JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

(Registered in U. S. Patent Office) (Copyright, 1952, by the American Chemical Society)

VOLUME 74 OCTOBER 9, 1952 NUMBER 19

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

The Photolysis of Di-*n*-propyl Ketone[1]

BY C. R. MASSON[2]

RECEIVED FEBRUARY 18, 1952

The decomposition of gaseous di-*n*-propyl ketone resulting from the absorption of λ3130 Å. radiation has been studied over a pressure range 8 to 115 mm., a temperature range 55 to 357° and a 3-fold variation in light intensity. The results support earlier conclusions by other workers that two kinds of primary process occur. For temperatures up to 161° the quantum yield of ethylene formation is independent of pressure, temperature and light intensity, while that of carbon monoxide formation varies only slightly with temperature and is independent of pressure and light intensity. The activation energy for the abstraction of a hydrogen atom from the ketone by a *n*-propyl radical has been found to be 6.5 kcal. per mole, assuming zero activation energy for the association of *n*-propyl radicals. It is estimated that, of the *n*-propyl radicals which mutually react, 17% disproportionate at 113°. Above 161° a chain reaction becomes increasingly important. This is explained in terms of the decomposition of the heptanonyl radical, and an activation energy of 10 kcal. has been assigned to this step. A value of 20 kcal. is found for the decomposition of the *n*-propyl radical into ethylene and methyl. In addition to the combination of *n*-propyl radicals, a further reaction leading to hexane formation at high temperatures is necessary to explain the results.

The photolysis of di-*n*-propyl ketone has been studied previously,[3] both in the vapor phase and in paraffinoid solution. It has been concluded that two types of primary process occur: (a) a direct decomposition into ethylene and methyl *n*-propyl ketone and (b) a split into carbon monoxide and free radicals. It was found that, in the vapor phase, the quantum yields of these processes were not greatly influenced by temperature over the range 0–100°; in solution, on the other hand, a marked temperature dependence was observed for process (b), while (a) was relatively unaffected. Propane was obtained as a product of the reaction in solution but not in the gas phase. It has also been demonstrated[4] that *n*-propyl radicals are formed in the photolysis.

This paper describes further work on the photolysis in the gas phase. New products have been identified and a fuller insight into the mechanism of decomposition is now possible.

Experimental

Di-*n*-propyl ketone (E. C. Matheson & Co., Inc.) was stored over drierite for about one month, then distilled through a 30-plate column in an atmosphere of dry nitrogen, the middle third (n^{20}D 1.4073, lit. 1.40732) being retained. This was introduced into the apparatus over drierite and distilled again *in vacuo*, the center portion being kept for use. Diethyl ketone was similarly purified, anhydrous copper sulfate being used as desiccant. Cylinder hydrogen, used in analysis, was purified by passage through a hot palladium thimble.

The light source used in all experiments was a Hanovia Quartz Alpine Sun Burner, type S-100, in conjunction with 1 mm. of Pyrex as light filter. The light was collimated by a single quartz lens and a series of stops. The wave lengths absorbed by the ketone consisted mainly of 3130 Å. with a little 3020 and 2967 Å. A cylindrical quartz reaction cell, 20 cm. in length and 2.2 cm. internal diameter was employed. In order to avoid, as far as possible, uncertainties in the interpretation of the data due to the diffusion of radicals out of the light path,[5,6] the light beam was arranged so that the intense central core of the beam just filled the cell completely. Light intensities were varied by means of neutral density filters of coated quartz.

The cell was surrounded by a cylindrical, electrically heated furnace 36 cm. in length, closed at each end with plane windows of either Pyrex or quartz. Temperatures were recorded near the center of the cell by either a thermometer or a copper–constantan thermocouple. The temperature was controlled manually to ±1° during a run, although for short runs up to about 10 or 15 min. duration temperature control was usually much better than this.

