The Photolysis of 1,1′-Azo-*n*-butane Vapor. The Reactions of the *n*-Butyl Free Radical[1]

Wayne E. Morganroth and Jack G. Calvert

Contribution from the Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210

Received August 1, 1966

Abstract: The vapor phase photolysis of 1,1′-azo-*n*-butane at 3660 A has been investigated as a function of reactant pressure, temperature, light intensity, and added gas. The sequence of reactions 1–7 of the text is consistent with the observed results. With the assumption that the rate constant for the reaction $2n\text{-C}_4\text{H}_9 \rightarrow n\text{-C}_8\text{H}_{18}$ is 2.2×10^{13} cc/mole sec, and that for the reaction $(n\text{-C}_4\text{H}_9)_2\text{N}_2{}^* + \text{M} \rightarrow (n\text{-C}_4\text{H}_9)_2\text{N}_2 + \text{M}'$ is 3.2×10^{14} cc/mole sec, the rate constants for the following reactions have been estimated: $(n\text{-C}_4\text{H}_9)_2\text{N}_2{}^* \rightarrow 2n\text{-C}_4\text{H}_9 + \text{N}_2$, $k_2 \cong 2.5 \times 10^9 e^{-3.8/RT}$ sec^{-1}; $n\text{-C}_4\text{H}_9 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5$, $k_5 \cong 3.7 \times 10^{13} e^{-2.87/RT}$ sec^{-1}; $n\text{-C}_4\text{H}_9 + (n\text{-C}_4\text{H}_9)_2\text{N}_2 \rightarrow n\text{-C}_4\text{H}_{10} + \text{C}_4\text{H}_8\text{N}_2\text{C}_4\text{H}_9$, $k_6 \cong 1.4 \times 10^{11} e^{-7.1/RT}$ cc/mole sec. The disproportionation to combination ratio for the *n*-C_4H_9 radical (k_3/k_4) is estimated as 0.14 from experiments using both steady-state and flash-photolysis conditions. Published rate data for the reaction $\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4 \rightarrow n\text{-C}_4\text{H}_9$ are combined with the results of this study to estimate the thermodynamic quantities for the *n*-C_4H_9 radical: $\Delta H_f{}^\circ \cong 15.7$ kcal/mole; $S^\circ \cong 77.3$ eu (standard state, 1 atm); $D_{n\text{-C}_4\text{H}_9-\text{H}} \cong 98.0$ kcal/mole.

The reactions of the *n*-butyl free radical have been studied little, and several major uncertainties exist in the published rate data for this species. For example, there is no consistency between the reported rate constant ratios (k_3/k_4) for the disproportionation and combination reactions of the *n*-butyl radical.

$$2n\text{-C}_4\text{H}_9 \xrightarrow{(3)} 1\text{-C}_4\text{H}_8 + n\text{-C}_4\text{H}_{10}$$
$$\xrightarrow{(4)} n\text{-C}_8\text{H}_{18}$$

The data obtained by Moore and Wall[2] in their study of the photolysis of the di-*n*-butylmercury gave a value of about 0.5 for k_3/k_4 at 320°. Kraus and Calvert[3] predicted this ratio to be about 0.9 near 100° from an extrapolation of the similar ratios of the other butyl radicals. Kerr and Trotman-Dickenson[4] derived values of k_3/k_4 ranging from 0.57 at 61° to 1.09 at 229° from the photodecomposition of *n*-valeraldehyde. Thynne[5] found $k_3/k_4 \cong 0.95$ from 75 to 186° from the methyl radical sensitized decomposition of *n*-butyl formate.

All of these estimates of k_3/k_4 seem inordinately high in view of the magnitude of the similar rate constant ratios for the other normal alkyl radicals: 0.12 ± 0.02 for the ethyl radical,[6] 0.14 ± 0.02 for the *n*-propyl radical,[7] and about 0.2 for the *n*-pentyl radical.[8] There is no obvious reason why the ratio of rate constants for the reactions of disproportionation to that for combination for the *n*-butyl free radical should be greatly different from that of the other simple normal alkyl radicals; certainly a more accurate redetermination of this ratio is needed.

A similar conflict of data exists with regard to the decomposition reactions of the *n*-butyl radical. Kerr and Trotman-Dickenson[4] concluded from their study of photodecomposition of *n*-valeraldehyde that both of the following decomposition modes occur at elevated temperatures.

$$n\text{-C}_4\text{H}_9 \xrightarrow{(5)} \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5$$
$$\xrightarrow{(11)} \text{C}_3\text{H}_6 + \text{CH}_3$$

They estimated that $E_5 = 22.0$ and $E_{11} = 27.1$ kcal/mole; $\log A_5 = 11.2$ and $\log A_{11} = 12.1$ (units of sec^{-1}). However, it appears to be quite unlikely that the source of propylene in their system was reaction 11, since Frey and Hepp[9] reported the virtual absence of this compound among the products from the thermal decomposition of di-*n*-butylmercury. Furthermore, the experimental activation energy attributed to reaction 5 is inconsistent with reasonable thermal data for the over-all reaction 5 and rate data for the reverse reaction

$$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4 \xrightarrow{(10)} n\text{-C}_4\text{H}_9$$

