should again give more information than the average. The helical content and the orientation of the helices in the molecule should be determinable.

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[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY, COLUMBUS]

A Kinetic Study of the *n*-Propyl Radical Decomposition Reaction

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Thermally equilibrated *n*-propyl radicals were generated homogeneously through the selective photolysis of azomethane at 3660 A. in *n*-butyraldehyde–azomethane mixtures. The decomposition reaction, $n\text{-C}_3\text{H}_7 \rightarrow \text{CH}_3 + \text{C}_2\text{H}_4$ (1), was followed by measurement of the rate of ethylene formation. The steady-state concentration of *n*-propyl radicals was gauged indirectly by the determination of the rates of butane formation, $\text{CH}_3 + n\text{-C}_3\text{H}_7 \rightarrow n\text{-C}_4\text{H}_{10}$ (5), and ethane formation, $2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ (6). From the temperature dependence of the rate function, $R_{\text{C}_2\text{H}_4}R_{\text{C}_2\text{H}_6}{}^{1/2}/R_{n\text{-C}_4\text{H}_{10}} = k_1k_6{}^{1/2}/k_5$ and the assumption $k_5 = k_6 = 2.2 \times 10^{13}$ cc./mole-sec., it is estimated that $k_1 \cong 2.85 \times 10^{16}e^{-34.9/RT}$ sec.$^{-1}$. From these data and Brinton's estimate of k_{-1}, we derive: $\Delta H_1 \cong 26.2$ kcal./mole; $\Delta S_1{}^0 \cong 15.4$ e.u. (near 200°). These and accurate thermal data suggest $D_{\text{CH}_3\text{-H}} - D_{n\text{-C}_3\text{H}_7\text{-H}} \cong 6.8$ kcal./mole; taking $D_{\text{CH}_3\text{-H}} = 102.0$ kcal./mole, $D_{n\text{-C}_3\text{H}_7\text{-H}} \cong 95.2$ kcal./mole. The agreement is good between the present kinetic estimates of the thermodynamic quantities related to reaction 1 and those estimated from "reasonable" thermal data. It is probable that the previous kinetic estimates of $E \cong 19$–21 kcal./mole are seriously in error.

The great divergence between the published kinetic data and "reasonable" thermal data for reaction 1

$$n\text{-C}_3\text{H}_7 \longrightarrow \text{CH}_3 + \text{C}_2\text{H}_4 \qquad (1)$$

is alarming. There are three independent determinations from photochemical and thermal kinetic experiments which suggest $E_1 \cong 19$–21 kcal./mole.[1-3] From measurements of the rate of methyl radical addition to ethylene, the reverse of reaction (1), Mandelcorn and Steacie[4] derive $E_{-1} \cong 7 \pm 1.5$ kcal./mole. Recently a more detailed study of this reaction by Brinton[5] has confirmed the "high" value for E_{-1}; he derives $E_{-1} \cong 8.7$ kcal./mole. Thus current kinetic data suggest $\Delta H_1 \cong E_1 - E_{-1} \cong 10$–$14$ kcal./mole. Contrast this estimate with that based on "reasonable" thermal data, $\Delta H_1 \cong 23$–26 kcal./mole.[6,7] The recent "high" values for E_{-1} appear to be well substantiated, but the accuracy of the kinetic estimates of E_1 should be questioned, as Mandelcorn and Steacie suggest.[4] Indeed the estimates of E_1 seem to be low in view of the recent findings of Trotman-Dickenson and Kerr.[8] The preliminary results of a study of the full arc, high temperature photolysis of *n*-butyraldehyde give: $E_1 \cong 25$ kcal./mole. Recently a re-evaluation of the earlier work relative to reaction 1 has been made,[9] and several possible sources of error have been noted.

The present study was designed to avoid many of the possible complications often encountered in the photochemical studies of radical decomposition reactions. Thermally equilibrated *n*-propyl radicals were generated homogeneously; the thermal decomposition of *n*-butyraldehyde was sensitized by the selective photolysis of azomethane at 3660 Å. in *n*-butyraldehyde–azomethane mixtures. It will be seen that the data from this system remove the apparent conflict between kinetic and thermal estimates of the thermodynamic quantities related to reaction 1.