Pressures were measured on a small U-tube mercury manometer constructed of precision bore 2 mm. tubing attached to the reaction system. The reaction system was isolated

(1) For detailed tables of data order Document 3628 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(2) (a) Maritime Regional Laboratory, National Research Council, Halifax, N. S., Canada. (b) This work was supported by Contract N6-onr-241, Task I with the Office of Naval Research, United States Navy. The author also wishes to thank the Drs. Camille and Henry Dreyfuss Foundation, Inc., for the award of a post-doctoral fellowship.

(3) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1504 (1935); 1531, 1544 (1938).

(4) T. G. Pearson and R. H. Purcell, *ibid.*, 253 (1936).

(5) W. A. Noyes, Jr., *J. Phys. Colloid Chem.*, **55**, 925 (1951).

(6) A. J. C. Nicholson, THIS JOURNAL, **73**, 3981 (1951).

from the remainder of the apparatus by a float-valve mercury cut-off. Since the vapor pressure of the ketone at 30° is only about 10 mm., all parts of the reaction system external to the furnace were electrically heated to a temperature of about 80°.

The gaseous products of the reaction were pumped off and measured by means of a combined Töepler pump, McLeod gage and gas buret. Non-condensable gases were removed through a pumped-down liquid nitrogen trap at −210°, CO being subsequently determined by oxidation over CuO at 200–220°. The remaining products were separated into convenient fractions by low-temperature distillation, using two columns of the type described by LeRoy.[7] C_2 Hydrocarbons were removed at −180°. C_3H_8 and C_3H_6 were generally pumped off at −135°, but in runs where C_4 hydrocarbons were also present in the products this fraction was taken off at −148° and the C_4 product removed at −120°.

Unsaturation in the C_2 and C_3 fractions was determined both by absorption in a Blacet–Leighton[8] apparatus, using the hydroxy-mercurial method of Pyke, Kahn and LeRoy,[9] and by micro-hydrogenation over a nickel catalyst employing the method of Moore and Taylor[10] as adapted by Kutschke.[11] Both methods gave consistent results, and the result obtained by the hydrogenation technique for an approx. 50/50 mixture of C_3H_8 and C_3H_6 agreed to within 4% with a mass spectrometric determination by Consolidated Engineering Corporation on the same sample.

The hexane vapors were töeplered over at −85° into a calibrated volume between two cut-offs, and measured on a small McLeod gage. Mass spectrometer analysis of this fraction showed that 98% of the hexanes consisted of *n*-hexane.

Attempts were made[12] to identify $CH_3COC_3H_7$, reported as a product by Bamford and Norrish.[3] A fraction having a vapor pressure intermediate between *n*-hexane and di-*n*-propyl ketone was isolated by prolonged töeplering at −50°, and although mass spectrometer analysis[13] showed it to contain less than 2% of the parent ketone, positive identification was not obtained.

For the determination of quantum yields diethyl ketone was used as an internal actinometer, Φ_{CO} for this ketone being taken as unity at 113° in the spectral region employed.[14,15]

Results

Products identified were CO, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, a C_4-hydrocarbon and n-C_6H_{14}: of these, CH_4, C_2H_6 and the C_4 fraction were found only in the products of runs at 240° or higher.

The complete results are listed in tables available through the American Documentation Institute.[1] Rates have been calculated on the basis of a reaction volume of 76.1 cc. Conversions were nearly always less than 1%.

From these results the following facts are obtained: (1) At 113° and constant incident intensity Φ_{CO} has a mean value of 0.31 (±0.03), independent of pressure from 8 to 47 mm. (2) At 113° the ratio C_2H_4/CO is essentially independent of pressure from 8 to 115 mm., as shown in Fig. 1. The slight decrease, if real, corresponds to a change in $\Phi_{C_2H_4}$ from 0.22 at 8 mm. to 0.20 at 115 mm. This is in marked contrast to the variation of the other ratios with pressure, also shown in Fig. 1. (3) The rates of formation of CO and C_2H_4 at 39 mm. and 113° are each directly proportional to the absorbed light intensity over the range $I_a = 0.276 \times 10^{12}$ to 2.71×10^{12} $h\nu$/cc./sec. For the other products, under the same conditions, the following intensity exponents are obtained: $R_{C_3H_8} \sim I_a^{0.75}$; $R_{C_3H_8-C_3H_6} \sim I_a^{0.73}$; $R_{C_3H_6} \sim I_a^{1.41}$; $R_{n\text{-}C_6H_{14}} \sim I_a^{1.49}$. These exponents refer to only a very limited range of intensities; the values may be expected to vary with intensity over a wider range. (4) At constant ketone concentration and constant I_a, Φ_{CO} and $\Phi_{C_2H_4}$ each vary very little with temperature from 55 to 161°. At higher temperatures a sharp increase occurs. This increase is observed also for the other products, being very marked in the case of propylene.

