5H_9 radical to butadiene was less than that of methyl radicals. By analogy one might expect that E_A for the addition of methyl radicals to methyl propenyl ketone would be of the order of 3 to 5 kcal./mole, with E_A for the $CH_3CH{=}CH$ radical somewhat larger. At the lower temperatures studied, addition reactions are highly favored over the competing abstraction and combination processes. Even at 275°, a rough material balance shows that a substantial percentage of the methyl and propenyl radicals add to the double bond to produce larger radicals which subsequently react to give a complex mixture of condensable products.

Kinetics and Mechanism.—It is evident from Fig. 1 that the pressure of the ketone has a pronounced effect upon the quantum yields of the non-condensable products at 2380 Å. Values of $1/\Phi$ plotted against pressure are straight lines for CO, methane, propene and butene at 275° and for CO at 200°. The points for $1/\Phi_{(C_2H_6)}$ may have some curvature, but within experimental error for the small values of $\Phi_{C_2H_6}$ a straight line is also reasonable. At 200° the quantum yields of the hydro-

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

carbons are too small to make similar plots highly significant, although the reciprocals of the quantum yields are approximately proportional to the pressure of the ketone. Several mechanisms possibly could be formulated that would give equations of the form $1/\Phi = a + bP$, but the following sequence of reactions in which the primary process is the formation of a photo-excited molecule seems the most consistent with the experimental results at 2380 Å. and 200 and 275°. For convenience the symbol KH refers to methyl propenyl ketone, either *cis* or *trans*.

$$\mathrm{KH}\ (\textit{trans}) + h\nu \longrightarrow \mathrm{KH}^* \quad (1)$$

$$\mathrm{KH}^* + \mathrm{KH} \longrightarrow 2\mathrm{KH}\ (\textit{cis}\ \text{or}\ \textit{trans}) \quad (2)$$

$$\mathrm{KH}^* \longrightarrow \mathrm{CH_3} + \mathrm{CO} + \mathrm{CH_3CH{=}CH} \quad (3)$$

$$\mathrm{KH}^* \longrightarrow \mathrm{KH} + h\nu \quad (4)$$

$$\mathrm{CH_3} + \mathrm{KH} \longrightarrow \begin{cases} \mathrm{CH_3CO} + \mathrm{C_4H_8} & (5) \\ \mathrm{CH_4} + \mathrm{K} & (6) \\ (\mathrm{C_6H_{11}O}) & (7) \end{cases}$$

$$\mathrm{CH_3CH{=}CH} + \mathrm{KH} \longrightarrow \begin{cases} \mathrm{C_6H_{10}} + \mathrm{CH_3CO} & (8) \\ \mathrm{CH_3CH{=}CH_2} + \mathrm{K} & (9) \\ (\mathrm{C_8H_{13}O}) & (10) \\ \mathrm{CH_3} + \mathrm{CH_3CH{=}CHCH{=}CHCOCH_3} & (11) \end{cases}$$

$$\mathrm{CH_3CO} \longrightarrow \mathrm{CH_3} + \mathrm{CO} \quad (12)$$

$$2\mathrm{CH_3} \longrightarrow \mathrm{C_2H_6} \quad (13)$$

$$2\mathrm{CH_3CH{=}CH} \longrightarrow \mathrm{C_6H_{10}} \quad (14)$$

$$\mathrm{CH_3} + \mathrm{CH_3CH{=}CH} \longrightarrow \mathrm{C_4H_8} \quad (15)$$

If one assumes the steady state, the rate of formation of CO in molecules/sec., R_{CO}, is given by

$$R_{\mathrm{CO}} = \Phi_{\mathrm{CO}} I_a = k_3\,(\mathrm{KH}^*) + k_5(\mathrm{CH_3})(\mathrm{KH}) + k_8\,(\mathrm{CH_3CH{=}CH})(\mathrm{KH}) \quad (16)$$

where I_a = quanta absorbed per sec.