Pinder and LeRoy,[10] Lampe and Field,[11] and Kerr and Trotman-Dickenson[12] have estimated E_{10} to be: 5.5, 5.5, and 8.6 kcal/mole, respectively. An average of these estimates coupled with the reasonable estimate of $\Delta H_5 \cong 23$ kcal/mole, suggest that $E_5 \cong 30$ kcal/mole. The results from the studies of the analogous decomposition radicals of the *n*-propyl[13,7d] and *sec*-butyl[14] are also inconsistent with the published kinetic data

---

[1] Presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., Sept 1964; submitted by W. E. M. in partial fulfillment of the requirements for the Ph.D. degree, The Ohio State University, 1965.

[2] W. J. Moore and L. A. Wall, *J. Chem. Phys.*, **17**, 1325 (1949).

[3] J. W. Kraus and J. G. Calvert, *J. Am. Chem. Soc.*, **79**, 5921 (1957).

[4] J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1602 (1960).

[5] J. C. J. Thynne, *Trans. Faraday Soc.*, **58**, 1533 (1962).

[6] For examples of the many studies of the ethyl system see: (a) K. O. Kutschke, W. H. J. Wijnen, and E. W. R. Steacie, *J. Am. Chem. Soc.*, **74**, 714 (1952); (b) R. K. Brinton and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1840 (1955); (c) D. G. L. James and E. W. R. Steacie, *Proc. Roy. Soc.* (London), **A244**, 289 (1958); (d) H. Cerfontain and K. O. Kutschke, *Can. J. Chem.*, **36**, 344 (1958); (e) D. P. Dingledy and J. G. Calvert, *J. Am. Chem. Soc.*, **85**, 856 (1963).

[7] (a) F. E. Blacet and J. G. Calvert, *ibid.*, **73**, 661 (1951); (b) S. G. Whiteway and C. R. Masson, *J. Chem. Phys.*, **25**, 233 (1956); (c) P. Ausloos and E. Murad, *J. Am. Chem. Soc.*, **80**, 5929 (1958); (d) J. A. Kerr and J. G. Calvert, *ibid.*, **83**, 3391 (1961).

[8] M. H. J. Wijnen, *ibid.*, **83**, 3752 (1961).

[9] F. E. Frey and H. J. Hepp, *ibid.*, **55**, 3357 (1933).

[10] J. A. Pinder and D. J. LeRoy, *Can. J. Chem.*, **35**, 588 (1957).

[11] F. W. Lampe and F. H. Field, *ibid.*, **37**, 995 (1959).

[12] J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1611 (1960).

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

[14] J. G. Calvert, *Chem. Rev.*, **59**, 569 (1959).

