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The Photolysis of Azo-*n*-propane; the Decomposition of the *n*-Propyl Radical

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The vapor phase photolysis of azo-*n*-propane has been studied from 24 to 291° at wave length 3660 Å. The product rate data suggest that there is a single photodecomposition mode in which *n*-propyl radicals and molecular nitrogen are formed. The rates of combination, disproportionation, H-atom abstraction and decomposition reactions of the *n*-propyl radical are derived from the results. A partial resolution of the conflicting estimates of the rate constant for the reaction $n\text{-}C_3H_7 \rightarrow C_2H_4 + CH_3$ (I) has been obtained. If one assumes the rate constant for the combination reaction of $n\text{-}C_3H_7$ radicals to be 10^{14} cc./mole-sec., from the present work $k_1 = 10^{15.36}\, e^{-34.5/RT}$ sec.$^{-1}$ for $[(C_3H_7)_2N_2] = 0.35$ μmole/cc.

Two independent studies of the rate constant for the *n*-propyl radical decomposition reaction 1 have been reported recently.[2,3] Kerr and Trot-

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

man-Dickenson[2] (K & TD) studied the photoinitiated chain decomposition of *n*-butyraldehyde; they derived $k_1 = 10^{11.7}\, e^{-25.2/RT}$ sec.$^{-1}$, assuming $k_2 = 10^{14}$ cc./mole-sec.

$$2\ n\text{-}C_3H_7 \longrightarrow n\text{-}C_6H_{14} \qquad (2)$$

Calvert and Sleppy[3] (C & S) investigated the selective photolysis of azomethane in azomethane-*n*-butyraldehyde mixtures; with similar assumptions it can be estimated from these data that $k_1 = 10^{15.8}\, e^{-34.9/RT}$ sec.$^{-1}$. The difference between these estimates is alarming, but the results can only be evaluated properly by comparing the Arrhenius plots, as in Fig. 2. It is seen that, for certain temperatures, there is much better agreement between the rate constants than the divergent Arrhenius parameters might suggest. K & TD found that k_1 was a function of the pressure of the system; it could be increased by increasing the initial concentration of *n*-butyraldehyde or by adding large pressures of carbon dioxide. C & S used a constant total concentration of reactants, approximately 3.0 μmole/cc. for the data shown in the Arrhenius plot of Fig. 2. K & TD maintained an aldehyde concentration of about 0.54 μmole/cc. Obviously some of the difference in the rate constants for the two studies is readily explained by the large difference in the conditions of pressure. Further it should be noted that the C & S results are calculated on the assumption that the rate constant for cross-combination of methyl and *n*-propyl radicals is twice the geometric mean of the rate constants for autocombinations of these radicals. While there is considerable justification for such an assumption,[4] any divergence from this assumed equality would affect the vertical position of the C & S line. The reasons for the large difference in the slopes of the K & TD and C & S plots remain obscure. The present work involving a third source of *n*-propyl radicals was undertaken in the hope of resolving these differences between the estimates of the rate constant k_1 for *n*-propyl radical decomposition.

(1) University College of Wales, Aberystwyth, Wales, U. K.

(2) J. A. Kerr and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, **55**, 572 (1959).

(3) J. G. Calvert and W. C. Sleppy, *J. Am. Chem. Soc.*, **81**, 1544 (1959).

(4) J. A. Kerr and A. F. Trotman-Dickenson, *Chemistry and Industry*, 125 (1959).

Experimental

Apparatus.—The photolysis system consisted of a cylindrical quartz cell (volume, 113 cc.), a mercury manometer, an all glass in-line circulating pump, a trap and an excess volume to keep the percentage conversion of reactant low. This system, which had a total volume of about 450 cc., was isolated by mercury cut-off valves. The photolysis cell was suspended in an aluminum block oven regulated to ±1°. 3660 Å. radiation was isolated from a Hanovia Type A (S-500) burner, by means of a Corning 5840 filter in combination with a 0.8 cm. thickness of plate glass.[5] The light beam completely filled the cell. In the runs with *n*-butyraldehyde–azomethane mixtures, a second lamp and filter system was placed at the rear of the photolysis cell to enhance the rates of radical combination reactions. At temperatures above 240° pyrolysis of azo-*n*-propane becomes measurable during the time of the photochemical run. The obvious precaution of rapid entry and removal of the azo-*n*-propane was taken in runs involving combined photolysis and pyrolysis.

Materials.—Azo-*n*-propane was a product of Merck (Montreal) and was shown to contain about 1% of *n*-hexane by gas chromatography. The hexane was removed from small samples of the azo-*n*-propane, sufficient for two or three photolytic runs, by prolonged pumping on the impure sample which was held at −60° in a Ward still. The purified compound was stored under vacuum at liquid nitrogen temperature. Carbon dioxide was commercial Dry Ice which was degassed and used without further purification. Trimethylamine was taken from the volatile fraction of the Eastman White label product and further purified by bulb-to-bulb distillation. Standard reference samples of the hydrocarbon gases were Philips research grade. Azomethane was prepared and purified as described by Renaud and Leitch[6] and shown to be pure by gas chromatography. *n*-Butyraldehyde was taken from a volatile fraction of the Eastman White Label product and further purified by bulb-to-bulb distillation.