Discussion

The Primary Process.—The above results afford support for the original postulate by Bamford and Norrish[3] that the ethylene arises by the non-free-radical primary process (1a)

$$C_3H_7COC_3H_7 = C_2H_4 + CH_3COC_3H_7 \qquad (1a)$$

The occurrence of this type of primary process for certain ketones, particularly methyl *n*-butyl ketone,[16] now seems to be quite definitely established.

The virtual constancy of Φ_{CO} with pressure, light intensity and temperature (up to 161°) indicates that, if CO formation occurs through the intermediacy of the *n*-butyryl radical C_3H_7CO, this radical must be so unstable as to decompose spontaneously before it can react in any way. In their study of the photolysis in paraffinoid solution, Bamford and Norrish[3] present evidence that the *n*-butyryl radical is sufficiently stable below 70° to react with the solvent or recombine with a *n*-propyl radical. It would therefore appear that the lifetime of this radical under ordinary conditions is less than the time between collisions in the gas phase (*ca.* 10^{-8} sec.) but greater than the corresponding time interval in the liquid phase (*ca.* 10^{-13} sec.). It depends upon our definition of the term "primary process" as applied to gas phase reactions whether we can regard the *n*-butyryl radical as being formed. From the point of view of the present work, the formation of CO is described by the over-all reaction (1b)

$$C_3H_7COC_3H_7 = 2C_3H_7 + CO \qquad (1b)$$

The sum of primary processes (1a) and (1b) accounts for only about half of the total light absorbed. In view of the absence of pressure effects, the reason for this low quantum efficiency is not obvious. In the only fluorescence study of this ketone[17] it is reported that no bands are visible at temperatures above about −50°. It has been suggested[3] that the excited ketone molecule must undergo a process of internal degradation of energy; this seems to be the only explanation for the low yields which fits the present facts.

(7) D. J. LeRoy, *Can. J. Research*, **B28**, 492 (1950).

(8) F. E. Blacet and P. A. Leighton, *Ind. Eng. Chem., Anal. Ed.*, **3**, 266 (1931).

(9) R. Pyke, A. Kahn and D. J. LeRoy, *Anal. Chem.*, **19**, 65 (1947).

(10) W. J. Moore and H. S. Taylor, *J. Chem. Phys.*, **8**, 466, 396 (1940).

(11) K. O. Kutschke, Ph.D. thesis, University of Rochester. See K. O. Kutschke, M. H. J. Wijnen and E. W. R. Steacie, THIS JOURNAL, **74**, 714 (1952).

(12) These experiments were performed by Mr. Peter Graf.

(13) The author wishes to thank Drs. D. W. Stewart and G. P. Happ of the Research Lab., Eastman Kodak Co., for kindly performing these analyses.

(14) W. Davis, Jr., THIS JOURNAL, **70**, 1868 (1948).

(15) K. O. Kutschke, M. H. J. Wijnen and E. W. R. Steacie, *ibid.*, **74**, 714 (1952).

(16) For a review, see W. Davis, Jr., *Chem. Revs.*, **40**, 245 (1947).

(17) S. C. Sirkar and B. M. Bishni (Calcutta), *Nature*, **156**, 333 (1945).