If one neglects the small amount of butene formed by the combination reaction 15 with respect to that formed by the displacement process 5 (this is justified subsequently in the Discussion), one can re-write (16) as

$$\Phi_{\mathrm{CO}} = \frac{k_3}{I_a}(\mathrm{KH}^*) + \Phi_{\mathrm{C_4H_8}} + \frac{k_8}{k_9}\Phi_{\mathrm{C_3H_6}} \quad (17)$$

The results in Table II show that the ratios $\Phi_{\mathrm{C_4H_8}}/\Phi_{\mathrm{CO}}$ and $\Phi_{\mathrm{C_3H_6}}/\Phi_{\mathrm{CO}}$ are constant over the entire pressure range from 2.5 to 38 mm. at 275°. This is also true at 200°, although for a smaller pressure range. Thus, in equation 17 in place of $\Phi_{\mathrm{C_4H_8}}$ and $\Phi_{\mathrm{C_3H_6}}$, respectively, one can substitute $(\Phi_{\mathrm{CO}})(C)$ and $(k_8/k_9)(C')(\Phi_{\mathrm{CO}})$, where C and C' are the constant values of these ratios. After making these substitutions, rearranging the equation and inserting the value for (KH*) obtained by assuming the steady state, one obtains the expression

$$\frac{1}{\Phi_{\mathrm{CO}}} = \frac{(k_3 + k_4)}{k_3}\left[1 - C - \left(\frac{k_8}{k_9}\right)C'\right] + \frac{k_2}{k_3}\left[1 - C - \left(\frac{k_8}{k_9}\right)C'\right](\mathrm{KH}) \quad (18)$$

At a given temperature, all quantities, other than the pressure of the ketone on the right hand side of (18), are constants. Hence the equation is of the proper form to fit the experimental results on carbon monoxide at 200 and 275°. Furthermore, since the ratios of the quantum yields of butene, propene and methane to the quantum yield of CO are all constants and independent of pressure, it follows that plots of $1/\Phi_{\mathrm{C_4H_8}}$, $1/\Phi_{\mathrm{C_3H_6}}$ and $1/\Phi_{\mathrm{CH_4}}$ should also vary in a linear fashion with pressure. It is clear from Fig. 1 that this is the case.

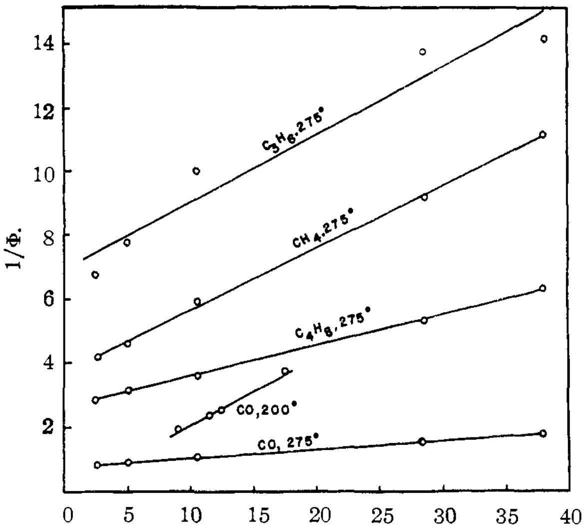

Fig. 1.—Pressure dependence of the reciprocals of the quantum yields at 2380 Å.

Since the photo-activated molecule KH* can presumably be deactivated by collision with any molecule, M, in the system a more general version of equation 18 would include (M) in place of (KH). As a check, run 54 was made with 10.5 mm. pressure of methyl propenyl ketone to which 22.5 mm. of the "inert gas" $\mathrm{CO_2}$ was added. It is evident from a comparison of results in Table II that addition of the inert gas had no effect on the ratios of butene, propene and methane to CO, although the absolute values of the quantum yields of all products were substantially decreased. The value of $1/\Phi_{\mathrm{CO}}$ for run 54 falls close to the line for $1/\Phi_{\mathrm{CO}}$ *vs.* pressure of ketone, if one takes for the abscissa the value of 33 mm. pressure (10.5 mm. of ketone and 22.5 mm. of $\mathrm{CO_2}$). Although more data are necessary, this result does indicate that the efficiency of collisional deactivation of KH* by carbon dioxide is of the same order as that for methyl propenyl ketone.

