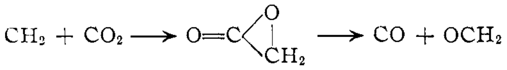
formaldehyde and the formation of an equivalent amount of carbon monoxide suggest that the mechanism of the reaction with carbon dioxide is



$$\mathrm{CH_2 + CO_2 \longrightarrow O{=}C\overset{O}{\underset{CH_2}{\langle}} \longrightarrow CO + OCH_2}$$

by analogy with the attack on ethylene[6] and on carbonyl compounds.[24] Under high radiation intensity some other reactions must also occur because of the excessive reduction of ethylene yields.

Summing up the results of this investigation, it must be regretfully admitted that few problems have been solved; however the extreme complexity of the reactions involved has been brought out more forcefully than hitherto.

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(24) C. D. Gutsche in R. Adams, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 364.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF ROCHESTER]

The Thermal Decomposition of Methyl *n*-Propyl Ketone[1]

BY WILLIAM B. GUENTHER[2]

RECEIVED SEPTEMBER 9, 1957

The liquid products of the gas-phase thermal decomposition of methyl *n*-propyl ketone in the range 500–530° have been examined. Large quantities of methyl vinyl ketone and some acetone were found. Analysis shows that at least 37% of the methyl *n*-propyl ketone decomposing forms methyl vinyl ketone at the start of decomposition. Previously proposed mechanisms are revised to contain these results.

Knowledge of the thermal decomposition of aliphatic ketones in the gas phase has been advanced in recent papers on methyl *n*-butyl ketone[3] and methyl *n*-propyl ketone.[4] Since only the gaseous products were determined for the methyl *n*-propyl ketone decomposition,[4a] it seemed of interest to examine the liquid products. Because of the similar free radical nature of the decompositions of these two ketones, one would look for the products methyl vinyl ketone and acetone which had been found in the methyl *n*-butyl ketone decomposition.

Experimental

Materials and Apparatus.—Two samples of methyl *n*-propyl ketone were obtained, one from Matheson, Coleman and Bell Division and one from Eastman Kodak, practical grade. The latter was used by Waring and Garik.[4a] It was purified as in the previous work[4a] through the bisulfite product and redistillation. Two separate purification batches of the Matheson material had b.p. 102.2 ± 0.2° and 102.0 ± 0.2° at 760 mm. pressure. The purified Eastman Kodak batch boiled at 101.9 ± 0.2°. This compares with recorded values, 102.35 to 102.4°[5] and 102.4°.[6] Waring and Garik[4a] found 101.7°. The bisulfite treatment did remove from the distilled Eastman Kodak ketone a substance which absorbed at 9.15 and 9.62 μ, probably an ester. The index of refraction of the Matheson ketone after purification was 1.3905 corrected[5] to 20°. This compares with 1.3901[5] and 1.3903[6] previously reported. Waring and Garik[4a] found 1.3898 for theirs.

The purification and properties are of special interest because the rates of pressure increase in Garik's thesis[7] are 1.8 times those observed in this work at 500, 510 and 520°. Therefore, the rate of pressure increase of C.P. acetone at 526° was used to check the apparatus. It was found to be about 20% faster in the present apparatus than reported before.[8] As no special purification of the acetone was attempted, this is satisfactory agreement. Thus, it does not seem that an error in the temperature measurement is responsible for our slower rate with methyl *n*-propyl ketone.

The apparatus was similar to that previously used in this Laboratory.[9] The volume of the reaction bulb was 309 ± 2 ml. A platinum *versus* platinum–13% rhodium thermocouple measured the temperature at the center of the reaction bulb. It was checked at the freezing point of zinc.