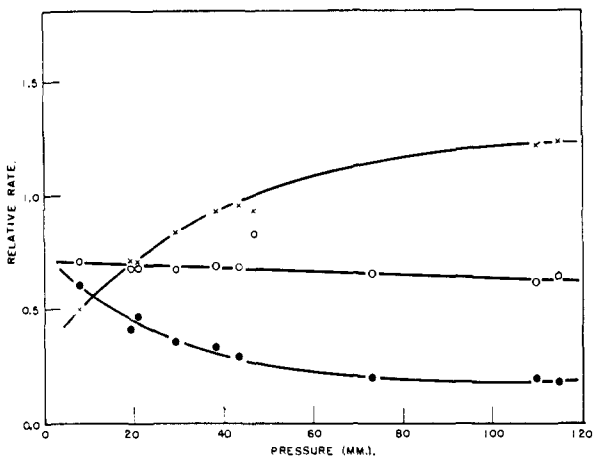

Fig. 1.—Variation of relative rates with pressure at 113°: O, C_2H_4/CO; ×, C_3H_8/CO; ●, C_6H_{14}/CO.

Secondary Reactions.—In addition to (1a) and (1b), reactions (2) to (12) are considered in explaining the results. Of these, (7) to (12) are required only for the high-temperature photolysis.

$$C_3H_7 + C_3H_7 = C_6H_{14} \quad (2)$$

$$C_3H_7 + C_3H_7 = C_3H_8 + C_3H_6 \quad (3)$$

$$C_3H_7 + C_3H_7COC_3H_7 = C_3H_8 + C_3H_7COC_3H_6 \quad (4)$$

$$C_3H_7 + C_3H_7COC_3H_6 = C_3H_7COC_6H_{13} \quad (5)$$

$$2C_3H_7COC_3H_6 = (C_3H_7COC_3H_6)_2 \quad (6)$$

$$C_3H_7COC_3H_6 = C_3H_7 + CO + C_3H_6 \quad (7)$$

$$C_3H_7 = C_2H_4 + CH_3 \quad (8)$$

$$CH_3 + C_3H_7COC_3H_7 = CH_4 + C_3H_7COC_3H_6 \quad (9)$$

$$CH_3 + CH_3 = C_2H_6 \quad (10)$$

$$CH_3 + C_3H_7 = C_4H_{10} \quad (11)$$

$$C_3H_7 + C_3H_7COC_3H_6 = C_6H_{14} + CO + C_3H_6 \quad (12)$$

Reaction (2) best explains the formation of *n*-hexane. Evidence for the occurrence of reaction (3) is found in the constant ratio of propylene to hexane for all runs at 113°, indicating that these products are formed mainly by related mechanisms. The slight difference (if real) in intensity exponent for these two products at 113° might be explained by the occurrence of reaction (7) to a slight extent at low intensities. From a mean value of the results in Table I it is concluded that, of the propyl radicals which mutually react, 17% disproportionate at 113°. This may be compared with the value of 10% at room temperature found by Blacet and Calvert.[18] Present data are not sufficiently accurate to permit an estimate to be made of the activation energy difference between reactions (2) and (3).

If reactions (2), (3) and (4) are the only methods of formation of C_6H_{14}, C_3H_6 and C_3H_8 relations (13), (14) and (15) are obtained

$$C_3H_6/C_6H_{14} = k_3/k_2 \quad (13)$$

$$\frac{C_3H_8 - C_3H_6}{C_6H_{14}} = \frac{k_4}{k_2^{1/2}} \frac{(\text{d.p.k.})}{R_{C_6H_{14}}^{1/2}} \quad (14)$$

$$\frac{C_3H_8}{C_6H_{14}} = \frac{k_3}{k_2} + \frac{k_4}{k_2^{1/2}} \frac{(\text{d.p.k.})}{R_{C_6H_{14}}^{1/2}} \quad (15)$$

where (d.p.k.) represents the ketone concentration, and the subscripts refer to the above reactions.

(18) F. E. Blacet and J. G. Calvert, THIS JOURNAL, 73, 661 (1951).