Product Analysis.—Gas chromatography was used throughout the work. The product were separated into two fractions; the first consisted of N_2 and CH_4 which was taken off with a Toepler pump with the traps at liquid nitrogen temperature; the second fraction, containing all the other products and unreacted azo-*n*-propane, was transferred in its entirety by high vacuum distillation to the inlet system of a gas chromatography system. The N_2 and CH_4 were analyzed on a 10 ft. × 1/4 in. diam. column packed with 30–60 mesh molecular sieves maintained at 75°. The molecular sieves were previously activated by heating at 400° for two days in a stream of dry nitrogen. The flow of helium carrier gas was constant at 35 ml./min. A Gow-Mac detector was used in conjunction with a Brown recorder. The column was calibrated using measured pure samples of the known products. The second fraction was analyzed on an alumina column, activated in the same way as before. The column consisted of 30–60 mesh alumina impregnated with 1% squalene, packed in a glass U-tube 5 ft. long and 1/4 in. diameter and contained in a fiber-glass jacket. A coil heater was placed along the length of the jacket and the temperature of the column was programmed from room temperature to 190° in the course of an analysis. The flow rate of the carrier gas was maintained at 25 ml./min. by means of a flow controller. The product peaks for C_2H_6,

(5) J. G. Calvert and J. T. Gruver, *J. Am. Chem. Soc.*, **80**, 1313 (1958).

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

TABLE I

PRODUCT RATE DATA FROM THE PHOTOLYSIS OF AZO-*n*-PROPANE AT 3660 Å.

Temp., °C.	[Azo], μmole/cc.	Product rates × 10^{12}, mole/cc.-sec.									Rate functions			% De-compn.	Mass balance, $N_2/(C_3/2 + C_6)$
		N_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	*n*-C_4H_{10}	*n*-C_5H_{12}	*n*-C_6H_{14}	II	III	IV × 10^6		
24.5	0.609	6.55	0.000	0.000	0.000	0.891	1.03	0 000	0.000	5.72	0.156	0.0954	0.00	0.5	0.981
24.3	.556	6.97	.000	.000	.000	.970	1.08	.000	.000	5.99	.162	.0808	.00	.7	0.993
37.6	.558	5.61	.000	.000	.000	.772	0.915	.000	.000	4.53	.170	.120	.00	.5	1.05
46.6	1.11	7.74	.000	.000	.000	1.02	1.48	.000	.000	6.56	.156	.162	.00	.2	0.991
50.1	1.02	7.31	.000	.000	.000	0.943	1.48	.000	.000	5.97	.158	.216	.00	.6	1.02
55.5	0.625	7.33	.000	.000	.000	.910	1.33	.000	.000	6.00	.152	.274	.00	.6	0.992
70.6	.808	7.57	.000	.000	.000	.904	1.70	.000	.000	6.33	.143	.392	.00	.4	.839
76.2	.533	5.85	.000	.000	.000	.875	1.47	.000	.000	5.80	.151	.464	.00	.5	.845
88.2	.515	7.23	.000	.000	.000	1.12	2.21	.000	.000	6.89	.163	.806	.00	.5	1.03
108.1	.556	8.48	.000	.000	.000	0.988	2.95	.000	.000	6.30	.157	1.41	.00	.5	1.19
124.5	.521	10.2	.000	.000	.000	.954	3.90	.000	.000	6.18	.154	2.28	.00	.6	1.18
154.2	.492	11.0	.000	.000	.000	.986	5.25	.000	.000	5.35	.184	3.88	.00	.6	1.30
180.1	.496	12.8	.000	.000	.000	1.54	7.57	.000	.000	3.95	.390	7.05	.00	.6	1.51
206.5	.549	15.4	.000	.000	.000	1.76	11.7	.000	.000	3.40	.518	11.0	.00	.6	1.52
215.2	.389	11.0	.049	.122	Trace	1.02	8.71	Trace	Trace	2.79	.366	12.7	.073	4.3	..
222.2	.385	11.8	.104	.213	Trace	1.21	9.68	Trace	Trace	3.10	.390	13.6	.121	2.3	..
232.4	.381	17.8	Lost	.575	Trace	1.50	11.4	Trace	Trace	3.08	.487	16.3	.328	2.8	..
241.5	.369	18.1	0.650	.918	0.578	1.90	14.1	0.136	0.280	3.16	.601	20.7	.516	3.3	..
249.9	.376	25.1	1.18	2.06	1.19	3.13	20.1	.369	.551	5.15	.608	22.6	.908	2.3	..
258.9	.369	33.8	2.36	4.05	1.73	4.30	28.1	.785	.885	7.11	.605	27.4	1.52	1.8	..
267.0	.351	62.5	6.05	9.18	3.30	7.31	39.6	2.10	2.12	13.4	.546	29.2	2.51	3.0	..
275.4	.355	101	12.1	19.3	5.90	13.4	71.5	4.91	4 10	28.1	.477	35.7	3.64	2.4	..
276.5	.371	135	15.2	26.0	7.11	16.9	74.7	6.27	5.61	34.5	.490	31.8	4.43	6.1	..
283.5	.355	214	25.5	50.0	12.0	27.2	106	13.7	9.06	57.8	.471	35.9	6.58	4.1	..
290.7	.347	392	46.0	96.9	18.1	48.8	194	35.1	18.1	122	.400	45.7	8.77	3.4	..