Table I. Product Rate Data from the Photolysis of 1,1′-Azo-*n*-butane at 3660 A

Run no.	$[Bu_2N_2]$, $M \times 10^4$	Temp, °K	I_a, einstein/cc sec $\times 10^{12}$	Φ_{N_2}	Rate formation of products, moles/cc sec $\times 10^{13}$: N_2	C_2H_4	C_2H_6	C_3H_8	*n*-C_4H_{10}	1-C_4H_8	*n*-C_6H_{14}	*n*-C_8H_{18}
1	0.974	298	3.61	0.14	4.91	0.00	0.00	0.00	0.737	0.447	0.00	3.70
2	1.05	298	4.27	0.16	6.61	0.0	0.0	0.0	0.922	0.632	0.0	4.34
3	1.02	318	3.74	0.16	6.11	0.0	0.0	0.0	1.05	0.552	0.0	4.69
4	2.83	324	9.77	0.09	8.31	0.0	0.0	0.0	2.11	0.688	0.0	5.33
5	2.58	350	8.98	0.11	10.2	0.0	0.0	0.0	3.37	0.724	0.0	6.23
6	2.50	353	9.70	0.13	12.5	0.0	0.0	0.0	4.44	1.11	0.19	6.43
7	4.75	358	15.4	0.06	8.83	0.0	0.0	0.0	4.26	0.633	0.0	4.11
8	4.75[a]	358	15.4	0.05	8.31	0.0	0.0	0.0	*a*	*a*	0.0	2.66
9	0.630	377	1.11	0.51	5.60	0.0	0.0	0.0	1.57	0.399	0.0	3.13
10	1.18	379	2.05	0.31	6.37	0.0	0.0	0.0	1.77	0.405	0.0	3.60
11	7.06	379	21.1	0.08	17.4	0.0	0.0	0.0	*b*	0.692	0.0	3.05
12	3.68	381	5.86	0.14	8.37	0.0	0.0	0.0	4.58	0.406	0.0	2.72
13	21.8	381	42.0	0.02	10.0	0.0	0.0	0.0	12.7	0.305	0.0	0.575
14	0.747	382	2.76	0.39	10.7	0.0	0.0	0.0	2.19	0.680	0.0	5.51
15	13.4	382	32.8	0.04	12.7	0.0	0.0	0.0	10.4	0.478	0.11	1.00
16	2.31	383	8.13	0.15	12.5	0.0	0.0	0.0	*b*	*b*	*b*	*b*
17	4.87	399	7.57	0.13	9.84	0.0	0.0	0.0	*b*	*b*	*b*	*b*
18	2.56	400	4.23	0.22	9.10	0.0	0.0	0.0	5.40	0.560	0.0	3.05
19	2.71	400	4.46	0.17	7.76	0.0	0.0	0.0	5.00	0.375	0.0	2.79
20	2.32	432	8.16	0.24	19.6	0.160	0.0	0.0	14.2	0.888	0.0	4.48
21	2.82	432	4.63	0.27	12.6	0.083	0.0	0.0	9.14	0.515	0.0	1.89
22	2.36	439	8.28	0.28	22.9	0.311	0.160	0.096	*b*	1.10	0.06	4.83
23	2.43	439	4.04	0.37	14.9	0.197	0.080	0.0	9.56	0.738	0.0	2.24
24	2.43	459	*b*	*b*	*b*	1.43	0.466	0.220	24.2	1.91	0.253	6.58
25	2.39	468	8.35	0.47	39.3	2.49	1.06	0.451	30.1	2.58	0.471	7.54
26[c]	1.56	475	1.09	0.96	10.5	1.43	0.704	0.212	8.23	0.649	0.326	1.60
27	2.34	475	4.33	0.74	32.2	3.58	1.39	0.542	25.2	2.05	0.777	5.48
28	2.40	475	4.43	0.77	33.9	2.69	1.39	0.498	24.9	2.07	0.831	6.11
29	2.63	476	9.13	0.55	49.8	4.42	1.85	0.809	39.0	3.34	0.927	9.06
30	1.50	480	2.86	0.85	24.4	3.72	1.45	0.421	16.2	1.49	1.17	*b*
31	2.52	487	8.80	0.61	53.6	10.9	4.30	1.42	43.6	3.86	1.72	9.51
32	2.53	501	8.84	0.64	56.3	21.1	9.60	2.82	53.7	4.48	2.42	7.64
33	2.41	505	8.43	0.64	53.7	24.6	11.3	*b*	52.2	4.74	2.61	6.77
34	2.45	520	8.58	0.64	54.8	64.0	33.4	8.37	71.4	9.70	6.59	8.55

[a] A pressure of 24 mm of CO_2 was added in this run and made impossible analysis for butane and butene. [b] Not determined because of analytical failures of one kind or another. [c] Uniform density filter (36.7% transmission) used in this run.

for reaction 5. The need for a redetermination of k_5 is evident.

The present work was initiated to obtain more reliable kinetic data to help clarify the conflicting published data on the *n*-butyl radical. In view of the past successes in the use of gaseous azo alkyl compounds as clean alkyl free-radical sources, the 3660-A photolysis of 1,1′-azo-*n*-butane was selected to generate *n*-butyl radicals in this work.

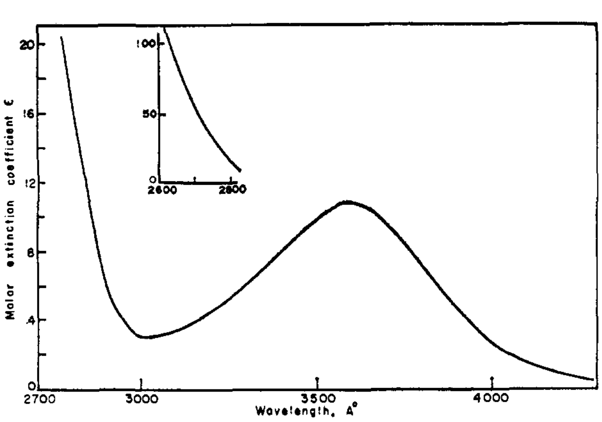

Figure 1. Ultraviolet absorption spectrum of 1,1′-azo-*n*-butane; $\epsilon = \log (I_0/I)/cl$ l./mole cm.

Experimental Section

The 3660-A photolysis system used for the quantitative rate studies was similar to that employed in this laboratory in previous studies.[15a] In the series of flash experiments the equipment was essentially that described by McQuigg.[15b] In this case the cell was surrounded with a glass jacket which limited the light from the flash to wavelengths greater than about 3000 A. The flash duration was 0.9 msec. A series of successive flashes were made usually on a given sample of the azo compound to provide sufficient products (0.18–0.95 μmole of octane) and thus ensure an accurate analysis. Column 2 of Table II represents the summation of the voltages squared from successive flashes in a given run, and it is proportional to the total energy of the flashes. Product analysis was accomplished through rather conventional mass spectrometric and chromatographic methods. The column was made from a 5-mm i.d. glass U-tube, 6 ft in length, packed with 20/60 mesh activated alumina with 2% by weight squalane.