Analysis of the Products.—Methyl vinyl ketone was identified in four ways. (1) Boiling point—the liquid products of a large number of static experiments at 510–530° and 150–300 mm. initial pressure were trapped at −78° after a pressure increase of about 80%. This product was distilled in a semi-micro column as done by Barry and Walters.[3] There was a good plateau at 81° in the distillation curve. (2) Infrared—the material boiling in the neighborhood of 81° had the characteristic sharp odor of methyl vinyl ketone and gave all the infrared absorptions of methyl vinyl ketone in the region 2.5–15.5 μ. Absorptions of other ketones assumed to be acetone or methyl propyl ketone were also present in this fraction of the products. Using the ultraviolet method described below, this fraction collected near 81° analyzed 53% methyl vinyl ketone. (Attempts to prepare the semicarbazone with this mixture failed. It was found that the semicarbazone would not form properly in the 81° fraction of a known mixture of the three ketones in the proportions expected.) (3) The very intense ultraviolet absorption of methyl vinyl ketone, $\epsilon = 1.07 \times 10^4$ l./mole cm. at 210 mμ was found in the product. The absorption was parallel to the pure methyl vinyl ketone band from 210 to 240 mμ. (4) The polarographic half-wave potential of a solution of the product in 0.1 *N* KCl in 10% methanol was 1.45 volts *versus* the saturated calomel electrode. 1.41–1.43 volts has been reported for aqueous solutions.[10] The current-voltage curve coincided with that for known solutions of methyl vinyl ketone.

Acetone[4b] was identified as the 57° fraction of the product distillation described above. It gave a fluffy semicarbazone like that with known acetone. This washed, dried derivative melted from 178–187° (not recrystallized). The commonly used value is 187°.

The ketene absorption at 4.6–4.7 μ occurred in the gaseous infrared spectrum of the total products but not in the

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(1) The work reported here was supported by a postdoctoral research grant from the Shell Companies Foundation, Inc., for the summer of 1957.

(2) Chemistry Department, University of the South, Sewanee, Tennessee.

(3) W. T. Barry and W. D. Walters, THIS JOURNAL, **79**, 2102 (1957).

(4) (a) C. E. Waring and V. L. Garik, *ibid.*, **78**, 5198 (1956). (b) Recent work (J. R. McNesby and A. S. Gordon, *ibid.*, **80**, 261 (1958)) on the photolysis of methyl *n*-propyl ketone at higher temperatures and the pyrolysis has shown the presence of acetone.

(5) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publ. Co., New York, N. Y., 1950, p. 362.

(6) P. Pomerantz, *et al.*, *J. Research Natl. Bur. Standards*, **52**, 59 (1954).

(7) V. L. Garik, Ph.D. thesis, Univ. of Connecticut, 1953. Univ. Microfilms Pub. No. 6328, Ann Arbor, Mich.

(8) F. O. Rice and W. D. Walters, THIS JOURNAL, **63**, 1701 (1941); C. H. Klute and W. D. Walters, *ibid.*, **67**, 550 (1945).

(9) D. W. Vanas and W. D. Walters, *ibid.*, **70**, 4035 (1948).

(10) E. I. Fulmer, J. J. Kolfenbach and L. A. Underkofler, *Ind. Eng. Chem.*, *Anal. Ed.*, **16**, 469 (1944).

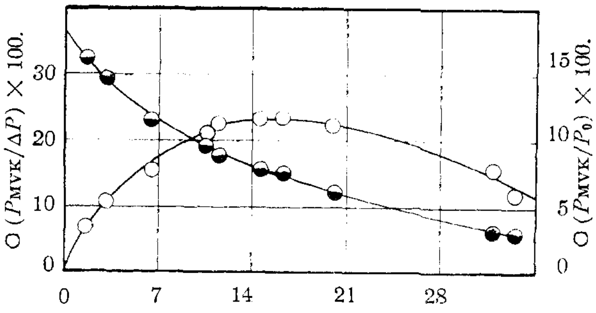

Fig. 1.—Methyl vinyl ketone present during the decomposition of methyl *n*-propyl ketone at 510°. P_0 of methyl *n*-propyl ketone from 130–200 mm. Points up to 11 minutes are averages of 2–3 analyses. The others are single results.

products trapped at −78°. This absorption is said to belong to the C=C=O group.[11] Thus, it seems possible that CH_2CO could be the only ketene present.