Experimental

Apparatus.—The photolysis system was similar to that described previously.[10] One significant change was made to obtain a higher light intensity and higher radical concentrations; these conditions favor the desired radical association products, ethane and butane, from which a measure of the *n*-propyl radical concentration may be had. An additional light source (Hanovia Type A, S-500, burner) and 3660 Å. filter system was placed on the optical path, outside the air thermostat, at the rear of the photolysis cell. In the runs at the highest temperatures both the arcs at the front and the rear of the cell were operated at maximum intensity. Under these conditions the rates of ethane and butane formation were sufficiently raised to make analysis for these products feasible, even though the products of the chain reactions, CO, C_3H_8, CH_4 and C_2H_4, were still dominant.

Materials.—Azomethane was prepared and purified as described by Renaud and Leitch.[11] *n*-Butyraldehyde was taken from a volatile fraction of the Eastman White Label product and further purified by bulb-to-bulb distillation at reduced pressure. Standard reference samples of the hydrocarbon gases were Phillips research grade.

Product Analysis.—By combined mass spectrometric and chromatographic analyses, identification of a number of products was made: CH_4, N_2, CO, C_2H_4, C_2H_6, C_3H_6, C_3H_8, $n\text{-C}_4\text{H}_{10}$ and $n\text{-C}_6\text{H}_{14}$. The products were divided into three fractions for convenience in analysis. The first fraction, N_2, CO and CH_4, was pumped off with a Toepler pump while the trap was maintained at liquid nitrogen temperature. This fraction was not analyzed in most of the runs, since these products offered no unique data which would justify the time expenditure required for the analyses.

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

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

[3] C. R. Masson, THIS JOURNAL, **74**, 4731 (1952).

[4] L. Mandelcorn and E. W. R. Steacie, *Can. J. Chem.*, **32**, 474 (1954).

[5] R. K. Brinton, *J. Chem. Phys.*, in press.

[6] E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. II, Reinhold Publ. Corp., 1954, p. 584.

[7] W. M. D. Bryant, *J. Polymer Sci.*, **6**, 359 (1951).

[8] A. F. Trotman-Dickenson and J. A. Kerr, University of Edinburgh, private communication.

[9] J. G. Calvert, "Symposium on Elementary Processes in Chemical Kinetics," Division of Physical Chemistry, 134th National Meeting of American Chemical Society, Chicago, Sept., 1958.

[10] J. G. Calvert and J. T. Gruver, THIS JOURNAL, **80**, 1313 (1958).

[11] R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954).

TABLE I

DATA FROM THE PHOTOLYSIS OF AZOMETHANE–BUTYRALDEHYDE MIXTURES AT 3660 Å.

Run no.	Temp., °C.	Pressure, mm. Me_2N_2		Rates, moles/cc.-sec. × 10^{11} C_2H_4			$\frac{R^{1/2}_{C_2H_6}R_{C_2H_4}}{R_{C_4H_{10}}} \times 10^7$
		Me_2N_2	C_4H_8O	C_2H_4	C_2H_6	n-C_4H_{10}	
1	198.0	53.2	31.2	1.35	0.819	5.93	0.508
2	207.6	53.7	41.1	4.00	0.876	7.27	0.763
3	217.3	62.6	35.3	2.86	1.77	6.42	1.48
4	223.8	68.0	33.3	7.66	2.23	8.86	2.20
5	224.8	70.4	30.4	6.74	2.83	9.43	2.46
6	237.1	62.0	36.0	8.44	7.82	8.77	8.19
7	241.3	66.2	29.0	16.7	10.5	10.9	12.4
8	248.4	64.4	37.7	16.4	26.6	24.7	13.8
9	262.0	62.0	31.3	42.6	52.1	33.8	31.8
10	266.4	78.5	37.8	61.3	106	52.0	50.5
11	276.6	69.3	30.3	82.2	367	140	75.1