It is interesting that well substantiated mechanisms for the photolysis of ketene[13] and methyl ketene[14] also include the formation of a photo-excited molecule in the primary process. With this postulate, as in the present study, kinetic expressions can be derived for each compound that satisfy the experimental fact that $1/\Phi_{\mathrm{CO}}$ is directly proportional to pressure.

In deriving equation 18, the quantity I_a cancelled out, and on this basis one would expect that the quantum yields of CO, butene, propylene and methane should be independent of intensity. In runs 52, 51 and 57 at constant pressure, the values of I_a were 2.08×10^{14}, 1.03×10^{14} and 0.36×10^{14} quanta absorbed/sec. while the corresponding

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[13] A. N. Strachan and W. A. Noyes, Jr., THIS JOURNAL, **76**, 3258 (1954).

[14] G. B. Kistiakowsky and B. H. Mahan, *ibid.*, **79**, 2412 (1957).

values of Φ_{CO} were 0.96, 0.99 and 1.2. Thus, a variation of a factor of six in light intensity produced little significant change in the quantum yield of CO, in agreement with the kinetic expression. Quantum yields of butene, propene and methane were not determined on the lowest intensity run, but it is evident from a comparison of results for runs 52 and 51 in Table I that a reduction of light intensity by a factor of two had no effect on these hydrocarbons. Again, this fact is in accord with the proposed mechanism.

In sharp contrast to the other non-condensable hydrocarbon products, the quantum yield of ethane dropped from 0.007 to 0.003 when the light intensity was reduced by a factor of two. Furthermore, the ratio $\Phi_{C_2H_6}/\Phi_{CO}$ was dependent upon the pressure of the ketone. The values of $\Phi_{C_2H_6}$ are too small to warrant extensive discussion of these effects, but they are compatible with the view that ethane is formed in the radical combination proposed in reaction 13. The very small yields of ethane indicate that the other radical combination processes, (14) and (15), are also of low probability. This seems reasonable in view of the high probability of the competing addition and abstraction reactions in this system.

Although little fluorescence was observed visually, reaction 4 is included to account in part for the very low quantum yields of gaseous products at all wave lengths in photolyses at room temperature. Collisional deactivation by reaction 2 seems very effective in reducing to negligible amounts the yields of gaseous products at 25°. The marked variations of the quantum yields of non-condensable gases with pressure, and the pronounced effect of an inert gas, afford good evidence for this view.

The postulate of a primary process in which a photo-excited molecule is formed is compatible with the observed effects of increasing the temperature and the energy of the absorbed radiation. As the amount of electronic and vibrational energy possessed by KH* is increased, on the basis of this mechanism one would expect that the ratio of decomposition to deactivation would increase, and, furthermore, that the pressure effect would become less pronounced. The strong increase in the quantum yields at 2380 Å. with temperature shown in Table I and the greater slope of the line $1/\Phi_{CO}$ *vs.* pressure at 200° compared to the slope at 275° are arguments for the validity of this postulate.

Some information concerning the ratios k_8/k_9 and k_2k_3 can be obtained by considering equation 18 in terms of the values of the slopes and intercepts of the experimental curves at 200 and 275° in Fig. 1. If one inserts the average values of the constant ratios $\Phi_{C_4H_8}/\Phi_{CO}$ and $\Phi_{C_3H_6}/\Phi_{CO}$ at the two temperatures and neglects k_4 with respect to k_3, which seems reasonable at 2380 Å. and elevated temperatures, expressions (19) and (20) result

200°:

$$1/\Phi_{CO} = [0.79 - 0.11\,(k_8/k_9)] + (k_2/k_3)\,[0.79 - 0.11\,(k_8/k_9)]\,(\mathrm{KH}) \qquad (19)$$

275°:

$$1/\Phi_{CO} = [0.71 - 0.11\,(k_8/k_9)] + (k_2/k_3)\,[0.71 - 0.11\,(k_8/k_9)]\,(\mathrm{KH}) \qquad (20)$$