1,1′-Azo-*n*-butane (stated 99% purity), purchased from Merck Sharp and Dohme, was purified in reduced red light by transpiring the hydrocarbon impurities (octane, butane, etc.) from the liquid sample (150–165°) with dry helium gas, and distillation at reduced pressures. Samples purified in this fashion showed no detectable impurities on the chromatograms of an amount of azo compound equivalent to that used in photolytic runs. The vapor pressure of the purified compound was measured at several temperatures in the range 294–361.2°K. The data fit well the least-squares equation: $\log P\ (\text{mm}) = -2.329 \times 10^3/T + 8.189$. From this equation the normal boiling point and the heat of vaporization of 1,1′-azo-*n*-butane are estimated to be: 439°K and 10.7 kcal/mole, respectively. The measured molar extinction coefficient [$\epsilon = \log (I_0/I)/cl$] at 3660 A

---

(15) (a) R. M. Smith and J. G. Calvert, *J. Am. Chem. Soc.*, 78, 2345 (1956); (b) R. D. McQuigg, Ph.D. Dissertation, The Ohio State University, 1964.

Table II. Product Yields from the Pyrex-Filtered Flash Photolysis of 1,1′-Azo-*n*-Butane at 80°

Run no.	(1) Pressure, Bu_2N_2, mm	(2) Σ (voltage)^2 $\times 10^{-8}$ v^2	(3) Moles of product $\times 10^6$ *n*-C_4H_{10}	(4) Moles of product $\times 10^6$ 1-C_4H_8	(5) Moles of product $\times 10^6$ *n*-C_8H_{18}	(6) [(3) + (4)]/ 2 × (5)	(7) (5) + [(3) + (4)]/2 / (2)(1) × 10^{17}
35	4.16	9.41	0.040	0.035	0.335	0.11	9.5
36	7.39	14.5	0.088	0.067	0.557	0.14	5.9
37	9.54	22.0	0.155	0.115	0.950	0.14	5.2
38	9.67	5.4	0.030	0.027	0.175	0.17	3.9
39	12.39	9.7	0.053	0.040	0.295	0.16	2.9
					Average	0.14	

was 7.9 l./mole cm. The ultraviolet absorption of the compound is shown in Figure 1.

Azomethane, used in actinometer experiments, was prepared from 1,2-dimethylhydrazine as described by Renaud and Leitch.[16] The hydrocarbon standard gases were Phillips research grade. The liquid hydrocarbons were obtained from Matheson Coleman and Bell.

The light intensity was estimated using azomethane photolysis as an internal actinometer. The measured fraction of light absorbed was matched closely with that found in experiments using azo-*n*-butane so that errors due to reflections were minimized. The quantum yield of nitrogen formation in azomethane was taken as unity.[17]

Several dark runs were made using 4.7–6.5 mm of 1,1′-azo-*n*-butane over the temperature range 203–255°. The apparent activation energies of nitrogen, ethylene, and *n*-butane formation were 47.5, 64.5, and 47.8 kcal/mole, respectively. Small corrections were made to the photochemical rate data at the highest temperatures. All data in Table I represent photochemical rates.

Results and Discussion

The rate data and quantum yields of nitrogen formation from the steady-state photolyses of azo-*n*-butane at 3660 A are summarized in Table I. The data from the high-intensity flash experiments are given in Table II.

The products of the photolysis of 1,1′-azo-*n*-butane and the rate data determined in this work are in accord with the following reaction mechanism.

$$(n\text{-}C_4H_9)_2N_2 + h\nu \longrightarrow (n\text{-}C_4H_9)_2N_2^* \qquad \text{(I)}$$

$$(n\text{-}C_4H_9)_2N_2^* + M \longrightarrow (n\text{-}C_4H_9)_2N_2 + M' \qquad (1)$$

$$(n\text{-}C_4H_9)_2N_2^* \longrightarrow 2n\text{-}C_4H_9 + N_2 \qquad (2)$$

$$2n\text{-}C_4H_9 \longrightarrow 1\text{-}C_4H_8 + C_4H_{10} \qquad (3)$$

$$\searrow n\text{-}C_8H_{18} \qquad (4)$$

$$n\text{-}C_4H_9 \longrightarrow C_2H_4 + C_2H_5 \qquad (5)$$

$$n\text{-}C_4H_9 + (n\text{-}C_4H_9)_2N_2 \longrightarrow n\text{-}C_4H_{10} + C_4H_8N_2C_4H_9 \qquad (6)$$

$$C_4H_8N_2C_4H_9 \longrightarrow 1\text{-}C_4H_8 + N_2 + n\text{-}C_4H_9 \qquad (7)$$

$(n\text{-}C_4H_9)_2N_2^*$ represents an electronically excited molecule.

Excited Molecule Participation. The quantum yields of nitrogen formation from 1,1′-azo-*n*-butane are considerably below unity at the lower temperatures. See the data of Table I. Furthermore in runs at a given temperature Φ_{N_2} decreases significantly as the concentration of the azobutane is increased; see Figure 2. Also the addition of carbon dioxide decreases the quantum yield of nitrogen and octane. Compare runs 7 and 8 of Table I. The results suggest the possible participation of a relatively long-lived electronically excited azobutane molecule and the collisional deactivation of a large fraction of these species at the lower temperatures. A test of the consistency of the data with the occurrence of eq I, 1, and 2 can be made readily assuming steady-state kinetics for the excited molecule intermediate. For conditions such that reaction 2 is the only important source of nitrogen, that is, the chain reaction step 7 is unimportant, one expects relation 8 to hold.

