[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Structure and Reactivity in the Vapor Phase Photolysis of Ketones. III. Methyl Cyclobutyl Ketone[1,2]

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The vapor phase photodecomposition of methyl cyclobutyl ketone at 2654 Å. is chiefly free radical in nature with CO, C_2H_4, CH_4 and cyclo-C_4H_8 the major products. The quantum yield of CO, Φ, remains 0.35 ± 0.02 from 100 to 250° whereas Φ C_2H_4 increases from 0.17 to 0.34. Cyclobutyl radicals are postulated to dissociate into ethylene, and vinyl radicals with an apparent activation energy of about 14 kcal. Minor products are methylcyclobutane, ethane, cyclobutene and traces of butadiene at the highest temperatures. These results differ drastically from methyl cyclopropyl ketone in which an intramolecular rearrangement to methyl propenyl ketone is the major mode of photolysis.

The photolysis of methyl cyclopropyl ketone in the vapor phase has been shown to result chiefly in an intramolecular rearrangement, with methyl propenyl ketone as the product.[4] The probability of this process is much higher than that of the competing free radical reactions characteristic of simple aliphatic ketones, since the quantum yield of formation of the α,β-unsaturated ketone is 0.31 compared to 0.12 for Φ_{CO} at 170°. The hydrocarbons formed following the radical primary processes have surprisingly small quantum yields and they are predominantly olefinic in character (*viz.*, butene, propylene and 1,5-hexadiene).

These results indicate that the cyclopropyl ring has profound effect upon the primary processes of this relatively simple ketone. Furthermore, in the cyclopropyl case the olefinic nature of the C_3 and larger hydrocarbons indicates that, if formed, the cyclopropyl radical rearranges rapidly to the allyl form.

In light of these facts it was of interest to investigate the next homolog in the methyl cycloalkyl series to determine whether or not the intramolecular rearrangement process is general for this type of methyl ketone, and to obtain some information concerning the vapor phase reactions of cyclobutyl radicals.

Experimental

The apparatus, experimental techniques and analytical procedures, employed in this investigation were essentially the same as those described in the previous paper.[4] However, a few alterations were made. In order to achieve higher temperatures and more accurate control, the reaction vessel was enclosed inside a cylindrical aluminum block furnace, which could be heated to 350° and automatically controlled to within about ±1.0°. The remainder of the reaction gas train was usually kept between 60 and 100° to prevent condensation of the ketone vapors.

A chemical filter containing bromine and chlorine vapor[4] was employed in the early runs. This filter was fairly effective in limiting the radiation to the 2654 Å. region. The 2537 Å. "line" was about one-half as intense as the 2654 Å. group. The filter was replaced later with a Farrand Model 300 ultraviolet Monochromator which effectively isolated the 2654 Å. band group. A type A Hanovia medium pressure mercury arc was used in all runs. The illuminated volume of the reaction cell was about 130 cc.

The sample of methyl cyclobutyl ketone was generously furnished by Professor R. P. Mariella and Dr. R. Raube, from a supply originally prepared by Dr. W. D. Huntsman in this Laboratory. The method of preparation and physical properties have been reported by the above authors.[5,6] The sample was purified by distillation in a micro-Podbielniak fractionating column. The center fraction (b.p. 134.2–134.8°, 755 mm.) was then distilled *in vacuo*, into the supply reservoir. Mass spectrometric analysis showed that compounds of molecular weight greater than the ketone were absent. The diethyl ketone, used as an internal actinometer, was purified as described previously.[4]

The cyclobutane and methylcyclobutane used as primary standards in the mass spectrometer analyses were prepared and generously supplied by Dr. H. Pines and co-workers of this Laboratory. Dr. E. Bobko synthesized the cyclobutene from a sample of 1,2-dibromocyclobutane,[7] by the method of Heisig.[8]

A Westinghouse Type LV mass spectrometer and a Blacet–Leighton micro-gas analysis apparatus were used to analyze the non-condensable gases.

Experimental Results

The Non-condensable Products.—The non-condensable products from the photolysis of methyl cyclobutyl ketone are carbon monoxide, cyclobutane, methylcyclobutane, cyclobutene, ethane, ethylene, methane and trace amounts of butadiene. The quantum yields of the above products as a function of temperature over the range 60–250° are shown in Table I. It should be noted that a quantitative separation of the C_4 and C_5 products from the large excess of unreacted ketone in the condensate was difficult to achieve; thus the reported quantum yields are probably low. The results from the runs in which the bromine–chlorine filter was used were in substantial agreement with those in Table I. The quantum yield of carbon monoxide was somewhat higher (Φ_{CO} = 0.33, 0.44 and 0.45, at 60, 120 and 170°, respectively), but this is reasonable in view of the large amount of 2537 Å. radiation present.