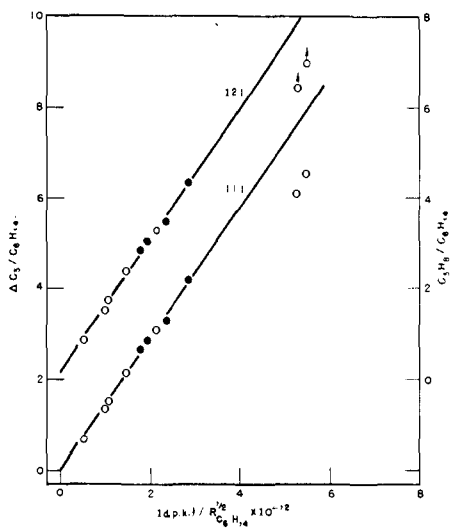

Fig. 2.—$\Delta C_3/C_6H_{14}$ *vs.* (d.p.k.)/$R^{1/2}_{C_6H_{14}}$ (curve 1) and C_3H_8/C_6H_{14} *vs.* (d.p.k.)/$R^{1/2}_{C_6H_{14}}$ (curve 2): temp., 113°; O, I_0 constant, (d.p.k.) varied; ●, I_0 varied, (d.p.k.) constant.

In Fig. 2 the ratios $(C_3H_8-C_3H_6)/C_6H_{14}$ (represented by $\Delta C_3/C_6H_{14}$) and C_3H_8/C_6H_{14} are each plotted against (d.p.k.)/$R^{1/2}_{C_6H_{14}}$ for all runs at 113° except one where the intensity was very low. Open circles represent runs where the pressure, and hence also I_a, were varied at constant incident intensity, while closed circles denote runs in which only the intensity was varied. In each case the majority of the points fall on a straight line, passing through the origin in the case of curve (1), and having a slight positive intercept on the ordinate in the case of curve (2), in agreement with the predictions of equations (14) and (15). The point representing the run of lowest intensity {(d.p.k.)/$R^{1/2}_{C_6H_{14}}$ = 10.5 × 10^{12}} lies slightly above an extension of the straight line in each case. A departure from linearity at high pressures is indicated in both sets of points. This is too large to be accounted for by an error in either propylene or hexane alone. It might be produced, however, by an approximately 3% error in the propane determination, since any propane not completely removed from the products at −135° would appear in the hexane fraction. In view of the relatively large volume of unreacted ketone in the high-pressure runs, the possibility of such an error cannot be excluded.

The value of k_3/k_2 obtained from the intercept of curve (2) in Fig. 2 is 0.15 ± 0.1; this agrees with the value of 0.21 given by the mean of the ratios C_3H_6/C_6H_{14} at 113°.

The slopes of the lines in Fig. 2 each give $k_4/k_2^{1/2}$. Values of this constant at other temperatures have been calculated by dividing $\Delta C_3/C_6H_{14}$ by (d.p.k.)/$R^{1/2}_{C_6H_{14}}$. For runs above 161°, the propylene formed by disproportionation has been neglected in comparison with the propane, and the ratio C_3H_8/C_6H_{14} has been used in place of $\Delta C_3/C_6H_{14}$ in the calculations. The values of $k_4/k_2^{1/2}$ obtained in this way are plotted logarithmically against $1/T$ in Fig. 3. The plot is linear for temperatures up to 161°. From this linear portion

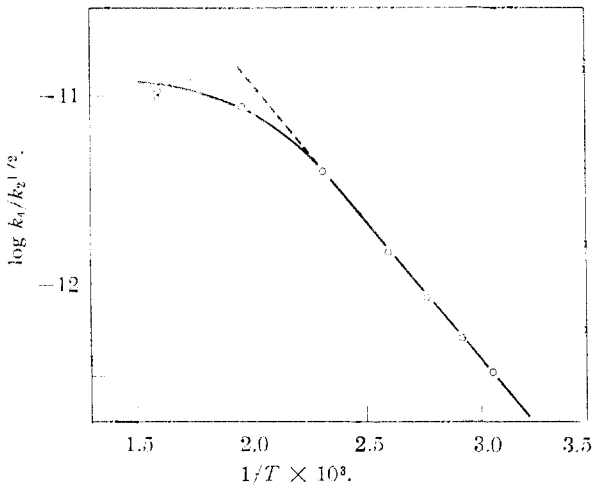

Fig. 3.—Log $k_4/k_2^{1/2}$ *vs.* $1/T$.