Since the observed intercepts of the lines at 275 and 200° are about 0.8 and 0.0, respectively, it is evident that k_8/k_9 at 200° must be significantly larger than at 275°. This points to a somewhat larger activation energy for the abstraction reaction 9 compared to the displacement process 8. Unfortunately quantitative determinations of the diolefin C_6H_{10} were not feasible in this research. This rules out a direct evaluation of k_8/k_9 with the available data. The slope of the line at 200° is significantly larger than that at 275° despite the fact that the quantity $[0.71 - 0.11(k_8/k_9)]$ at 275° is greater than $[0.79 - 0.11\,(k_8/k_9)]$ at 200°. This indicates that k_2/k_3 at 275° must be substantially less than k_2/k_3 at 200°, an observation compatible with the previous suggestion that an increase in temperature should favor the decomposition reaction (3) over deactivation, (2).

The free radical displacement process (5) has been discussed in detail elsewhere.[15,16] However, considerable information concerning its existence and importance can be derived from a brief consideration of the results of this investigation. The quantum yields of ethane are small at all temperatures and the ratio of ethane to carbon monoxide decreases rapidly with increasing temperature and pressure. In contrast, the ratio of 2-butene to carbon monoxide is independent of pressure at 200 or 275° and increases sharply at temperatures above 200°. Furthermore, the quantum yield of 2-butene is always significantly larger than that of methane and a factor of twenty or more greater than that of ethane. These facts indicate that most of the 2-butene must be formed by a process other than radical dimerization. Formation of 2-butene in a direct primary process seems to be eliminated on the basis of the strong temperature dependence of $\Phi_{C_4H_8}$.

The most satisfactory explanation for the behavior of the butene yields is to postulate that 2-butene is formed by the displacement process 5. At elevated temperatures, the acetyl radical decomposes rapidly into methyl radical and CO by (12) and the elements of a chain are set up. Evidence for a short chain is the fact that Φ_{CO} exceeds unity at 275° and pressures of ketone of the order of 10 mm. or less. Subsequently, further proof of (5) was obtained from the pyrolysis of mixtures of di-*t*-butyl peroxide and methyl propenyl ketone[15] and the photolysis of mixtures of CD_3COCD_3 and methyl propenyl ketone.[16] The process now seems to be well established. No unequivocal evidence is available for (8) except that a hexadiene is a product of the photolysis. Primarily, reaction (8) is included by analogy with reaction (5).

In addition to the reactions listed for the high temperature photolyses, several other processes having a direct effect on the yields of non-condensable products must take place in the region 25 to 125°. These include

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(15) J. N. Pitts, Jr., R. S. Tolberg and T. W. Martin, THIS JOURNAL, **76**, 2834 (1954).

(16) J. N. Pitts, Jr., D. D. Thompson and R. W. Woolfolk, Presented before the Division of Physical and Inorganic Chemistry at the Spring Meeting of the American Chemical Society, Miami, 1957. THIS JOURNAL, **79**, 6370 (1957).

$$KH^* \longrightarrow CH_3 + CH_3CH{=}CHCO \quad (21)$$

$$KH^* \longrightarrow CH_3CH{=}CH + CH_3CO \quad (22)$$

$$CH_3CH{=}CHCO \longrightarrow CH_3CH{=}CH + CO \quad (23)$$

Reactions (21) and (22) are analogous to free radical dissociations of the aliphatic ketones that occur at the lower temperatures.[3] At elevated temperatures, processes (21) and (22) followed by the rapid dissociation of CH_3CO and $CH_3CH{=}CHCO$ radicals in (12) and (23) would be equivalent to the over-all process (3). The quantum yields of methane and of propene are virtually identical at 125° and over the entire pressure range at 200°. Although this fact may be in part coincidental since the mechanism is quite complex, it does appear that the $CH_3CH{=}CHCO$ radicals decompose at a rate of the same order of magnitude as the acetyl radicals which are known to decompose rapidly at temperatures above 100°.[3]

Unfortunately, little is known about the products of β-addition by methyl or propenyl radicals to methyl propenyl ketone except that complex mixtures of condensable products are ultimately produced. It is unwarranted to speculate here about reactions resulting in these products, except to mention briefly reactions for which there is some experimental evidence.