A detailed check of the non-condensables using micro-chemical and mass spectrometric methods failed to disclose any significant amounts of butenes or pentenes. The analyses for cyclobutene and butadiene were not very accurate since they were based on the relatively small m/e 54 and 53 peaks that remained after corrections were made for the contributions from cyclobutane and methyl cyclobutane. However, qualitatively it appears that cyclobutene predominates at temperatures be-

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[1] Presented at the Chicago Meeting of the American Chemical Society, September, 1953.

[2] Taken from the doctoral dissertation of I. Norman, Northwestern University, 1953. Eastman Kodak Predoctoral Fellow, 1952–1953.

[3] Division of Physical Sciences, University of California, Riverside, California.

[4] J. N. Pitts, Jr., and I. Norman, THIS JOURNAL, **76**, 4815 (1954).

[5] R. P. Mariella and R. R. Raube, *ibid.*, **74**, 58 (1952).

[6] W. D. Huntsman, Doctorate Thesis, Northwestern University, 1950.

[7] Kindly given to the authors by Professors J. D. Roberts and W. Saunders.

[8] G. B. Heisig, THIS JOURNAL, **63**, 1698 (1941).

TABLE I

THE EFFECT OF TEMPERATURE ON THE QUANTUM YIELD OF GASEOUS PRODUCTS FROM METHYL CYCLOBUTYL KETONE PHOTOLYSIS AT 2654 Å.

Temp., °C.	60	100	150	200	200	250
Pressure, mm.	28.5	23.3	35.5	38.5	36.5	44.2
Intensity, quanta/sec., 10^{-4}	4.40	4.35	3.27	3.39	3.02	3.34
Fraction absorbed	0.554	0.464	0.538	0.448	0.494	0.495
Time, sec. 10^{-4}	1.97	1.62	1.65	1.44	3.36	1.54
Quantum yields, Φ						
Carbon monoxide	0.27	0.34	0.35	0.37	0.37	0.37
Methylcyclobutane	.045	.016	.013	.00	.00	.00
Cyclobutane	.075	.092	.109	.094	.11	.066
Cyclobutene	.018	.012	.001	.004	.000	.000
Butadiene	.00	.00	.000	<.01	<.01	.01
Ethane	.030	.028	.004	<.01	<.01	<.01
Ethylene	.134	.165	.21	.30	.32	.34
Methane	.072	.186	.24	.29	.26	.25

tween 60 and 200°, while butadiene is formed at higher temperatures. Some qualitative mass spectrometric evidence also pointed to the presence of traces of propylene and a C_5 diene among the reaction products.

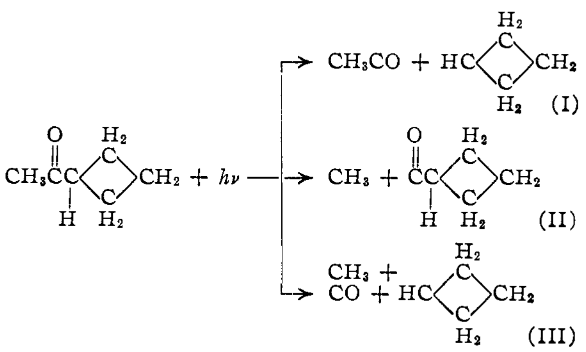
The Condensable Fraction.—Considerable effort was spent in checking the condensate for methyl vinyl ketone and 3-hexene-2-one since these α,β-unsaturated ketones are possible reaction products.[9] However, analyses with the mass spectrometer and infrared and ultraviolet spectrophotometers showed no trace of them. Actually, identification of methyl vinyl ketone is a difficult problem under most circumstances because of its tendency toward polymerization, particularly in the presence of free radicals.[10] Thus, it should still be considered as a possible product. However, the analytical results seem to eliminate the possibility of formation of substantial amounts of 3-hexene-2-one since the analogous compound, methyl propenyl ketone, was readily determined as a photolysis product of methyl cyclopropyl ketone.[4]

Discussion

The photochemistry of this ketone differs in a qualitative and a quantitative sense from that of methyl cyclopropyl ketone. In the latter case the major product was methyl propenyl ketone with a quantum yield of 0.31 whereas the analogous α,β-unsaturated ketone, 3-hexene-2-one was not formed from the cyclobutyl compound. Furthermore, the quantum yields of the non-condensable products are much larger in methyl cyclobutyl ketone photolysis, with $\Phi_{CO} = 0.36$ at 170°, compared to 0.13 for the cyclopropyl analog.