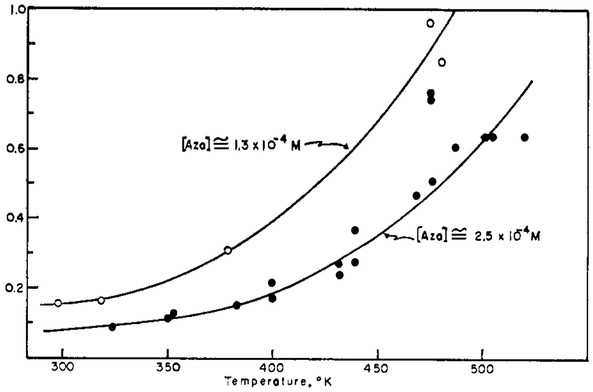

Figure 2. The effect of temperature on the quantum yield of nitrogen in the 3660-A photolysis of 1,1′-azo-*n*-butane.

$$\frac{1}{\Phi_{N_2}} = \frac{1}{\phi_I} + \frac{k_1[M]}{k_2\phi_I} \qquad (8)$$

The quantum yield data are plotted in Figure 3 as a test of relation 8. The data at 380°K are the most extensive and show a reasonably good fit to the form of the relation. The intercept of 0.8 ± 0.2 suggests that ϕ_I is near unity and that reactions of $(n\text{-}C_4H_9)_2N_2^*$ other than (1) and (2) are relatively unimportant for these conditions. Assuming ϕ_I equals unity then the slopes of the lines drawn in Figure 3 give estimates of k_1/k_2. With the less extensive data at the four other temperatures shown in Figure 3, the lines were drawn through the points for the particular temperature and through the intercept for the 380° data. Using this procedure values of k_1/k_2 (mm^{-1}) were estimated to be: 0.40 at 435°K, 0.78 at 380°K, 1.5 at 354°K, and 3.2 at 298°K. The data from the highest temperature are not precise enough to allow a meaningful estimate for these conditions. The Arrhenius plot of these data (Figure 4) gives $k_1/k_2 \cong 1.26 \times 10^5 e^{3.8/RT}$ cc/mole. If k_1 is assumed to be the magnitude of the collision number, 3.2×10^{14} cc/mole sec, then $k_2 \cong 2.5 \times 10^9 e^{-3.8/RT}$ sec^{-1}. The product yields from the flash studies shown in Table II reflect the identical behavior.

---

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

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

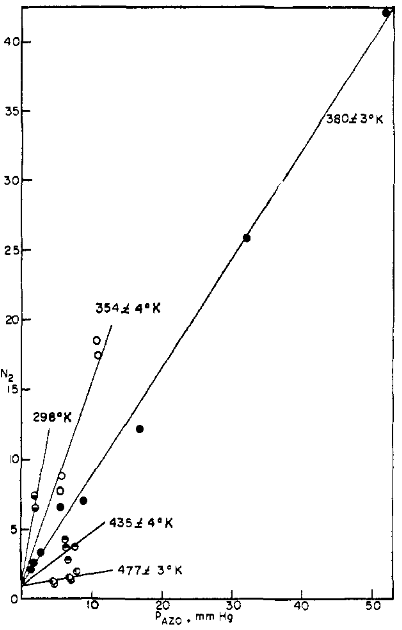

Figure 3. Effect of pressure of azobutane on $1/\Phi_{N_2}$ at various temperatures; slopes of the lines are in theory related to k_1/k_2.

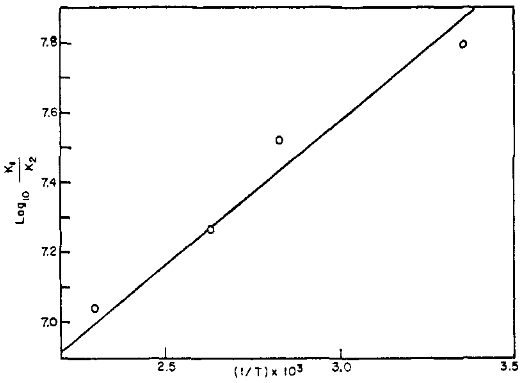

Figure 4. Arrhenius plot of the ratio of rate constants for the deactivation of excited azobutane and its decomposition, k_1/k_2.

The number of quanta created by the flash is proportional to the energy or the square of the voltage to which the condenser bank is charged, and the absorption of the light by the azo compound is directly proportional to the azo compound pressure for these conditions of low concentration and short path length; thus column 7 of Table II is expected to be proportional to the nitrogen quantum yield. The decrease in the figure in column 7 with increase in azo compound pressure is very similar to that observed from the nitrogen quantum yield data of the steady-state experiments at the same temperature.