C_2H_4, C_3H_8, C_3H_6, *n*-C_4H_{10}, *n*-C_5H_{12}, *n*-C_6H_{14} and other products were resolved cleanly, and the elution of all products through hexane was accomplished in about 30 min. The azo-*n*-propane came off the column very slowly with a retention time of about 2 hr. The column was kept at 190° and helium passed overnight after each analysis. In this way the lifetime of the column was greatly increased.

Discussion

The Mechanism of the Low Temperature 3660 Å. Photolysis of Azo-*n*-propane.—No previous work on the photolysis of azo-*n*-propane has been reported, but from the results for azomethane, azoethane and azo-isopropane, one is tempted to predict that a major primary photodecomposition mode of azo-*n*-propane would involve the formation of *n*-propyl radicals and nitrogen. Indeed the product data of the present study support this expectation; see Table I. Below 215° the noncondensable fraction consists entirely of nitrogen and the only hydrocarbon products in the condensable fraction are propane, propylene and *n*-hexane. The following mechanism is suggested to explain the low temperature photolysis results

$$C_3H_7N{=}NC_3H_7 + h\nu \longrightarrow 2\ n\text{-}C_3H_7 + N_2 \quad (1)$$

$$2\ n\text{-}C_3H_7 \longrightarrow n\text{-}C_6H_{14} \quad (2)$$

$$2\ n\text{-}C_3H_7 \longrightarrow C_3H_6 + C_3H_8 \quad (3)$$

$$n\text{-}C_3H_7 + C_3H_7N{=}NC_3H_7 \longrightarrow C_3H_8 + C_3H_6N{=}NC_3H_7 \quad (4)$$

$$C_3H_6N{=}NC_3H_7 + R \longrightarrow RC_3H_6N{=}NC_3H_7 \quad (5)$$

$$C_3H_6N{=}NC_3H_7 \longrightarrow C_3H_6 + N_2 + C_3H_7 \quad (6)$$

$$n\text{-}C_3H_7 + C_3H_7N{=}NC_3H_7 \longrightarrow (C_3H_7)_2N{-}NC_3H_7 \quad (7)$$

$$(C_3H_7)_2N{-}NC_3H_7 + R \longrightarrow (C_3H_7)_2N{-}N(R)C_3H_7 \quad (8)$$

R = any radical in the system.

The absence of other than C_3 and C_6-hydrocarbon products excludes a primary process analogous to the Norrish Type II split common for carbonyl compounds containing γ-H-atoms. There are not sufficient definitive data to evaluate the importance of the collisional deactivation and internal conversion of light excited azo-*n*-propane molecules, although these reactions might be expected in view of the results of azo-ethane[7-9] and azo-isopropane[10,11] photolyses. The major interest of the present work was in the study of the reactions of the *n*-propyl radical; the lack of knowledge of the extent of excited molecule deactivation reactions does not lead to any ambiguity with regard to the reactions of the propyl radical, since hexane formation, reaction 2, could be used in each experiment to monitor the propyl radical concentration directly.

The Disproportionation and Combination of *n*-Propyl Radicals.—If reactions 2 and 3 are the only sources of hexane and propylene, then the ratio of rate constants k_3/k_2 will be given by rate function II.

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

It is seen from the data of column 12 of Table I that the function II is approximately constant independent of azo-*n*-propane pressure and temperature up to about 130°. This suggests that reaction 6 is unimportant to 130°. The mean value of $k_3/k_2 = 0.157$ is in excellent agreement with the two most recently published values of this ratio: 0.15 by Ausloos and Murad[12] and 0.16 found by K & TD.[2] The data show $E_3 - E_2 \cong 0$ as reported for the analogous activation energy differences for most of the alkyl radicals.[13,14] At about 150° the function II increases from the

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(9) H. Cerfontain and K. O. Kutschke, *Can. J. Chem.*, **36**, 344 (1958).

(10) R. W. Durham and E. W. R. Steacie, *ibid.*, **31**, 377 (1953).

(11) R. H. Riem and K. O. Kutschke, *ibid.*, **38**, 2332 (1960).

(12) P. Ausloos and E. Murad, *J. Am. Chem. Soc.*, **80**, 5929 (1958).

(13) A. F. Trotman-Dickenson, *Ann. Rep. Chem. Soc.*, 36 (1959).