These facts indicate that photolysis of methyl cyclobutyl ketone primarily involves free radicals, whereas an intramolecular rearrangement is the most probable mode of photolysis of methyl cyclopropyl ketone. The following series of postulated primary processes is in accord with this idea.

Primary processes I, II and III are characteristic of all simple aliphatic ketones. At room temperature all three no doubt occur, but at temperatures exceeding 120° the acetyl and cyclobutyryl radicals dissociate so rapidly that the over-all effect can be represented by III alone. Undoubtedly a "hot atom" effect at 2654 Å. also contributes to the decomposition of these acyl radicals.



If one takes Φ_{CO} to be a measure of the extent of decomposition into radicals, then it is obvious that primary processes I, II and III account for only 35% of the quanta absorbed. This inefficiency in radical production is in sharp contrast to acetone. methyl ethyl ketone, diethyl ketone[11] and diisopropyl ketone,[12] which have quantum yields of unity under comparable conditions. This low value of Φ TOTAL for methyl cyclobutyl ketone is, however, in line with values obtained for other methyl ketones that possess a γ-hydrogen atom and which are known to photodissociate into an olefin and acetone. The remaining 65% of the quanta must lead to the formation of activated molecules or initiate other primary processes, or both. Deactivation of the excited molecules through fluorescence, collisional deactivation, or internal degradation would certainly lead to a lowering of the quantum yield, perhaps by as much as 65%, but unfortunately with the available data no quantitative assessment of these effects is possible. Another possibility is a primary process in which an α,β-bond is broken and then the biradical recyclizes to give the original material. However, there is no direct evidence for or against this process.

The possibility of other primary processes, not

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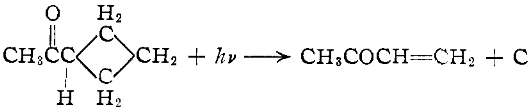
[9] In a private communication, Professor W. D. Walters and Dr. L. Daignault report finding methyl vinyl ketone and ethylene among the pyrolysis products of methyl cyclobutyl ketone.

[10] T. T. Jones and H. W. Melville, *Proc. Roy. Soc.* (*London*), **A187**, 19 (1946).

[11] E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Vol. II, Reinhold Publ. Corp., New York, N. Y., 1954, p. 509.

[12] S. G. Whiteway and C. R. Masson, THIS JOURNAL, **77**, 1508 (1955).

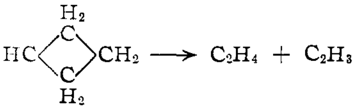
leading to carbon monoxide, cannot be overlooked. One such process that seems likely is an intramolecular reaction to give ethylene and methyl vinyl ketone, IV. Both of these are products of the pyrolysis of methyl cyclobutyl ketone,[9] and ethylene is a major product from the photolysis. However, the results to date indicate that IV is not a major primary process. In the first place, an extensive search failed to reveal any α,β-unsaturated ketones in the condensate. But, this is not conclusive evidence against IV because methyl vinyl ketone may have been formed which rapidly polymerized and thus escaped detection by the spectrophotometric procedures employed. The strongest argument against IV being a major source of the ethylene is the poor material balance this gives for the hydrocarbons in the non-condensable products, particularly at the higher temperatures. On the other hand, an excellent hydrocarbon balance is achieved if one assumes that all the ethylene arises from the thermal decomposition of cyclobutyl radicals into ethylene and vinyl radicals, and that the vinyl radicals abstract H atoms to form more ethylene. It seems best at this time to conclude that IV may occur to a limited extent, but that it is much less probable than the free radical processes I, II and III.


(IV)

It has been pointed out that the major mode of photolysis of methyl cyclopropyl ketone is to form methyl propenyl ketone.[4] A detailed search for the analogous compound, 3-hexene-2-one, was carried out in this research but no evidence was obtained for its formation. This does not seem unreasonable in view of the considerably lower carbon–carbon bond dissociation energy in the cyclopropyl as compared to the cyclobutyl rings.[13]

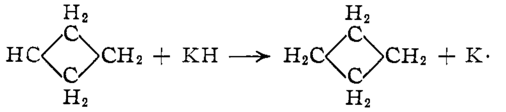
Secondary Reactions.—The usual abstraction and combination reactions of the radicals formed in primary processes I, II and III explain the non-condensable products methane, ethane, cyclobutane and methylcyclobutane. Combination reactions between large radicals leading to products remaining in the condensed phase also occur, but analytical difficulties prevented their detection and estimation. The traces of cyclobutene and butadiene probably arise from disproportionation reactions of cyclobutyl and vinyl radicals, but the small yields preclude a detailed discussion of their mode of formation.