The data presented here are in general accord with those found by Kutschke and co-workers. Cerfontain and Kutschke[6d] found that the activation energy for the decomposition of azoethane excited with 3660 A was 2.1 kcal/mole; Riem and Kutschke[18] found a similar value of 2.3 kcal/mole for azoisopropane excited at 3660 A. In general the photochemical behavior of the 1,1′-azo-*n*-butane, and specifically the deactivation of electronically excited molecules, is consistent with that observed for all of the azo compounds which have been studied that have a complexity greater than that of azomethane.

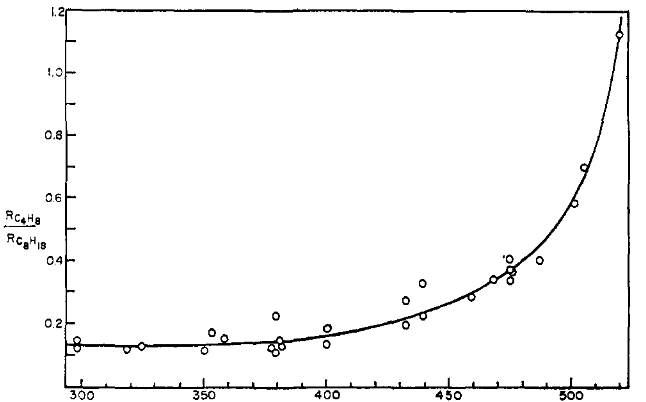

Figure 5. Effect of temperature on the ratio of rates of 1-butene and *n*-octane in 1,1′-azobutane photolysis at 3130 A.

Disproportionation to Combination Ratio for the *n*-Butyl Radical. Significant products of the photolysis of 1,1′-azo-*n*-butane include 1-butene and *n*-octane. Likely sources of these products are reactions 3 and 4. In runs made at 358°K with 24 mm of added oxygen, only a trace of octane product was formed. In an otherwise similar run made without oxygen but with 24 mm of added carbon dioxide (run 8 of Table I) only a 50% reduction of the octane was found. This is the expected magnitude to the collisional deactivation which would result from 24 mm of added oxygen. Hence it is probable that octane is not formed in an intramolecular process, but its major source is reaction 4. In previous studies of the disproportionation and combination reactions of free radicals there is general agreement that the ratio of rate constants for these two reactions is nearly temperature independent. Indeed the ratio of the rate of butene formation to that of octane formation found in this work is seen to be essentially constant up to about 400°K (see Figure 5). A significant increase in the butene to octane ratio occurs in runs above 400°K. Presumably this reflects the increasing importance of reaction 7, an additional source of butene, as the temperature rises above 400°K. It seems reasonable to assign the average ratio of butene to octane, 0.14, observed in the experiments below 400°K to the ratio k_3/k_4. As a check on this assignment photolyses at very high light intensity were made. It is apparent that the additional butene forming reaction 7 must be preceded by the H-atom abstraction reaction 6. Presumably the radical with the specific structure, $CH_3CH_2\dot{C}HCH_2$-$N_2C_4H_9$, only one of three species formed by secondary H-atom abstraction, is the major source of the 1-butene. It was reasoned that any possible contribution of reactions 6 and 7 to butene formation could be eliminated readily by employing a flash source such that very high radical concentrations would be created, and radical–radical reactions 3 and 4 of very low activation energy would dominate over radical–molecule reactions of significant E_a such as 6. The results of the flash experiments, summarized in Table II, bear out this expectation. The moles of butane are nearly equal to those of butene found in a given experiment, and the average ratio of moles of products, $[(C_4H_8 +$

---

(18) R. H. Riem and K. O. Kutschke, *Can. J. Chem.*, 38, 2332 (1960).

$C_4H_{10})/2]/C_8H_{18}$, can be taken as an independent estimate of k_3/k_4. This yields $k_3/k_4 \cong 0.14$ in excellent agreement with the estimate from the low-temperature steady-state experiments. This estimate is in good accord with that observed for the *n*-propyl radical (0.14 ± 0.02)[7] and the *n*-pentyl radical (0.2).[8] It is in striking contrast to the much higher estimates for k_3/k_4 for the *n*-butyl radical which have been made previously; however, these systems were much more complex, and alternative sources of butene cannot be ruled out in the previous studies.

The Decomposition Reaction of the *n*-Butyl Radical. An inspection of the data of Table I shows that the rates of ethylene and ethane formation become significant in runs at temperatures above 430°K. Hexane also appears as a significant product under these conditions. A probable precurser to these products is the *n*-butyl radical decomposition (reaction 5). Presumably ethane is formed through H-atom abstraction reactions involving a proportion of the ethyl radicals formed in (5). The hexane probably arises largely from the ethyl–butyl radical combination reaction. A mass balance test between ethyl radicals and ethylene formed in (5) is impossible since an unknown fraction of the ethyl radicals formed is expected to add to the azobutane double bond; the analogous reaction has been observed in the other azo compounds.