The quantitative analyses for methyl vinyl ketone were done as before,[3] spectrophotometrically and polarographically. The two methods agreed within about 10% in checks. The analyses reported in the figure are spectrophotometric.

Results and Discussion

The previously reported[4a] major gas products are methane, carbon monoxide, ethylene and propylene. There were small amounts of ketene, carbon dioxide and hydrogen. These, together with the methyl vinyl ketone and acetone found in the present study, suggest that abstraction of any one of the hydrogen atoms in methyl propyl ketone can occur during the free radical chain decomposition as first predicted by Rice.[12] Indeed, the only major revision of his postulated mechanism needed is to write the radical $CH_3COCHCH_2CH_3$ forming methyl vinyl ketone and CH_3 rather than ethyl ketene and CH_3. One can then adapt Rice's[12] chain steps, where the radicals on the left are formed as other radicals abstract hydrogen atoms from methyl propyl ketone, as

$$CH_3COCH_2CH_2CH_2 \longrightarrow CH_3COCH_2 + CH_2CH_2 \quad (1)$$

$$CH_3COCH_2CHCH_3 \longrightarrow CH_3 + CO + C_3H_6 \quad (2)$$

$$CH_3COCHCH_2CH_3 \longrightarrow CH_3COCHCH_2 + CH_3 \quad (3)$$

$$CH_2COCH_2CH_2CH_3 \longrightarrow CH_2CO + CH_2CH_2 + CH_3 \quad (4)$$

The relative importances of these steps were estimated as 3:4:8:6 by assuming that secondary hydrogens are twice as reactive as primary and that those alpha to the carbonyl are doubled in reactivity.[12] This scheme gives qualitative agreement with the initial products. Acetone can form through hydrogen abstraction by the acetonyl radical of step 1, as suggested also in work reported in ref. 4b. Also, in view of recent results with biacetyl[13] the possibility of a skeleton breaking reaction by methyl radical on methyl propyl ketone or methyl vinyl ketone to give acetone should not be excluded.

Quantitatively, this scheme suggests a larger amount of ketene than was observed.[4a] Ketene was also only a minor product from methyl *n*-butyl ketone.[3]

The analyses for methyl vinyl ketone are shown in the figure. Its production was about first order with respect to methyl propyl ketone. With methyl butyl ketone,[3] it was found that the pressure change and methyl vinyl ketone production were both about 1.3 order. The subsequent decomposition of methyl vinyl ketone[14] causes its relative amount to decrease with time. The plot of methyl vinyl ketone pressure/ΔP *versus* time extrapolates to about 37% at the start of the reaction. If, according to steps 1 and 3 above, one mole of methyl propyl ketone produces two moles of gas, this would correspond to 37% of the methyl propyl ketone going through step 3 at the start. If more than two moles of gas are produced for each mole of methyl propyl ketone, (as will be the case if reactions 2 and 4 are important) this yield would be even higher. If, as it seems to be, steps 2 and 3 are the most important, the approximation that one mole of methyl *n*-propyl ketone forms 2.5 moles of product gives about 55% as the yield of methyl vinyl ketone. It is interesting that Rice's[12] rough estimate of relative reactivities, above, gives 8/21 or 38% for step 3.