The product of most interest is ethylene. As has been pointed out earlier, the most likely source is the decomposition of cyclobutyl radicals into ethylene and vinyl radicals, reaction 1. The vinyl radicals then abstract hydrogen atoms from the substrate to form more ethylene, as in (2).


(1)

$$C_2H_3 + KH \longrightarrow C_2H_4 + K\cdot \qquad (2)$$

A strong argument in favor of this reaction sequence can be based on the observed temperature dependence of ethylene and cyclobutane. If the cyclobutyl radical were stable in the range 60–250°, then it would react chiefly by the H-atom abstraction process (3), and cyclobutane would show a strong increase with temperature, as is observed for Φ_{CH_4}


(3)

Actually the quantum yields of methane and cyclobutane both start at about 0.07 at 60°, but Φ_{CH_4} rises rapidly to 0.24 at 150° and then levels off, whereas the quantum yield of cyclobutane climbs to only 0.11 at 150° and then drops off to 0.07 at 250°. This maximum in the quantum yield of cyclobutane is consistent with the idea that reactions (1) and (3) are competing and that the dissociation process has a somewhat higher energy of activation than the abstraction reaction.

An approximate kinetic treatment of the available data gives an experimental value of 4 ± 1 kcal./mole for $E_1 - E_3$. The calculation is based on the assumption that (2) is the only important reaction of the vinyl radicals formed in (1). One can then derive the expression

$$\frac{k_1}{k_3} = \frac{R_{C_2H_4\,(\text{ketone})}}{2R_{C_4H_8}}$$

and estimate $E_1 - E_3$ from a plot of log k_1/k_3 *vs.* $1/T$ for temperatures above 100° where the proportion of radicals that react by combination is negligible.[14] If E_3 is assumed to be 10 kcal., the experimental value for the activation energy of the decomposition of the cyclobutyl radical becomes 14 ± 1 kcal. It is interesting to compare this value with the one obtained from calculations involving the heats of formation of the reacting species, and the C–H bond dissociation energy in cyclobutane. If this $D_{(C-H)}$ is estimated to be 96 ± 2 kcal., ΔH_1 is 15 ± 2 kcal./mole. Thus, if the activation energy of the reverse of reaction 1, the addition of vinyl radicals to ethylene, is assumed to be zero, $\Delta H_1 = E_1 = 15 \pm 2$ kcal./mole. Actually there is probably a significant activation energy involved in this radical addition to a double bond.[11] If the energy of activation is assumed to be of the order of 4 ± 2 kcal. as seems to be the case for methyl addition to double bonds,[11] then E_1 becomes 19 ± 4 kcal./mole.

Unfortunately, a further uncertainty enters these calculations. The value calculated for ΔH_1 depends not only on $D_{(C-H)}$ for cyclobutane but it also involves the value for the heat of formation of vinyl radicals, which is currently in doubt. Estimation of the latter quantity involves $D_{(C-H)}$ for ethylene, and, whereas Stevenson reports this to be 91 kcal.,[15] Field gives 122 kcal.[16] Stevenson's value was used in the calculations described above, and the fact that the experimental and calculated values for the decomposition of cyclobutane do not differ greatly may be evidence for the lower value for

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(13) F. H. Seubold, Jr., *J. Chem. Phys.*, **22**, 945 (1954).

(14) The authors are indebted to Dr. F. H. Seubold for helpful discussions on these calculations.

(15) D. P. Stevenson, THIS JOURNAL, **65**, 209 (1943).

(16) F. H. Field, *J. Chem. Phys.*, **21**, 1506 (1953).

$D_{(C-H)}$ in ethylene since the value of 122 kcal. gives $E_1 = 39 \pm 2$ kcal., which seems unduly large.

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[CONTRIBUTION FROM CALIFORNIA RESEARCH CORPORATION]

The Thermal Decomposition of Mono-2-ethylhexyl Polypropylene Glycol

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The thermal decomposition reactions of mono-2-ethylhexylpolypropylene glycol were studied. The decomposition is free radical in nature and is catalyzed by oxygen or peroxides. The behavior of the free radical polymer molecule is controlled by the ease with which ether bonds are broken in the formation of carbonyl groups. This effect also controls the production of volatile products arising from radical fragments of the original molecules.