The second fraction, primarily C_2H_6 and C_2H_4, was pumped from a modified Ward still which was regulated automatically to −155 ± 2°. Very small amounts of C_3H_8 and C_3H_6 were removed also in this fractionation procedure, and suitable correction for these compounds was necessary in the treatment of the mass data. Precise mass spectrometric analysis of the C_2H_6 and C_2H_4 product mixture was possible for the runs at temperatures above 190°. Below this temperature the ratio of ethane to ethylene in the products was too great to ensure accurate C_2H_4 estimates by our analysis method. The third fraction of the products, a large excess of $(CH_3)_2N_2$ and n-C_3H_7CHO with C_3H_8, C_3H_6, n-C_4H_{10} and other products condensed at −155°, was distilled from the Ward still and analyzed in its entirety by vapor–liquid partition chromatography. This system was the same as that described previously.[12] The column was packed with C-22 firebrick (John–Manville) covered with Dow Therm "A" and was operated at 22°. The column provided an excellent resolution of the *n*-butane peak from the peaks of the reactants and other products, and quantitative analysis for this product could be made easily. Propane and propylene peaks were only partially resolved, and the minor product, n-C_6H_{14}, gave a small, broadened peak characteristic of its relatively long elution time; with our system it was impossible to determine accurately the C_3H_8, C_3H_6 and C_6H_{14} in the products.

Product Rate Data.—The duration of each run was regulated so that less than about 3% of the original reactants underwent change. Hence the measured rates should correspond closely to initial rates of product formation. The rate data for C_2H_6, C_2H_4 and n-C_4H_{10}, those products for which quantitative analyses were made, are summarized in Table I. The rates of product formation in the thermal, unsensitized reaction were negligible up to the highest temperature recorded in Table I, 276° (run 11). In runs at 300° the thermal reaction was appreciable and precluded useful experimentation at this temperature. The units on the rate function given in the last column of Table I are (moles/cc.-sec.)$^{1/2}$.

The Mechanism of Product Formation in 3660 Å. Photolysis of Azomethane–*n*-Butyraldehyde Mixtures.—Azomethane, the only 3660 Å. light absorbing species in this system, is photodissociated as shown in primary process I

$$(CH_3)_2N_2 + h\nu \longrightarrow 2CH_3 + N_2 \qquad (I)$$

In our system the methyl radicals formed in I initiate the thermal decomposition of *n*-butyraldehyde. Only those reactions which are likely sources of the products, n-C_4H_{10}, C_2H_6 and C_2H_4 need be considered here.

$$CH_3 + n\text{-}C_3H_7CHO \longrightarrow CH_4 + n\text{-}C_3H_7CO \qquad (2)$$

$$n\text{-}C_3H_7CO \longrightarrow n\text{-}C_3H_7 + CO \qquad (3)$$

$$n\text{-}C_3H_7 + n\text{-}C_3H_7CHO \longrightarrow C_3H_8 + n\text{-}C_3H_7CO \qquad (4)$$

$$n\text{-}C_3H_7 \longrightarrow CH_3 + C_2H_4 \qquad (1)$$

$$CH_3 + n\text{-}C_3H_7 \longrightarrow n\text{-}C_4H_{10} \qquad (5)$$

$$2CH_3 \longrightarrow C_2H_6 \qquad (6)$$

It is highly probable that reaction 1 is the source of ethylene in this system. Ethylene is undetectable in the products of low temperature (<150°), photolyses, so one can exclude as a possibility its formation from the decomposition of electronically excited *n*-butyraldehyde, n-$C_3H_7CHO^* \rightarrow C_2H_4 + CH_3CHO$.[13] Conceivably the butyraldehyde might become electronically excited by resonance transfer of azomethane excitation or by direct absorption of 3340 or 3130 Å. impurity in the "3660 Å." light. Furthermore, it is highly unlikely that a significant amount of ethylene results from the decomposition of the possible transient radical, $CH_2CH_2CH_2CHO$; at the temperatures used in this work the acyl-H and secondary-H atoms in *n*-butyraldehyde would be abstracted much more readily than the primary-H atoms which must be removed to form this radical. With this reasoning we conclude that reaction 1 is the dominant source of ethylene in this system.