A test of this mechanism of ethylene formation is possible using the rate of octane formation as a monitor of *n*-butyl radical concentrations. Relation 9 should apply if reactions 4 and 5 are the only sources of octane and ethylene.[19]

$$\frac{R_{C_2H_4}}{(R_{C_8H_{18}})^{1/2}} = \frac{k_5}{k_4^{1/2}} \qquad (9)$$

In Figure 6 an Arrhenius plot is made of this function calculated from the data of Table I. The data follow a reasonably good linear plot, and a least-squares treatment leads to the following estimate of $k_5/k_4^{1/2}$.

$$k_5/k_4^{1/2} \cong 7.94 \times 10^6 e^{-28.7/RT}\ (\text{mole/cc sec})^{1/2}$$

Taking k_4 as 2.2×10^{13} cc/mole sec, the association constant for methyl, an estimate of k_5 is found: $k_5 \cong 3.73 \times 10^{13} e^{-28.7/RT}$.

A check on the consistency of this estimate can be made using the measured rate constant for the reverse of reaction 5

$$C_2H_5 + C_2H_4 \longrightarrow n\text{-}C_4H_9 \qquad (10)$$

and suitable thermal data. There is good agreement on the magnitude of the rate constant for (10) from previous studies;[10–12] for example, at 111°, common to all

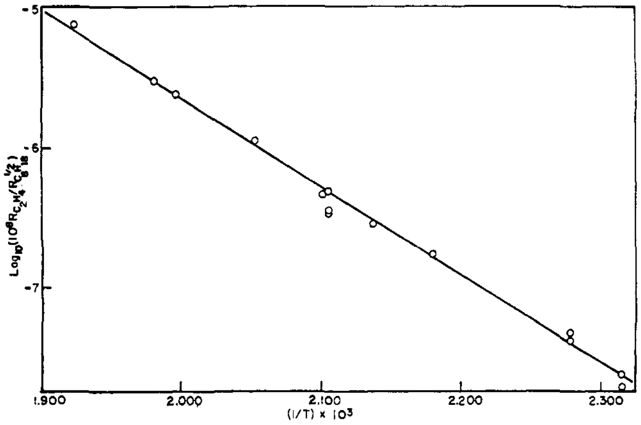

Figure 6. Arrhenius plot of the rate function theoretically equal to $k_5/k_4^{1/2}$.

the studies, estimates of $k_{10} \cong 6.73 \times 10^6$, 3.76×10^6, and 7.04×10^6 cc/mole sec are derived from the data of Kerr and Trotman-Dickenson, Pinder and LeRoy, and Lampe and Field, respectively. If one takes as a best estimate of E_{10} the average value of the three studies, 6.5 kcal/mole, then the Arrhenius *A* factor can be estimated from this value and the average k_{10} at 111°. With this method, $k_{10} \cong 2.91 \times 10^{10} e^{-6.5/RT}$ cc/mole sec. The relation between the ratio of preexponential factors for forward and reverse reactions and the over-all entropy change for the reaction $\Delta S_5 = R \ln (A_5/A_{10})$ yields $\Delta S_5 = 14.2$ eu for the standard state of 1 mole/cc and 34.3 eu for the choice of 1 atm as the standard state. This is in excellent agreement with the estimate of $\Delta S_5 = 34.7$ eu derived from reasonable thermal data for 25° and 1 atm.[20] The enthalpy change of the reaction 5 should in theory relate to the difference in activation energies between the forward and reverse reactions, $\Delta H_5 = E_5 - E_{10} + RT$. With this relation the kinetic data give $\Delta H_5 \cong 23.0$ kcal/mole; reasonable thermal data suggest $\Delta H_5 \cong 22.8$ kcal/mole at 25°.[20] The high consistency of the rate constant k_5 determined in this work and the published data for k_{10} with reasonable thermal data points to a common transition state for reactions 5 and 10 and tends to substantiate the present interpretation of the kinetic data. From the present data we can estimate for the n-C_4H_9 radical at 25° and 1 atm, $\Delta H_f^\circ \cong 15.7$ kcal/mole and $S^\circ \cong 77.3$ eu. These data can be used with the heats of formation of n-C_4H_{10} and the H atom to estimate the heat of dissociation of the primary H bond in n-C_4H_{10} to be about 98.0 kcal/mole.

The absence of propylene and methane in the products of 1,1′-azo-*n*-butane photolysis at all temperatures used in this study shows the unimportance of reaction 11 for our conditions. It seems likely to us that the

$$n\text{-}C_4H_9 \longrightarrow C_3H_6 + CH_3 \qquad (11)$$

propylene and methane products of *n*-valeraldehyde photolysis, attributed to this reaction by Kerr and Trotman-Dickenson,[4] had their origin in some other radical decomposition reaction (*e.g.*, $CH_3\dot{C}HCH_2CH_2CHO \rightarrow C_3H_6 + \cdot CH_2CHO$).