The polypropylene glycols comprise a class of synthetic polymeric materials possessing many interesting physical properties. Their chemical behavior is informative because their structure offers unique opportunity for studying the ether linkage. This paper reports a study of the thermal decomposition of a mono-2-ethylhexylpolypropylene glycol having an average molecular weight of about 1000.

Experimental

Materials.—The polypropylene glycol was prepared by polymerization of propylene oxide. The reaction was initiated with 2-ethylhexanol and catalyzed by sodium 2-ethylhexanolate. This material was purified and topped in the usual manner yielding number average molecular weights of 1000 and 920, determined by end group analysis and freezing point lowering, respectively. The polymer viscosity at 100° was 11.4 centistokes. To ensure that the results obtained with this material were typical of the class of compounds, several critical measurements were repeated with a sample of polypropylene glycol P-1200 obtained from the Dow Chemical Company. No significant differences were noted.

Thermal Decomposition Measurements.—The rate of thermal decomposition was determined by measuring the rate of increase of pressure in a closed system due to the formation of highly volatile products. A weighed amount of the material (10 g. in all cases) was introduced into the reaction tube, which was heated by a vapor bath, and the gas handling system was filled to a pressure of 20 mm. with oxygen-free N_2. The system was designed so that all of the lower molecular weight products, except those highly volatile, were maintained in the tube by reflux. Measurements were started at a given time after the reflux level of the vapor bath reached a fixed position. The temperature of the bath was determined separately with a mercury thermometer, and the pressure was determined with a mercury manometer. By closing appropriate stopcocks, gas samples for analysis were obtained in a sample bulb contained in the gas handling system.

Catalytic Effect of Oxygen.—Determination of the catalytic effect of oxygen was carried out in apparatus very similar to that described above, except that the reaction tube was equipped with an inlet line at the bottom so that gas pumped by a Sigmamotor pump could be circulated through the system. The gas, composed of nitrogen and oxygen in predetermined proportions, was initially near atmospheric pressure. The reaction was followed by observing the change in pressure.

Catalytic Effect of Peroxides.—The catalytic effect of peroxide upon the thermal decomposition reaction was determined by decomposing a given quantity of di-*t*-butyl peroxide in the polyglycol and then stripping off the peroxide decomposition products plus any low molecular weight polyglycol fragments produced by reaction of free radicals derived from the peroxide. The weight loss of polymer and the viscosity change of the residual material were determined. The residual material was examined by infrared analysis to determine the principal functional groups produced.

Analyses.—Gas analysis for all components, with the exception of formaldehyde, was carried out using infrared and mass spectrometry. Acetaldehyde, propylene, carbon monoxide and acetone were identified and determined quantitatively using a Perkin–Elmer Model 21, dual beam, infrared spectrometer.[1] These values were confirmed by mass spectrometric analyses and determination made of propionaldehyde. Formaldehyde was determined polarographically[2] in an aqueous solution obtained by extracting the sample bulb with water. In the experiments designed for the determination of formaldehyde, the apparatus was heated to ensure that all condensation took place in the sample bulb. The presence of formaldehyde was confirmed by ultraviolet and infrared analysis in experiments wherein the gaseous products were fed into heated cells which prevented condensation from occurring.

Carbonyl determinations on the residual liquid samples were made by a modification of the method of Stillman and Reed.[3] Hydroxyl determinations were made using acetyl chloride and pyridine, while unsaturation was determined by the method of DuBois and Skoog.[4]

Molecular weights of degraded samples were determined by a freezing point lowering method.

Results

Thermal Decomposition.—The decomposition rates of the polypropylene glycol at two temperatures are shown in Fig. 1, where the volume of gaseous decomposition products measured in cubic centimeters at normal temperature and pressure per 10 g. of oil is plotted against time in minutes. Detailed analyses of the gaseous products from a number of runs at 338° were made, the average result of which are given in Table I. The average sample was collected after 7.5 minutes. The actual pressure of gaseous products in the system at this point was 80 mm. This low sample collection pressure was used to avoid condensation. The average results of analyses of the liquid residues remaining after formation of the gas sample discussed above are also given in Table I.

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[1] J. T. Neu, *J. Opt. Soc.*, **43**, 520 (1953).

[2] G. C. Whitnack and R. W. Moshier, *Ind. Eng. Chem.*, *Anal. Ed.*, **16**, 496 (1944).

[3] A. C. Stillman and R. M. Reed, *Perfumery Essential Oil Record*, **23**, 228 (1932).

[4] H. D. DuBois and D. A. Skoog, *Anal. Chem.*, **20**, 624 (1948).