(14) J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1062 (1960).

TABLE II

RATE CONSTANT FACTORS FOR THE REACTIONS R + RN=NR → RH + R'N=NR

($k = 10^{14}$ cc./mole-sec. for all combination reactions, 2R → R_2, is assumed)

R	RN=NR	E, kcal./mole	log A, cc./mole-sec.	log k at 100°	Ref.
CH_3	$CH_3N{=}NCH_3$	7.6	11.3	6.8	15
		6.9	10.8	6.7	16
		7.3	11.0	6.7	17
		8.4	11.8	6.8	18
C_2H_5	$C_2H_5N{=}NC_2H_5$	7.5	11.2	6.8	8
		8.0	11.6	6.9	9
iso-C_3H_7	(*iso*-$C_3H_7)_2N_2$	6.5	10.4	6.6	10
		6.7	10.5	6.6	11
n-C_3H_7	(*n*-$C_3H_7)_2N_2$	7.9	11.6	6.9	This work

TABLE III

RATE CONSTANT FACTORS FOR *n*-PROPYL RADICAL H-ATOM ABSTRACTION REACTIONS

($k = 10^{14}$ cc./mole-sec. is assumed for the combination reaction, $2C_3H_7 \rightarrow C_6H_{14}$)

Reaction	E, kcal./mole	log A, cc./mole-sec.	Ref.
n-C_3H_7 + *n*-C_3H_7CHO → C_3H_8 + *n*-C_3H_7CO	6.7	11.3	2
n-C_3H_7 + *n*-C_3H_7CHO → C_3H_8 + C_3H_6CHO	10.8	11.3	2
n-C_3H_7 + $(n\text{-}C_3H_7)_2CO$ → C_3H_8 + $C_3H_6COC_3H_7$	6.5	10.7	19
n-C_3H_7 + $(n\text{-}C_3H_7)_2N_2$ → C_3H_8 + $C_3H_6N{=}NC_3H_7$	7.9	11.6	Present work

constant value of the lower temperatures; this is attributed to the onset of reaction 6. The consistency between the k_3/k_2 ratios found here and those from other systems seems to indicate that the photolysis of azo-*n*-propane at 3660 Å. in the normal pressure range produces thermally equilibrated *n*-propyl radicals. This observation coupled with the evidence that there appears to be but one primary photodecomposition mode for azo-*n*-propane, process I, shows the photolysis of azo-*n*-propane at 3660 Å. as the cleanest source of *n*-propyl radicals yet reported.

The H-Atom Abstraction Reaction of the *n*-Propyl Radical.—If one assumes that reactions 2, 3 and 4 are the only sources of propane and hexane in the system, then relation III should hold.

$$\frac{R_{C_3H_8} - R_{C_3H_8(3)}}{(R_{C_6H_{14}})^{1/2}[\text{azo}]} = k_4/k_2^{1/2} \qquad \text{(III)}$$

$R_{C_3H_8(3)}$ represents the rate of propane formation in reaction 3; this can be calculated for a given run from the measured value of $R_{C_6H_{14}}$ and the known low temperature ratio of k_3/k_2. The values of the rate function III are given in Table I column 13 (units cc./mole-sec$^{1/2}$), and an Arrhenius plot of the data is shown in Fig. 1. The least squares treatment of the data gives $\log(k_4/k_2^{1/2}$ (cc./mole-sec.)$^{1/2}) = 11.6 - 7.85 \times 10^3/2.303RT$. It is interesting to compare this estimate with others

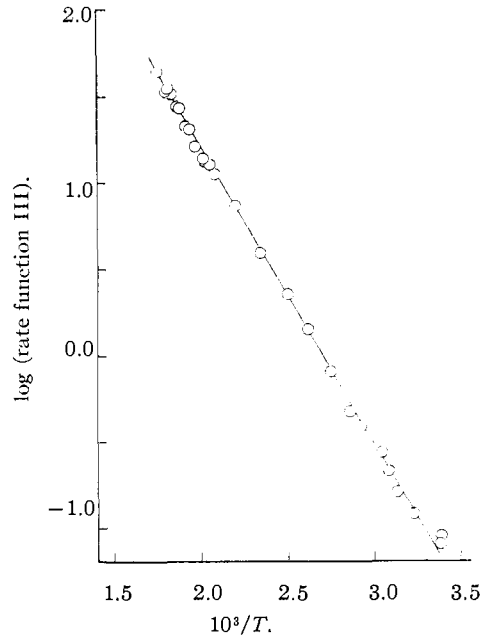

Fig. 1.—An Arrhenius plot of the rate function III, $[R_{C_3H_8}\text{-}R_{C_3H_8(3)}]/[\text{Azo}](R_{C_6H_{14}})^{1/2}$. The data are from 3660 Å. photolysis of azo-*n*-propane. The two points at the lowest temperature are the least accurate since the function III involves the difference between two product rates which are near equal at this temperature. Rate constants are in the units cc., mole, sec.