one obtains $E_4 - {}^1/_9E_2 = 6.5$ kcal./mole. The calculated ratio of steric factors $p_4/p_2^{1/2}$ is 9.03 $\times 10^{-12}$. $\sigma_{(2)}/\sigma^2_{(4)}$ where $\sigma_{(2)}$ and $\sigma_{(4)}$ are the collision diameters for reactions (2) and (4), respectively. Taking values of 5.4 and 6.2 Å., respectively, for these diameters, one obtains $p_4/p_2^{1/2} = 1.3 \times 10^{-4}$. This is of the same order of magnitude as the values found for methyl radical reactions.[19]

No direct evidence is available for the occurrence of reactions (5) and (6). Reaction (5) must, however, be included to account for the observation that $\Phi_{C_3H_8} + \Phi_{C_3H_6} + 2\Phi_{C_6H_{14}}$ is always less than $2\Phi_{CO}$. Reaction (6) is included by analogy with the corresponding reaction in the acetone photolysis.[20]

The High Temperature Reaction.—It is obvious from the results in Table I (b)[1] that a chain reaction sets in at high temperatures. The rapid and parallel increase of Φ_{CO} and $\Phi_{C_3H_6}$ with increase in temperature above 161° strongly suggests the occurrence of reaction (7) as a chain-propagating step. A corresponding reaction has been proposed to account for certain aspects of the diethyl ketone photolysis.[15]

The CO formed by reaction (7) above 161° has been calculated by subtracting the CO estimated from the primary process alone. The C_3H_6 arising from reaction (7) has also been estimated by assuming $E_2 = E_3$ and subtracting 21% of the hexane from the total propylene. The resulting rates of chain production of CO and C_3H_6 are compared in Table II. The agreement is within experimental error for most runs.

The increase in $\Phi_{C_2H_4}$ with temperature above 161° and the simultaneous appearance of CH_4, C_2H_6 and C_4 hydrocarbons in the products are explained by reaction (8), followed by (9), (10) and (11). The rate of formation of C_2H_4 by reaction (8) ($R_{C_2H_4'}$) has been determined in the same way as for $R_{\text{chain CO}}$. According to equations (8) to (11), $R_{C_2H_4'}$ should be equal to $R_{CH_4} + 2R_{C_2H_6} + R_{C_4H_{10}}$. As shown in Table II, good agreement is obtained between these quantities.

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

(20) W. A. Noyes, Jr., and L. M. Dorfman, *ibid.*, **16**, 788 (1948).

TABLE II

COMPARISON OF RATES

(d.p.k.) ≈ 5.3×10^{17} molecules cc.$^{-1}$; $I_a \approx 1.7 \times 10^{12}$ $h\nu$ cc.$^{-1}$ sec.$^{-1}$

Run	33	34	36	37	39
Temp., °C.	240	307	357	357	357
Rates (molecules cc.$^{-1}$ sec.$^{-1}$) $\times 10^{-12}$					
Chain CO	0.47	4.06	12.4	17.8	13.3
Chain C_3H_6	.59	4.11	12.3	17.4	15.2
C_2H_4'	.127	1.86	10.3	..	12.2
$CH_4 + 2C_2H_6 + C_4H_{10}$	.155	1.88	10.6	..	12.0

The deviation from linearity of the plot shown in Fig. 3 can be explained only by a further reaction leading to hexane formation above 161°. Reaction (12) is suggested as a possible explanation. To account for the curvature, this reaction would be required to yield approximately 25% of the hexane formed at 357°; it would affect the yields of CO and C_3H_6 by only about 2%.