We believe that reactions 5 and 6 are the only sources of butane and ethane, respectively, since there are no attractive alternatives to these reactions. It has been well demonstrated that ethane is not formed from azomethane in a primary photochemical process.[14] Since the quantum yield of nitrogen formation in azomethane photolysis is near unity at the temperatures and pressures used in this study, ethane formation in the possible chain sequence $CH_3 + (CH_3)_2N_2 \rightarrow C_2H_6 + CH_3N_2$, $CH_3N_2 \rightarrow CH_3 + N_2$, is ruled out.[15] Butane formation in a similar chain sequence, $CH_3 + n\text{-}C_3H_7CHO \rightarrow n\text{-}C_4H_{10} + CHO$, $CHO + M \rightarrow CO + H + M$, $H + n\text{-}C_3H_7CHO \rightarrow H_2 + n\text{-}C_3H_7CO$, cannot be important since hydrogen was not detected in the products.

Derivation of the Rate Constant for the Reaction 1: n-$C_3H_7 \rightarrow CH_3 + C_2H_4$.—In terms of the relatively unambiguous reaction mechanism suggested, the rate function 7 may be derived

$$R_{C_2H_4}R_{C_2H_6}{}^{1/2}/R_{C_4H_{10}} = k_1k_6{}^{1/2}/k_5 \qquad (7)$$

The values of the rate function 7 are given with the product rate data in Table I for experiments from 198–276°. A least squares treatment of the Arrhenius plot of the function 7, shown in Fig. 1, gives $k_1k_6{}^{1/2}/k_5 = 10^{8.783}\,e^{-34.9/RT}$ (moles/cc.-sec.)$^{1/2}$. If

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[12] J. W. Kraus and J. G. Calvert, THIS JOURNAL, **79**, 5921 (1957).

[13] F. E. Blacet and J. G. Calvert, *ibid.*, **73**, 661, 667 (1951).

[14] G. R. Hoey and K. O. Kutschke, *ibid.*, **33**, 496 (1955).

[15] M. H. Jones and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 1018 (1953).

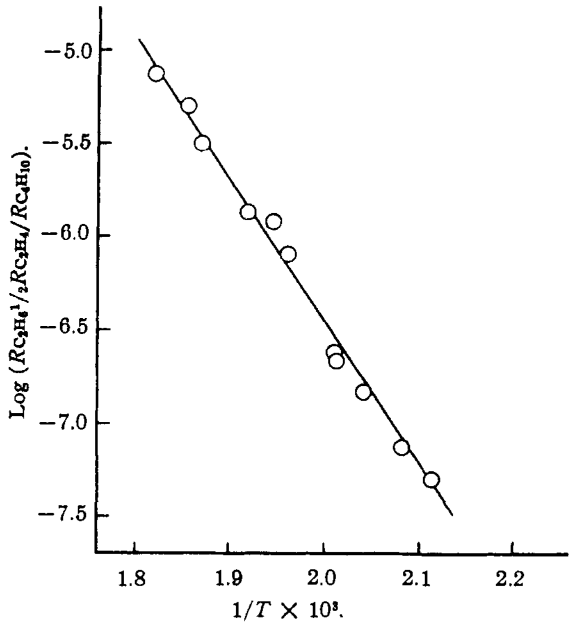

Fig. 1.—An Arrhenius plot of the rate function theoretically equal to $k_1k_6{}^{1/2}/k_6$. The data are from the selective photolyses of azomethane at 3660 Å. in *n*-butyraldehyde–azomethane mixtures.

we assume $k_6 = k_5 = 2.2 \times 10^{13}$ cc./mole-sec.[16] we estimate

$$k_1 \cong 2.8_5 \times 10^{16}\, e^{-34.9/RT}\ \text{sec.}^{-1}$$

Our estimate of $E_1 \cong 34.9$ kcal./mole is in serious disagreement with the first estimates of this quantity ($E_1 \cong$ 19–21 kcal./mole). However, it is likely that the accuracy of the previous estimates is low.[9] The results of the present work should be considerably more reliable since the interpretation of the data is much less uncertain in this case.