For a rough comparison of product quantities, one can subtract the pressures of carbon monoxide and ethylene from the total methane to find the methane from step 3. This should equal the pressure of methyl vinyl ketone. For 100 mm. of methyl propyl ketone carried to 30% pressure increase at 550° (ref. 7, p. 35 and 61), these pressures yield 8.5 mm. of methane equivalent to methyl vinyl ketone. In the present work at 510° and 30% pressure increase, there was 7.5 mm. of methyl vinyl ketone formed per 100 mm. of initial methyl propyl ketone. This treatment assumes that step 1 is either negligible or that methane is formed from CH_3COCH_2 or CH_3COCH_3 at these temperatures. A significant part of the methyl vinyl ketone has probably decomposed.[14] The good agreement should only be considered an indication that the methyl vinyl ketone results fit into the gas analyses of Waring and Garik.[4a,7]

It would seem more likely to form methyl vinyl ketone than its isomer, ethyl ketene, in step 3 if one assumes that methyl vinyl ketone is the more stable product because of the possibility of resonance with its alternate double bonds. The similar bond system in crotonaldehyde does show an increased stability or resonance energy of as much as 7.3 kcal./mole after correcting for polar and hyperconjugation effects.[15] Ethyl ketene may be compared with the adjacent double bonds of allene which actually shows a decrease in stability.[16]

Since acetone,[8] methyl vinyl ketone[14] and ketene[17] all decompose at the temperatures used and the pressure change for the last two gives an erro-

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[11] H. M. Randall, N. Fuson, R. G. Fowler and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., New York, N. Y., 1949, p. 43.

[12] F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," Johns Hopkins Press, Baltimore, Md., 1935, pp. 91, 108 and 111.

[13] W. B. Guenther, C. A. Whiteman and W. D. Walters, THIS JOURNAL, **77**, 2191 (1955).

[14] R. E. Wellman, Ph.D. thesis, Univ. of Rochester, 1955.

[15] M. M. Kreevoy and R. W. Taft, Jr., THIS JOURNAL, **79**, 4016 (1957).

[16] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 111.

[17] W. B. Guenther, Ph.D. thesis, Univ. of Rochester, 1954.

neous idea of the amount of decomposition, it does not seem likely that pressure measurements will have a simple relationship to the amount of methyl propyl ketone decomposed in any part of the reaction.

Ethylene and propylene also react and decrease greatly in amount during the decomposition.[4a] Since propylene inhibits the decomposition,[4a] that effect will operate to increase the complexity of the process. As with methyl *n*-butyl ketone,[3] one must conclude that a complete kinetic analysis of the free radical chain mechanism is not possible with the data available. However, the great similarity of the behaviors of these two ketones is apparent. It is seen that the chain steps above are analogous to those advanced for methyl *n*-butyl ketone.[3]

It is likely that the carbon dioxide reported by Waring and Garik[4a] is produced by the reactions of ketene since carbon dioxide is a major product of the ketene decomposition at these temperatures.[17]

Combining the analyses here with those of Waring and Garik,[4a,7] one can see that, if the above steps 1–4 represent the decomposition, steps 2 and 3 are most important.

Acknowledgment.—The author wishes to acknowledge the many helpful comments of Dr. W. D. Walters who suggested this problem. The gaseous infrared analyses were performed by Mr. C. A. Whiteman.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

The Exchange of Hypochlorite and of Hypobromite Ions with Water

BY M. ANBAR AND H. TAUBE

RECEIVED FEBRUARY 23, 1956

The reaction of ClO^- and BrO^- with NO_2^- proceeds with almost complete transfer of hypohalite oxygen to nitrite. This reaction has been applied in the isotopic analysis of ClO^- and BrO^- undergoing exchange with water. The exchange of ClO^- and water in alkaline solution proceeds by the paths $k_A[(ClO^-)/(OH^-)]$ and $k_B[[(ClO^-)(Cl^-)]/(OH^-)]$. Paths of similar kinetic form are indicated for the exchange of BrO^- and water, and Cl^- as well as Br^- can catalyze the exchange. The reactions reverse to the k_B paths are the attack of Cl_2, Br_2 or BrCl by OH^-, and the specific rates for these reactions have been calculated. The mechanisms of the reactions and the mode of action of H^+ in reactions of oxy-ions are discussed.