of the general type, R + RN=NR → RH + R'N=NR. For the purposes of comparison it is somewhat useful to make the arbitrary assumption that the rate constants for combination of the various simple free radicals are the same and equal to 10^{14} cc./mole-sec. The absolute values for the combination constants for ethyl, *n*-propyl and isopropyl radicals are not known with great precision, but indirect evidence from cross-combination and disproportionation studies[20,21] suggests that they are near equal. Data derived in this fashion are shown in Table II. The most striking feature of Table II is the similarity of the rate constants at 100° (about the mid-point of the experimental ranges). An explanation of this observation is not apparent from a simple consideration of the nature of the bonds which are formed and broken in these reactions. However, this rather unexpected result is not unique; the similarity in the reactivities of methyl, ethyl, *n*- and isopropyl and the butyl radicals in H-atom abstraction from aldehydes has been noted recently by Birrell and Trotman-Dickenson.[22] Table III compares the rate factors for the published *n*-propyl abstraction reactions.

There is no direct evidence for the occurrence of reactions 5, 7 and 8, but these seem to be reasonable reactions for temperatures above 130° where there is an appreciable unbalance in the nitrogen/hydrocarbon ratio of the products; see column 16

(15) M. H. Jones and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 1018 (1953).
(16) S. Toby, *J. Am. Chem. Soc.*, **82**, 3822 (1960).
(17) P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 39 (1955).
(18) S. Toby and K. O. Kutschke, *ibid.*, **37**, 672 (1959).
(19) C. R. Masson, *J. Am. Chem. Soc.*, **74**, 4731 (1952).
(20) J. W. Kraus and J. G. Calvert, *J. Am. Chem. Soc.*, **79**, 5921 (1957).
(21) J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1609 (1960).
(22) R. N. Birrell and A. F. Trotman-Dickenson, *ibid.*, 4218 (1960).

of Table I. The analogous reactions have been well established in the case of azomethane, but because of the very long retention time of the hydrazines and azo-compounds on the alumina column used this work, identification of the expected products was impossible here.

High Temperature Photolysis and Pyrolysis of Azo-*n*-propane; *n*-Propyl Radical Decomposition Reaction.—At a temperature above 200° methane and ethylene appear in the products. The obvious possible source of these products is the reactions 1 and 9

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

$$CH_3 + C_3H_7N{=}NC_3H_7 \longrightarrow CH_4 + C_3H_6N{=}NC_3H_7 \quad (9)$$

The amount of ethylene is always considerably greater than the methane; conceivably this may be a consequence of the importance of reaction 10, the analog of reaction 7.

$$CH_3 + C_3H_7N{=}NC_3H_7 \longrightarrow C_3H_7(CH_3)N{-}NC_3H_7 \quad (10)$$

However, there are two other possible sources of ethylene at high temperature in the present system which must be considered: (1) possible formation of ethylene in a heterogeneous thermal reaction; (2) ethylene formation from the decomposition of intermediate free radicals other than *n*-propyl, *e.g.*, $CH_2CH_2CH_2N{=}NC_3H_7$. If the present rate data are to be used to derive information about reaction 1, the possible contribution of these other sources of ethylene must be evaluated.

In experiments above 240° pyrolysis of azo-*n*-propane sets in and at 300° it is much faster than the photolysis for the light intensity employed in this work. The steady-state concentration of *n*-propyl radicals increases accordingly, as shown by the rates of formation of *n*-hexane in column 11 of Table I. The change from photochemical to thermal generation of radicals does not affect the calculated rate functions of the *n*-propyl H-atom abstraction reaction; this is apparent from Fig. 1 where no change in the Arrhenius plot of the function can be seen as one progresses from pure photolytic to thermal-photolytic experiments. The result is good evidence that *n*-hexane and propane are formed only in reactions 2, 3 and 4 under both photolytic and thermal conditions. Concurrent with the onset of pyrolysis, ethane, *n*-butane and *n*-pentane appear in the products in significant amounts; see Table I. The following conventional reactions might be considered in explanation of these products