Kinetic Estimates of the Enthalpy and Entropy Change of Reaction 1: n-$C_3H_7 \rightarrow CH_3 + C_2H_4$.—The thermodynamic quantities related to (1) can be derived from these results and those of Brinton[5] which relate to the reverse of reaction 1, $CH_3 + C_2H_4 \rightarrow n$-$C_3H_7$. He finds $k_{-1}/k_6{}^{1/2} = 3.3 \times 10^{-7}\, e^{-8.66/RT}$ (cc./molec.-sec.)$^{1/2}$. Changing the units to moles-cc.-sec. and again using Shepp's value for k_6 we derive

$$k_{-1} \cong 1.20 \times 10^{12}\, e^{-8.66/RT}\ \text{(cc./mole-sec.)}$$

The rate constant which we estimate for the forward reaction 1 appears to be reasonably consistent with Brinton's data for the reverse of (1). The data suggest (for temperatures near 200°) $\Delta H_1 \cong E_1 - E_{-1} \cong 34.9 - 8.7 \cong 26.2$ kcal./mole; $\Delta S_1{}^0 \cong R \ln(A_1/A_{-1}) \cong R \ln(2.85 \times 10^{15}/1.20 \times 10^{12}) \cong$ 15.4 e.u. (standard state, 1. mole/cc.). These estimates check well with the values of $\Delta H_1 \cong 26.4$ kcal./mole and $\Delta S_1{}^0 \cong 12.1$ e.u. (25°) calculated from Bryant's thermal data summary and his theoretical estimates of the entropies of the n-C_3H_7 and CH_3 radicals.[7] The observed difference in the experimental and theoretical values for $\Delta S_1{}^0$ corresponds to a factor of 5.3 in the ratio of the pre-exponential factors, A_1/A_{-1}, or about 1.7 kcal./mole in the difference $E_1 - E_{-1}$. Thus the divergence from "theory" is well within the experimental error and the simplifications involved in this comparison.

From our estimate of ΔH_1 and standard enthalpy for methane, ethane and ethylene, it can be shown that $D_{CH_3-H} - D_{n-C_3H_7-H} \cong 6.8$ kcal./mole. If we assume with Bryant[7] that $D_{CH_3-H} = 102.0$, then we estimate that $D_{n-C_4H_7-H} \cong 95.2$ kcal./mole.

We may conclude that the kinetic data for k_1 reported in this work reaffirm our faith in the thermal estimates of ΔH_1 and establish the inaccuracy of the previous "low" kinetic estimates of E_1 and ΔH_1.

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[16] A. Shepp, *J. Chem. Phys.*, **24**, 939 (1956).

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

Photoisomerization Processes in Cyclic Ketones. I. Cyclopentanone and Cyclopentanone-2,2,5,5-d_4[1]

BY R. SRINIVASAN

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4-Pentenal has been identified as one of the products of the vapor phase photolysis of cyclopentanone at 3130 Å. Quantum yields for the formation of 4-pentenal have been obtained at various temperatures and in the presence of added oxygen and carbon dioxide. The photolysis of cyclopentanone-2,2,5,5-d_4 has been found to give tetradeutero-4-pentenal, the structure of which is most probably $CD_2{=}CHCH_2CD_2CHO$. On the basis of these results, it is deduced that the photoisomerization of cyclopentanone to 4-pentenal involves a direct transfer of a hydrogen atom from a β-carbon to the carbonyl group in an excited state of the ketone molecule.

Introduction

The vapor phase photolysis of cyclopentanone has been investigated by Saltmarsh and Norrish,[2] by Benson and Kistiakowsky[3] and more recently by Blacet and Miller.[4] The products of photolysis are carbon monoxide, ethylene, cyclobutane and

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[2] O. D. Saltmarsh and R. G. W. Norrish, *J. Chem. Soc.*, 455 935).

[3] S. W. Benson and G. B. Kistiakowsky, THIS JOURNAL, **64**, 80 (1942).

[4] F. E. Blacet and A. Miller, *ibid.*, **79**, 4327 (1957).