If reactions (1) to (12) completely describe the photolysis, a rough estimate may be made of the activation energy difference $E_7 - {}^1/_2E_6$. From reactions (6) and (7) relationship (16) is obtained

$$R_{\text{chain CO}}/R_D^{1/2} = R_{\text{chain } C_3H_6}/R_D^{1/2} = k_7/k^{1/2} \quad (16)$$

where D represents $(C_3H_7COC_3H_6)_2$. Consideration of reactions (1) to (12), omitting (10), leads to the expression for R_D

$$R_D = R_{C_3H_8} + R_{C_6H_{14}} + {}^1/_2(R_{CH_4} + R_{C_4} + R_{C_2H_4'}) - R_{CO} \quad (17)$$

R_D calculated by (17) is subject to large error, so that the values of $k_7/k_6^{1/2}$ thus obtained must be considered as very approximate. An Arrhenius plot gives E, $- {}^1/_2E_6 = 10$ kcal. If E_6 is small, this will be an approximate value for the activation energy of reaction (7).

From reactions (4) and (8) one obtains

$$R_{C_2H_4}\ (\text{d.p.k.})/R_{C_3H_6} = k_8/k_4 \quad (18)$$

A plot of log k_8/k_4 against $1/T$ gives a value of 15 ± 1 kcal. for $E_8 - E_4$. In conjunction with the value of 6.5 kcal. for $E_4 - {}^1/_2E_2$ this gives $E_8 - {}^1/_2E_2 = 21.5 \pm 1.5$ kcal.

Alternatively, $E_8 - {}^1/_2E_2$ may be found by estimating the rate of formation of hexane by reaction (2) ($R_{C_6H_{14}'}$) and using the expression

$$R_{C_2H_4'}/R_{C_6H_{14}'}^{1/2} = k_8/k_2^{1/2} \quad (19)$$

to calculate values of $k_8/k_2^{1/2}$. $R_{C_6H_{14}'}$ has been calculated from an extension of the linear portion of the plot in Fig. 3. The resulting Arrhenius plot for $k_8/k_2^{1/2}$ gives $E_8 - {}^1/_2E_2 = 20 \pm 1$ kcal. It is of interest to note that, had reaction (12) been omitted from the mechanism and the total rate of hexane formation used instead of $R_{C_6H_{14}'}$ in calculating $k_8/k_2^{1/2}$, the apparent value found for $E_8 - {}^1/_2E_2$ would have been approx. 17 kcal., which is undoubtedly too low.

If E_2 is assumed to be zero, the above values are equal to the activation energy of reaction (8).

These are in good agreement with the values of 19 and 20 kcal.[21,22] found by previous workers.[23]

The present work does not provide a means of deciding which hydrogen atom is abstracted from the ketone in reaction (4). By analogy with methyl radical reactions[19] it is most probable that the abstraction occurs in either the α- or β-position to the carbonyl group. At high temperatures, however, the possibility of abstraction in the γ-position must be considered. If this occurred, the resulting heptanonyl radical might be expected to yield, on decomposing, the trimethylene biradical. It has been shown[24] that this radical may undergo ring closure in the gas phase to form cyclopropane. The presence of cyclopropane was therefore sought in the products of a run at 357°. Mass spectrometer analysis, however, showed that this compound was not formed in detectable amount, thus providing indirect evidence that the value of 6.5 kcal. found for E_4 refers to secondary hydrogen abstraction.

Acknowledgment.—The author wishes to express his thanks to Dr. W. A. Noyes, Jr., for his interest in this work and for much helpful advice and stimulating discussion.

(21) R. W. Durham, G. R. Martin and H. C. Sutton, *Nature*, **164**, 1052 (1949).

(22) S. Bywater and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 319 (1951).

(23) Note added in revision: These values for E_3 indicate a high value for the C–H bond strength in propane (ref. 22). This is in agreement with recent findings by C. H. Leigh and M. Szwarc, *ibid.*, **20**, 407 (1952), and by D. P. Stevenson (quoted in Leigh and Szwarc).

(24) C. E. H. Bawn and R. F. Hunter, *Trans. Faraday Soc.*, **34**, 608 (1938).

