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The Photolysis of Methylethyl Ketone

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The nature of the products from the photochemical decomposition of methylethyl ketone at temperatures from 90 to 200° has been re-examined. In contrast with earlier results, the formation of ethane, propane, and butane parallels the frequency of the corresponding free radical collisions. At the higher temperatures, however, production of ethane and especially of methane becomes predominant. The influences on the product distribution of secondary reactions, the lifetimes of the free radical collision complexes, and the activation energies and entropies, are considered.

THE photochemical decomposition of methylethyl ketone has previously been investigated by Norrish and Appleyard[1] using radiation in the near ultraviolet absorption region around 3000A, and more recently by Ells and Noyes[2] who worked in the region around 1850A. Both these investigations suggested that equivalent amounts of ethane, propane, and butane occurred in the reaction products, together with an amount of methane which increased markedly with increasing temperature. This result was indeed surprising, since if the hydrocarbons were formed by interaction of free radicals produced in the primary process, one would expect the ratio ethane : propane : butane to be approximately 1 : 2 : 1. The present experiments were undertaken to check this anomalous result, using a method of analysis for hydrocarbons which had proved reliable in previous studies of free radical reactions.[3]

EXPERIMENTAL DETAILS

The photolyses were carried out in a static system identical with that used for our studies of metal alkyl decompositions.[3] Ketone at forty mm pressure was irradiated with the unfiltered output of a high pressure arc of the mercury-in-quartz type, operating hot at 55 volts and 3.5 amp. d.c., until about fifty percent was decomposed. The methylethyl ketone used was a product of the Eastman Kodak Company, purified by treatment with anhydrous copper sulfate, and careful fractional distillation. A fraction boiling within a tenth of a degree at around 79.5° was retained; its refractive index was $n_D^{15}=1.38118$, compared with a reported value for the pure compound[4] of $n_D^{15}=1.38140$.

The products, amounting to about five cc of gas, were analyzed as follows:

1. A fraction pumped off from liquid air was burned over cupric oxide at 310°, converting carbon monoxide to dioxide, from which methane could be pumped off at liquid-air temperature; the carbon dioxide was pumped off at $-78°$, and any residual vapor was assumed to be water.
2. A fraction pumped off at $-138°$ (m.p. of ethyl chloride) was hydrogenated on nickel at 100° to determine ethylene, then cracked over nickel at 310° to methane, thus giving the average carbon content of the fraction. This fraction is made up of C_2 and C_3 hydrocarbons.
3. A fraction at $-78°$, consisting of C_3 and C_4 hydrocarbons, was similarly analyzed.

EXPERIMENTAL RESULTS

The observations were extended over a temperature range of from 90 to 200°. At the lowest temperature there was observed a small amount of diketone formation, evidenced by the appearance of a yellow oil and the typical odor of diketones in the reaction vessel. At the higher temperatures, however, no diketone formation was detected. Tests for acetaldehyde with Schiff's reagent were negative. There was evidently some polymer formation at all temperatures, and after pumping off products volatile at $-78°$, an odor resembling that of mesityl

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[1] Norrish and Appleyard, J. Chem. Soc. 874 (1934).
[2] Ells and Noyes, J. Am. Chem. Soc. **60**, 2031 (1938).
[3] Moore and Taylor, J. Chem. Phys. **8**, 396 (1940).
[4] J. Timmermans and F. Martin, J. chim. phys. **25**, 411 (1928).

oxide was distinctly noticeable; there was insufficient residue, however, to make possible the identification of the responsible compound or compounds.

The results of the analyses of the volatile products are given in Table I.

We note that at the lower temperatures considerably more propane is formed than either ethane or butane, but that at 200° the formation of methane and ethane is of primary importance.

TABLE I. *Percentage composition of photolysis products of* MeEtCO.

TEMP. °C	90	110	155	200
H_2	0.4	0.1	0.3	0.0
CO	47.5	49.0	47.0	48.5
CH_4	3.4	4.4	9.0	18.0
C_2H_4	2.2	0.5	1.7	3.0
C_2H_6	11.5	13.0	14.5	12.5
C_3H_8	19.1	20.0	18.6	11.0
C_4H_{10}	13.2	13.0	9.0	7.0
C_4H_8	1.5	—	0.0	—

GENERAL DISCUSSION

If, as a first approximation, we disregard the reactions of acetyl and propionyl radicals possibly arising in the primary process, the reactions with which we are concerned are as follows:

$$CH_3+CH_3=C_2H_6, \qquad (1a)$$

$$CH_3+C_2H_5=C_3H_8, \qquad (1b)$$

$$C_2H_5+C_2H_5=C_4H_{10}, \qquad (1c)$$

$$CH_3+CH_3COC_2H_5=CH_4+CH_3COC_2H_4, \qquad (2a)$$

$$C_2H_5+CH_3COC_2H_5=C_2H_6+CH_3COC_2H_4. \qquad (2b)$$

At 110° the hydrocarbon products probably arise principally from the interactions of free radicals. The ratio of the numbers of collisions of types 1a : 1b : 1c is roughly 1.00 : 1.74 : 0.83, while the observed formation of ethane, propane, and butane are in the ratio 1.00 : 1.54 : 1.00. Assuming equal activation energies for the reactions (1), there are two other factors which may influence the relative recombination rates of the free radicals.

The lifetime of the quasi-molecule formed in the free radical collisions will increase from (1a) to (1c). The entropy of activation should decrease in going from (1a) to (1c), since it is less for reactions between more complex radicals.[5] A proper evaluation of these factors would perhaps suffice to explain the observed deviations from the purely kinetic theory ratios.

In addition, and especially at higher temperatures, the secondary reactions (2) will be of importance, leading to the formation of methane and ethane at the expense of the other hydrocarbons. A detailed kinetic analysis of these reactions is difficult and not very informative, since we can already follow qualitatively the effect of the decreased radical concentrations in decreasing the amount of recombination of radicals as compared with secondary reaction with ketone molecules.

It is interesting to note that methane is formed from methylethyl ketone considerably more easily than from acetone.[6] This difference may most reasonably be ascribed to the lowered energy of activation for the reaction of a methyl radical with $-C_2H_5$ to form C_2H_4, as compared with the reaction with $-CH_3$ to form CH_2.

It appears also that methyl radicals are more effective in polymerizing ethylene than are ethyl radicals, since much greater amounts of ethylene remain in the photochemical decomposition of diethyl ketone than are found with methylethyl ketone.[2,7] This is in accord with the results of experiments by Yeddanapalli and Jungers[8] on the relative efficiencies in ethylene polymerization of methyl and ethyl radicals prepared by reaction of the corresponding iodides with mercury vapor.

The formation of an oxygen-containing polymer from such fragments as $CH_3COC_2H_4$ would also account for the small amount of ethylene formation, this possibility being also suggested by the characteristic odor of the nonvolatile photolysis products.

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[5] Bawn, Trans. Faraday Soc. **31**, 1536 (1935).

[6] Taylor and Rosenblum, J. Chem. Phys. **6**, 119 (1938).

[7] Noyes and Ells, J. Am. Chem. Soc. **61**, 2492 (1939).

[8] J. C. Jungers and L. M. Yeddanapalli, Trans. Faraday Soc. **36**, 483 (1940).