---

[19] An additional source of ethylene which should be considered in this system is the decomposition of the radical, $\cdot CH_2CH_2CH_2CH_2N_2C_4H_9$, one of the possible structural forms of the $C_4H_8N_2C_4H_9$ radical product of the H-atom abstraction reaction 6. Since a primary H atom must be abstracted to form this radical, it is probably an unimportant species in this system. There is good evidence that the secondary H-atom positions are attacked. The 1-butene chain reaction at high temperatures probably arises from the decomposition of the radical, $CH_3CH_2\dot{C}HCH_2N_2C_4H_9$. Possibly the propane product reflects decomposition of the radical, $CH_3CH_2CH_2\dot{C}HN_2C_4H_9$; see the section of the text on the mechanism of propane formation. Since propylene is absent among the products the possible radical $CH_3\dot{C}HCH_2CH_2N_2C_4H_9$ seems to be less favored as a product of reaction 6. The radical $\cdot CH_2CH_2CH_2CH_2N_2C_4H_9$ would be even less favored because of the higher activation energy required for its formation.

[20] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 819.

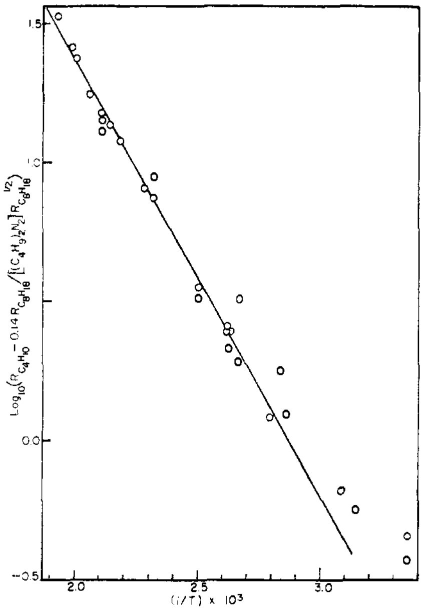

Figure 7. Arrhenius plot of the rate function theoretically equal to $k_6/k_4^{1/2}$.

H-Atom Abstraction by *n*-Butyl Radicals. The formation of *n*-butane can be explained satisfactorily by reactions 3 and 6. Using the *n*-octane rate as a butyl radical monitor again, one can estimate k_6 from the data assuming this mechanism.

$$k_6/k_4^{1/2} = \frac{(R_{C_4H_{10}})_{\text{total}} - (R_{C_4H_{10}})_3}{[(n\text{-}C_4H_9)_2N_2]R_{C_8H_{18}}^{1/2}} \qquad (12)$$

The terms in the numerator of (12) refer to the total butane rate and the rate of butane formed only in reaction 3, respectively. The latter term should equal $R_{C_8H_{18}}(k_3/k_4) \cong 0.14R_{C_8H_{18}}$. An Arrhenius plot of the function 12 derived in this fashion is shown in Figure 7. All but the points at the lowest temperatures fit the expected linear relationship. In seven runs at the lowest temperatures, the $(R_{C_4H_{10}})_3$ term is near equal to the total butane rate; under these conditions the numerator of relation 12 is very inaccurate. The least-squares line, excluding the data from these seven experiments, is given by

$$k_6/k_4^{1/2} \cong 3.02 \times 10^4 e^{-7.1/RT} \text{ (cc/mole sec)}^{1/2}$$

Taking $k_4 = 2.2 \times 10^{13}$ cc/mole sec, $k_6 \cong 1.42 \times 10^{11}e^{-7.1/RT}$ cc/mole sec. The estimate shows that H-atom abstraction reactions of the *n*-butyl radical are very similar to the analogous reactions of the smaller normal alkyl radicals. Compare the data of Table III.

Table III. Rate Constant Factors for the Reactions $R + RN{=}NR \longrightarrow RH + R'N{=}NR$

R	E_a, kcal/mole	Log *A*, cc/mole sec	Log *k*, cc/mole sec (100°)	Ref
CH_3	7.6	11.0	6.6	17
	6.9	10.5	6.5	*a*
	7.3	10.7	6.4	*b*
	8.4	11.5	6.6	*c*
C_2H_5	7.5	10.9	6.5	*d*
	8.0	11.3	6.6	6d
n-C_3H_7	7.9	11.3	6.7	7d
n-C_4H_9	7.1	11.2	7.0	This work

[a] S. Toby, *J. Am. Chem. Soc.*, **82**, 3822 (1960). [b] P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **32**, 593 (1954). [c] S. Toby and K. O. Kutschke, *ibid.*, 37, 672 (1959). [d] P. Ausloos and E. W. R. Steacie, *Bull. Soc. Chim. Belges*, **63**, 87 (1954).

The Mechanism of Propane Formation. The rate of propane formation becomes measurable in 1,1′-azo-*n*-butane photolysis in runs at 439°K and above. Although it is a relatively minor product, it is unexpected and not explainable with the limited mechanism given. Conceivably it may have its origin in propyl radicals formed by the thermal decomposition of one of the radicals of the general formula $C_4H_8N_2C_4H_9$, formed from the azo compound by H-atom abstraction by radicals (reaction 6). Possibly the radical $CH_3CH_2CH_2CHN_2C_4H_9$ could give n-C_3H_7, HCN, and NC_4H_9 by decomposition. Sufficient data are not now available to choose between this and other possibilities or to present a more definitive mechanism for propane formation.

Acknowledgment. The authors are grateful for the support of this work through a research grant from the Air Pollution Division, Bureau of State Services, U. S. Public Health Service, Bethesda, Md.