In the course of tracer work on the reactions of oxy-anions with nitrite ion in water, it was observed that when ClO^- or BrO^- are the oxidizing agents, almost complete transfer of oxygen to the reducing agent takes place. The reactions with nitrite provide a means of isotopic analysis of the hypohalites and therefore of following the rate at which oxygen exchanges between them and water. While the method thus made available is far from ideal, the exchange reactions in question are of such interest in themselves, as well as for comparison with other substitution or oxidation-reduction reactions of the hypohalites, that it was considered worthwhile to obtain even data of the quality of those reported in this paper. This decision was not reached without making an extensive survey[1] of other reactions which might be exploited for oxygen isotope sampling, but none was discovered superior to that adopted here. Some of the disadvantages of the present sampling method could be avoided by sampling the solvent by distillation. This method, however, is not accurate for dilute solutions of the solute.

Experimental

Reagents.—The hypochlorite solution was prepared by passing Cl_2 through ice-cooled 5 *M* NaOH, then gradually adding freshly prepared Ag_2CO_3 until Ag_2O, recognizable by its color, began to form. The solution at $pH > 13$ was stored in a refrigerator. The hypobromite was prepared in a similar manner, but because of the greater rate of decomposition, was used within 24 hr. Other chemicals were of A.R. quality, used without further purification.

Procedure.—Solutions in O^{18}-enriched water, each of total volume *ca.* 20 ml. were prepared, containing the hypohalite as well as appropriate amounts of H_2SO_4 and NaH_2PO_4 and kept in a thermostat. The adjustment of *p*H was made, using a Beckman *p*H meter, with a special electrode for alkaline solution. Measurements were reproducible to *ca.* 0.03 *p*H unit. Aliquots were withdrawn at intervals for isotopic assay of the hypohalite. Each sample immediately after being withdrawn was mixed with enough sodium nitrite solution to leave the oxidizing agent in slight excess and then was added with stirring to 100 ml. of water buffered to a *p*H of 1. After reaction, which was found to be complete within 10 sec., H_2O_2 was added to remove the excess hypohalite. Solid Ag_2SO_4 and $Ba(OH)_2$ were now added, and the solution was adjusted to *p*H 9 using NaOH. After filtration, which removes sulfate, phosphate, halide and silver from the system, the *p*H of the solution was adjusted to between 5 and 6 with acetic acid, and nitron (diphenylenedianelohydrotriazole) reagent was added. The solution was left for about 12 hr. for crystallization of nitron nitrate. This was filtered off, digested with ammonium hydroxide and was reprecipitated. After digesting the precipitate again with ammonium hydroxide, the remaining nitron base was extracted with ethyl acetate. The solution was then evaporated to dryness, the final drying being done under vacuum. The N_2O for isotopic analysis was obtained by decomposition of the NH_4NO_3 comprising the residue, the gas first being purified by storage over solid NaOH.

In spite of pains to improve the method of isotopic analysis, specific rates calculated from results for successive aliquots of a given reaction mixture are found to differ by as much as a factor of 2. These fluctuations do not correspond to real changes in rate, since they follow no trend with time, and furthermore the data within a precision of a factor of 2 or so conform to a simple and reasonable rate law, over a very wide range in rate. It has been shown by direct experiments that the handling of the nitrate is not responsible for the fluctuations. The principal error seems to be incurred in the reaction of nitrite and hypohalite, for the conditions necessary to make this reaction rapid also increase the rate of exchange between hypohalite and water. Partial exchange intervenes from time to time. This causes an apparent reduction in the rate of exchange, because the environment during the quenching reaction has nearly the isotopic composition of the initial hypohalite. To conform to this analysis, the theoretical line in Fig. 1 has been drawn through a high density of points corresponding to the higher

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(1) The results of these tracer experiments will be described in a separate article.