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Rates, Equilibrium and Temperature Coefficients in the Reversible Hydration of Gaseous 1-Methylcyclopentene-1 by Dilute Nitric Acid[1]

BY ROBERT W. TAFT, JR., JOSEPH B. LEVY, DAVID AARON AND LOUIS P. HAMMETT

RECEIVED APRIL 2, 1952

The rate of hydration to 1-methylcyclopentanol-1 of 1-methylcyclopentene-1 by dilute aqueous nitric acid is 3.64 times faster at 35° than is that of isobutene to *t*-butyl alcohol, and 3.05 times faster at 45°. The enthalpy of activation for the cyclic olefin is 3.50 ± 0.27 kcal. less than that of isobutene, the entropy of activation is 9.0 ± 0.9 cal./deg. less. The small difference in rate between the two olefins arises therefore from a difference in entropy of activation which almost completely compensates a difference in enthalpy of activation which would by itself make the reaction of the cyclic compound 300 times faster than that of isobutene. The reaction of the methylcyclopentene is considerably less complete than is that of isobutene, and precise values for the rate of dehydration of the alcohol and for the equilibrium constant have been obtained. The dehydration has an unusually high temperature coefficient and a positive entropy of activation, 9.6 ± 0.8 cal./deg.

We have studied the reversible conversion of 1-methylcyclopentene-1 in the gas phase to 1-methylcyclopentanol-1 dissolved in dilute aqueous nitric acid both by "hydration" measurements, *i.e.*, measurements starting from the gaseous olefin, and by "dehydration" measurements, which start from the dissolved alcohol. Although the hydration of this olefin, in contrast to that of isobutene,[2] is markedly reversible, the equations and procedures used in article I for computing the specific rates from experimental data on the rate of the drop in pressure apply without alteration to the present hydration measurements.

Our treatment of the dehydration case is based upon the considerations which follow. We use the same symbols as in article I, namely: P = partial pressure of olefin at time t; C_a = concentration of alcohol at time t; P^0, C_a^0 and P^e, C_a^e are corresponding values at time 0 and at equilibrium, respectively; r = (volume of gas phase)/(volume of solution); h = distribution constant C/P of olefin between phases; k_p = rate of conversion of olefin to alcohol at unit pressure of olefin; k_{-1} = rate of conversion of alcohol to olefin at unit concentration of alcohol. The basic relation, eq. (I-1), of article I still applies but the material balance relation, eq. (I-2), is replaced by

$$C_a = C_a^0 - P(h + r/RT) \qquad (1)$$

By manipulations which parallel those of article I one can obtain the relation

$$s \equiv -\frac{\mathrm{d} \ln (P^e - P)}{\mathrm{d}t} = \frac{k_p}{h + r/RT} + k_{-1} \qquad (2)$$

which differs from eq. I-5 of the hydration case only in the replacement of $P - P^e$ by $P^e - P$. By eliminating the quantities k_p and C_a^e between eq. 2, I-4, and the relation

$$C_a^e = C_a^0 - P^e(h + r/RT) \qquad (3)$$

which is an obvious corollary of eq. (1), one gets

$$\frac{C_a^0 RT}{sP^e r} = \frac{1}{k_{-1}} + \frac{h}{k_{-1}} \frac{RT}{r} \qquad (4)$$

If then a series of measurements of the slope are made with varying values of the ratio r of the volumes of gas and liquid, and if the initial concentration C_a of alcohol and the equilibrium partial pressure P^e of olefin are determined in each case the value of k_{-1} can be obtained as the reciprocal of the intercept of a plot of the left side of eq. (4) against

(1) The work reported herewith was carried out as project NR 956-062 under contract N6onr-271 between the Office of Naval Research and Columbia University. Reproduction in whole or in part permitted for any purpose of the United States Government.

(2) J. B. Levy, R. W. Taft, Jr., D. Aaron and L. P. Hammett, THIS JOURNAL, **73**, 3792 (1951). This will be referred to as article I, and the equations in it will be referred to as eq. (I-1), etc. The sign of the second term on the right of eq. (I-7) was incorrectly transcribed, and the equation should read

$$\frac{RT}{r(s - k_{-1})} = \frac{1}{k_p} + \frac{h}{k_p} \frac{RT}{r}$$