$$2CH_3 \longrightarrow C_2H_6 \quad (11)$$

$$CH_3 + n\text{-}C_3H_7 \longrightarrow n\text{-}C_4H_{10} \quad (12)$$

$$n\text{-}C_3H_7 + C_2H_4 \longrightarrow n\text{-}C_5H_{11} \quad (13)$$

$$n\text{-}C_5H_{11} + RH \longrightarrow n\text{-}C_5H_{12} + R \quad (14)$$

If reactions 11 and 12 are the only sources of ethane and *n*-butane then $(R_{C_4H_{10}})^2/(R_{C_2H_6}R_{C_5H_{12}})$ should be approximately equal to 4; in every run this ratio is very much less than 4. As suggested previously it is likely that hexane is formed only in reaction 2, and thus ethane must be produced by some reaction in addition to 11; butane may be formed entirely or in part by reaction 12. The contribution of the possible reaction sequence 13 and 14 can be calculated from known estimates of k_{13}.[2] Such calculations suggest that reactions 13 and 14 are unimportant in this system. Indeed this is what one would expect since the concentration of ethylene was kept low by allowing only small conversions of azo-*n*-propane. Confirmation of this conclusion was obtained experimentally by carrying out two runs under the same conditions of temperature and concentration but one with doubled run time. The $R_{C_2H_4}$ values from the two runs were equal within the experimental error. Obviously the reactions 11–14 cannot account satisfactorily for all of the ethane and pentane formed, and in this regard the mechanism is uncertain. Some heterogeneous path for the formation of these products seems most likely as evidenced in the following observations. When the low temperature photolyses were started, the first few runs (not included in Table I) gave ethane, *n*-butane and *n*-pentane (but no ethylene), as well as the expected products, propane, propylene and *n*-hexane. After several runs, however, ethane, *n*-butane and *n*-pentane formation ceased completely. This suggests that these products were formed heterogeneously on the unconditioned walls of the cell; the wall later became conditioned and the reaction ceased. At the higher temperatures later employed in the work, adsorbed azo-*n*-propane on the surface of the cell may have been decomposed heterogeneously to yield the unexplained products. The possibility of significant ethylene formation in the heterogeneous reaction at high temperatures seems unlikely for two reasons: first, there is no abrupt change in the rate of formation of ethylene when ethane, butane and pentane appear in the products; secondly, ethylene was completely absent in the products of the early low temperature heterogeneous reactions in which ethane, butane and pentane were observed.

The possibility of ethylene formation in the sequence 15 and 16 should be considered also

$$n\text{-}C_3H_7 + CH_3CH_2CH_2N{=}NC_3H_7 \longrightarrow C_3H_8 + CH_2CH_2CH_2N{=}NC_3H_7 \quad (15)$$

$$CH_2CH_2CH_2N{=}NC_3H_7 \longrightarrow C_2H_4 + CH_2N{=}NC_3H_7 \quad (16)$$

If these reactions occurred to any significant extent, one would expect curvature in the Arrhenius plot for the abstraction of an H-atom from azo-*n*-propane (see Fig. 1), since at low temperatures abstraction must be exclusively from the secondary-H positions in the azo-*n*-propane. No such curvature is found over the entire temperature range. Therefore reactions 15 and 16 are considered to be unimportant in the present work. The decomposition of other radicals formed in 4 and 9 ($CH_3CHCH_2N_2C_3H_7$ and $CH_3CH_2CHN_2C_3H_7$) to give ethylene is considered unimportant; for the temperature range employed in this study the gas phase decomposition of the simple alkyl radicals commonly occurs without H-atom migration.[23]

Reaction 1 remains as the only probable source of ethylene in these experiments. With this assumption function IV can be derived.

$$R_{C_2H_4}/R_{C_6H_{14}}^{1/2} = k_1/k_2^{1/2} \quad (IV)$$

(23) F. P. Lossing and J. B. deSousa, *J. Am. Chem. Soc.*, **81**, 281 (1959); isomerization of *n*-pentyl and higher *n*-alkyl free radicals by internal H-atom abstraction is well established; see A. S. Gordon and J. R. McNesby, *J. Chem. Phys.*, **31**, 853 (1959).

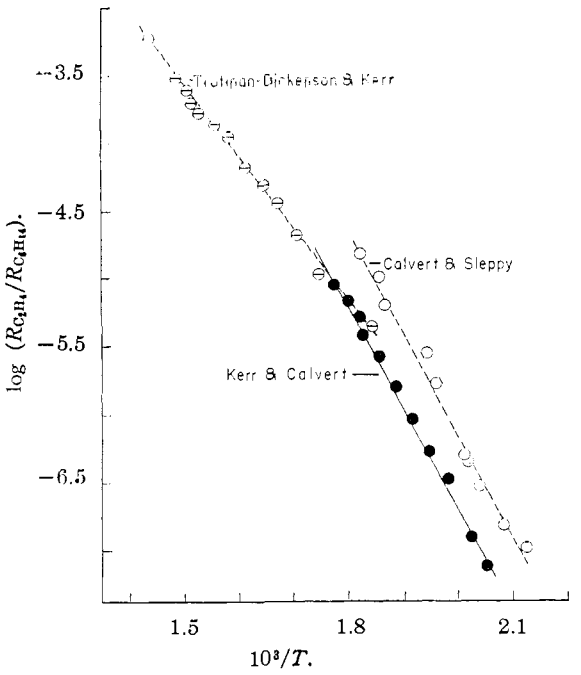

Fig. 2.—An Arrhenius plot of the rate function IV, $R_{C_2H_4}/R_{C_6H_{14}}^{1/2}$, theoretically equal to $k_1/k_2^{1/2}$. The estimates of Trotman-Dickenson and Kerr[2] were derived from the photoinitiated chain decomposition of *n*-butyraldehyde; the points of Calvert and Sleppy[3] were calculated from their results from the selective photolysis of azomethane in azomethane–*n*-butyraldehyde mixtures; the results of the present work (Kerr and Calvert) are from the high temperature photolysis of azo-*n*-propane. Rate constants are in the units cc., mole, sec.