Reaction 11 is included in the mechanism to account for the fact that there is a marked increase in the methane/carbon monoxide and 2-butene/carbon monoxide ratios at temperatures above 200° whereas no such increase occurs in the propene/CO ratio. Presumably the reaction goes through an intermediate radical as shown in (11′) which is fairly stable at 200° but dissociates rapidly at 275°

$$\begin{aligned} &CH_3CH{=}CH + KH \longrightarrow \\ &\quad [CH_3COCHCH(CH{=}CHCH_3)CH_3] \longrightarrow \\ &\qquad CH_3 + CH_3COCH{=}CHCH{=}CHCH_3 \quad (11') \end{aligned}$$

to produce methyl radicals. The methyl radicals may subsequently act as a source of additional 2-butene by the displacement process (5), or methane by the abstraction reaction (6). A similar effect might be expected to occur when methyl radicals add to the β-carbon at high temperatures. In this instance decomposition of the complex radical would simply give the starting materials. However, this process would serve to increase the steady-state concentration of methyl radicals at 275° relative to that at 200° since they would no longer be permanently "trapped" by addition to the double bond, as they are presumed to be at the lower temperature. This in turn would result in an increase in the ratios $\Phi_{\text{Butene}}/\Phi_{CO}$ and Φ_{CH_4}/Φ_{CO} at 275°.

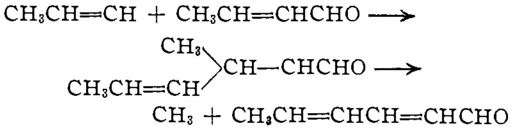
Several compounds with larger molecular weights than methyl propenyl ketone were detected in mass spectra of the condensable products. In one case the mass spectrum, after correction for the methyl propenyl ketone present, gave significant peaks at *m/e* 85, 58 and 57 which compared favorably with those for 4-methyl-2-pentanone. This would be a logical product from the beta addition of a methyl radical followed by a hydrogen abstraction reaction.

Crotonaldehyde.—The photochemistry of crotonaldehyde is similar in many respects to that of *trans*-methyl propenyl ketone. This aldehyde is unusually stable toward dissociation into non-condensable products at 3130 Å.,[10,11] but at 2380 Å. and 265° the quantum yield of carbon monoxide is of the order of 1.5. Furthermore there is a pronounced effect of pressure upon the quantum yield of carbon monoxide, although for the aldehyde it seems to follow the form $\Phi_{CO} = a + b/P$.[17] In view of the fact that Blacet and LuValle reported small amounts of methane as a product,[11] it was decided to make a brief study of the non-condensable products of crotonaldehyde to see whether some 2-butene might be formed as a result of a methyl displacement process analogous to reaction (5) with methyl propenyl ketone.

$$\begin{aligned} &CH_3 + CH_3CH{=}CHCHO \longrightarrow \\ &\qquad CH_3CH{=}CHCH_3 + HCO \quad (24) \end{aligned}$$

This idea was verified by mass spectrometric analysis of non-condensable products from two photolyses which showed that 2-butene was a reaction product and that the yield was a factor of about nine greater than ethane. Recent detailed studies on the photolysis of crotonaldehyde and crotonaldehyde–acetone mixtures[16] confirm the validity of process (24).

Blacet and LuValle[11] proposed that the methyl radicals could be formed in a direct primary process or by the decomposition of the propenyl radical. In either case at elevated temperatures acetylene might be expected to be a reaction product, but it was not detected in the photolysis of either crotonaldehyde or methyl propenyl ketone. An alternative method for producing methyl radicals would be a reaction analogous to reaction 11 in the ketone mechanism



$$\begin{aligned} &CH_3CH{=}CH + CH_3CH{=}CHCHO \longrightarrow \\ &\quad \left.\begin{matrix} CH_3 \\ CH_3CH{=}CH \end{matrix}\right\rangle CH{-}CHCHO \longrightarrow \\ &\qquad CH_3 + CH_3CH{=}CHCH{=}CHCHO \end{aligned}$$

(25)

This reaction could explain the formation of methyl radicals without the necessity of having acetylene as a product.

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[17] J. N. Pitts, Jr., R. W. Woolfolk and D. D. Thompson, unpublished results.