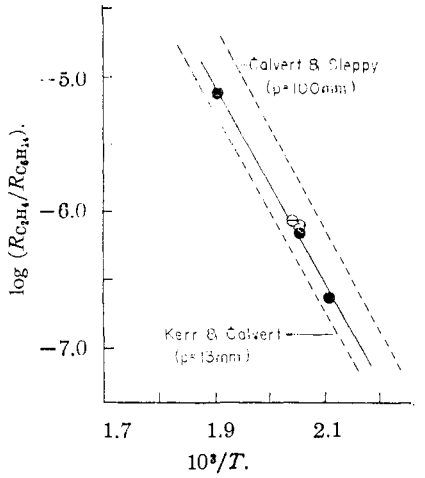

Fig. 3.—The effect of pressure on the rate function IV, $R_{C_2H_4}/R_{C_6H_{14}}^{1/2}$, theoretically equal to $k_1/k_2^{1/2}$. The data which determine the upper dotted line (Calvert and Sleppy[3]) were found in experiments using a total pressure of azomethane and *n*-butyraldehyde of about 100 mm.; the lower dotted line is from the present work for which the pressure of azo-*n*-propane was about 13 mm.; the darkened circles are from this work for which the pressure of azo-*n*-propane was about 25 mm.; the open circles are from runs with 25 mm. of azo-*n*-propane and 300 or 450 mm. of CO_2; the divided circle is for a run with the pressure of azo-*n*-propane equal 25 mm., with 70 mm. of added $(CH_3)_3N$. Rate constants are in the units cc., mole, sec.

Values of the rate function IV are given in Table I and the Arrhenius plot of the data in Fig 2. The least squares treatment of the Arrhenius plot of function IV gives log $k_1/k_2^{1/2}$ (mole/cc.-sec.)$^{1/2}$ = 8.36 − 34.5/2.303RT, for an approximately constant concentration of 0.35 μmole/cc. of azo-*n*-propane. The position of the data relative to those of the previous studies is interesting. It is seen from Fig. 1 that there is excellent agreement between the rate constants derived here and those of K & TD; in both studies the experiments were at comparable pressures. Although the rate constants agree well in the temperature range which is common to both studies, the slopes of the two lines are significantly different. K & TD were unable to determine hexane yields directly in their high temperature experiments, but these were estimated from the measured rates of propane and an extrapolated H-atom abstraction function for propyl attack on *n*-butyraldehyde. It is possible that some error was incurred by this procedure. Any error in the extrapolation would be reflected ultimately in an error in the rate constant for propyl decomposition. Since the present data could be used directly to derive the function IV, we place a greater confidence in the slope determined in the present work. There is excellent agreement between the slope of the present propyl decomposition data and that of C & S. Differences between the rate constants in this case were thought to be the result of the large pressure difference between the two systems. Experiments were carried out to test the expected effect of pressure. These results are shown in the Arrhenius plot of Fig. 3. By approximately doubling the initial pressure of azo-*n*-propane, k_1 was increased to about 1.4 times the value at 0.35 μmole/cc. These high pressure azo-*n*-propane points determine a line of slope near equal to that determined by the low pressure points. Rate theory predicts an insensitivity of activation energy to pressure for a molecule in which the effective number of normal vibration modes is small.[24] Unfortunately this was the highest pressure of azo-*n*-propane (the saturated vapor pressure at room temperature) which could be handled by the present apparatus. The addition of large pressures of carbon dioxide also increased the rate constant, as shown in Fig. 3. The rather small effect of this gas is attributed to its inefficiency as an activator of *n*-propyl radical through collision. In an attempt to find a more efficient activator, trimethylamine was added to the azo-*n*-propane; 70 mm. of trimethylamine increased the rate of decomposition of *n*-propyl radical to about the extent noted for 450 mm. of carbon dioxide. Larger pressures of trimethylamine flooded the gas chromatography column. Attempts to remove trimethylamine chemically were unsuccessful. No completely satisfactory molecule could be found which would extend the pressure range further yet not interfere with the analysis. Thus it was not possible for us to check quantitatively the consistency of the present

(24) N. B. Slater, "Theory of Unimolecular Reactions," Methuen, London, 1959, p. 186.

rate constants and those of C & S by increasing the pressure in the azo-*n*-propane system.

The problem was approached in another way. The work of C & S was repeated in part, with the hope of lowering the pressure of the azomethane–*n*-butyraldehyde system to that comparable to the azo-*n*-propane studies. It was hoped that a direct analysis of the product *n*-hexane might be made so that the identical rate constant function IV might be evaluated without any assumptions concerning rates of combination reactions of radicals; this proved to be impossible since the large excess of azomethane came off the chromatography column at the same time as the *n*-hexane, so the same rate function calculated by C & S had to be employed again. At the same pressures of *n*-butyraldehyde and azomethane as that used by C & S, excellent agreement with their values for k_1 and E_1 were obtained. When the pressure was halved, however, the calculated rate constants k_1 increased somewhat, although the activation energy remained the same. Runs with a further decrease in pressure did not yield sufficient radical combination products to provide a reasonable accuracy. The apparent increase in k_1 with decrease in pressure was most surprising; it may be the result of non-homogeneous light absorption in the azomethane mixtures at the higher pressures used by C & S. Although the results lack the quantitative character desirable, the qualitative observations of this work show that the difference in pressure between the C & S and the present work is a factor in the difference between rate constants derived in the two studies.

The present work suggests the "high" value for the activation energy of the *n*-propyl radical decomposition in reaction 1. $E_1 \cong 35$ kcal./mole is consistent with the thermochemical estimates of $\Delta H_1 \cong 23$–26 kcal./mole and $E_{-1} \cong 8.6$ kcal./mole reported by Brinton for methyl addition to ethylene.[25,26] The entropy change, $\Delta S_1 \cong 14.2$ e.u., calculated[27] from the present data and those of Brinton, may be compared with that obtained from thermal entropy data and theoretical data: Bryant's[28] data give $\Delta S_1 \cong 12.1$ e.u. The difference between the two ΔS_1 estimates corresponds to a factor of 2.9 in the ratio of A_1/A_{-1} or an error of $\pm$ 1 kcal./mole in the difference $E_1 - E_{-1}$. In view of the uncertainties involved in the calculations and the present rate data and those of Brinton, the agreement is considered to be satisfactory and lends support to the "high" pre-exponential factor (about 10^{15} sec.$^{-1}$) for reaction 1. High A-factors have been reported also for the radical decomposition reactions of the *sec*-butyl[29] and the *t*-butyl free radicals.[22] It is difficult to rationalize the "high" A-factors in terms of the Slater theory of unimolecular reactions; the Slater theory in its approximate form[24] restricts the limiting rate of unimolecular decomposition to the highest frequency normal vibration within the molecule. The model based on the theories of Hinshelwood, Kassel, Rice, Rainsperger and Marcus,[30] which allows free energy exchange between the different energy modes, can account satisfactorily for these "high" A-factors.

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Alkyl Radicals," "Progress in Reaction Kinetics," edited by G. Porter, Pergamon Press, London, in press.

(26) R. K. Brinton, *J. Chem. Phys.*, **29**, 781 (1958).

(27) The ΔS_1 was estimated from the pre-exponential factors for the forward and the reverse of reaction 1 using the relation $\Delta S_1 = R \ln (A_1/A_{-1})$. In the calculation we have assumed $k_2 = k_{11}$, and we have used the results of the highest pressure experiments derived in this work, conditions which match most closely those of Brinton.[26] The standard state is taken as 1 mole/cc.

(28) W. M. D. Bryant, *J. Polymer Sci.*, **6**, 359 (1951).

(29) J. G. Calvert, *Chem. Revs.*, **59**, 569 (1959).

(30) (a) R. A. Marcus and O. K. Rice, *J. Phys. Chem.*, **55**, 894 (1951); (b) R. A. Marcus, *J. Chem. Phys.*, **20**, 352, 255, 359 (1952).

(25) J. A. Kerr and A. F. Trotman-Dickenson, The Reactions of

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[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY, BATON ROUGE, LOUISIANA]

Local Field Effect and Failure of the Double Layer Correction in Electrode Kinetics

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Failure of the theory of the diffuse double layer is to be expected for mixtures of electrolytes with different ionic valences because of local variations of potential in the plane of closest approach. Experimental evidence for this *local field effect* is given for the discharge of Ga^{+3} on mercury in perchlorate medium containing uni- or divalent positive ions (Na^+, Mg^{+2}) whereas no local field effect was detected for Ga^{+3} discharge in presence of Al^{+3}. Classical theory accounts for the variations of overvoltage—at constant current density—with the concentration of indifferent electrolyte for Al^{+3} but fails for Mg^{+2} and, especially, for Na^+. Alternate explanations are also considered. The corrected Tafel plot of $\ln I + (zF/RT)\Delta\varphi$ against $E - \Delta\varphi$ (z ionic valence of species being discharged; $\Delta\varphi$ difference of potential across the diffuse double layer; I, E, F, R and T as usual) is suggested for the double layer correction in the absence of specific adsorption.

Introduction

It was pointed out recently by Parsons[2a] that the classical theory of the diffuse double layer does not account for variations of potential in planes parallel to the electrode because the Poisson equation is solved for one dimension. The difference between

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(2) (a) R. Parsons, "Advances in Electrochemistry and Electrochemical Engineering," Vol. I, P. Delahay, Editor, Interscience Publishers, Inc., New York, N. Y., 1961, Ch. 1, pp. 1–64. (b) A. N. Frumkin, N. Nikolajeva and R. Ivanov, *Can. J. Chem.*, **37**, 253 (1959).