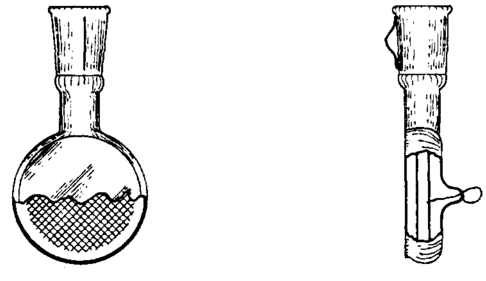

Figure 5. Electrochemiluminescence cell employed in the integrating-sphere studies.

Quantum-Yield Measurements. A 10-in. sphere was coated on the inner side with barium sulfate sphere paint[39] to give a surface with reflectance of 95% or better from 400 to 700 mμ.[40,41] A 1-in. diameter hole and a 1.5-in. diameter hole were cut into the sphere so as to be on the same great circle, having an arc of 180° between centers. A 1P28 photomultiplier detector was mounted on a holder having a 1-in. diameter tubulation extending 0.6 cm into the sphere. A ground-glass plate was attached to the end of the tube which extended into the sphere, and provision was made for inserting metallic screens into the tube to control the light level observed by the detector. The readout unit and power supply for the photomultiplier was an Aminco No. 10-213 microphotometer. The 1.5-in. diameter opening of the sphere was positioned on top so that the ecl cell (*cf.* Figure 5) could be suspended vertically into the center of the sphere. The platinum grid electrodes of the ecl cell were 80 mesh, 2.5 cm in diameter, and spaced 1 mm apart. The electrical leads acted as a suspension with terminals ending at a cap resting in the sphere opening. The sphere thus assembled was light tight, and essentially all of the light emitted impinged on the sphere wall, to be integrated, before measurement.

In order to calibrate the intensity of the emission recorded with the photomultiplier in terms of einsteins emitted, the cell shown in Figure 5 less its platinum electrodes was filled with a chemiluminescent solution,[27] containing N-butyl-4-butylaminonaphthalimide (Calofluor Yellow 7G^{R}) as the emitting species and placed in the integrating sphere. Simultaneously, this solution was poured into a cell of a chemiluminescence apparatus[27] in which the quanta per second emitted by the sample could be measured. The values obtained were correlated with the light-intensity measurements obtained on the photomultiplier attached to the integrating sphere to obtain a constant, *k*, by which the photomultiplier reading would be converted to quanta per second. In instances where the spectral distribution of the ecl emission differed significantly from the chemiluminescence standard, *k* was changed to reflect the known spectral response curve of the photomultiplier tube. A small lamp (grain of wheat) operated at known low voltage was inserted into the sphere periodically to check the constancy of the readout of the sphere assembly.

Acknowledgments. Thanks are due to J. B. Gallivan, J. Koren, and B. G. Roberts for assistance with the spectroscopic studies and P. Geiseke and J. Kriz for the integrating sphere investigations. We are also grateful to T. B. Reddy for his aid in measuring the ac current and to E. F. Ullman for discussion on the photooxidation studies. Thanks are also due to G. W. Kennerly for his encouragement and advice.

---

[39] Reflectance grade barium sulfate (Bausch & Lomb) with an acrylic latex binder was employed.

[40] Measured by comparison with a National Bureau of Standards reflectance standard.

[41] The use of reflectance spheres is described in "Absolute Calibration of Reflectance Standards," ASTM Designation E306,1966.

The Photolysis of 1,1′-Azoisobutane Vapor at 3660 A. The Reactions of the Isobutyl Free Radical[1]

David H. Slater, Susan S. Collier, and Jack G. Calvert

Contribution from the Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210. *Received August 25, 1967*

Abstract: The vapor-phase photolysis of 1,1′-azoisobutane was studied in experiments at wavelength 3660 A and at various temperatures and pressures. The product rate data fit well the suggested reaction scheme involving an excited azoisobutane molecule and reactions of the isobutyl free radical. The ratio of rate constants for the disproportionation and combination reactions of the isobutyl radical was estimated to be 0.075 ± 0.007 (25–168°). Rate constants for the H-atom abstraction and the decomposition reactions of the isobutyl radical were derived assuming the rate of the isobutyl combination reaction to be 2.2×10^{13} cc/mole sec: $i\text{-}C_4H_9 + (i\text{-}C_4H_9)_2N_2 \rightarrow i\text{-}C_4H_{10} + C_4H_8N_2C_4H_9$ (3), $k_3 \cong 3.2 \times 10^{10}e^{-6.7/RT}$ cc/mole sec; $i\text{-}C_4H_9 \rightarrow C_3H_6 + CH_3$ (5), $k_5 \cong 2.4 \times 10^{12}e^{-31 \pm 2/RT}$ sec^{-1}. These rate data were used with published data for the *sec*-butyl decomposition reaction, enthalpy and entropy data, to predict the kinetic reason for the dominance of reaction 10 over 9 [$CH_3 + C_3H_6 \rightarrow sec\text{-}C_4H_9$ (10), $CH_3 + C_3H_6 \rightarrow i\text{-}C_4H_9$ (9)]; the data suggest that it is largely the result of an *A*-factor difference between the two reactions. From the effects of pressure and temperature on the quantum yield of nitrogen, an estimate was obtained for the rate constant for the excited azo molecule decomposition reaction: $(i\text{-}C_4H_9)_2N_2^* \rightarrow 2i\text{-}C_4H_9 + N_2$ (B), $k_B \leq 4.5 \times 10^{9}e^{-4.8/RT}$ sec^{-1}. If the excited singlet were the reactant in B, then fluorescence emission should be observable from the azoisobutane. No emission was detectable even in experiments at −180°.

There is now very little quantitative information available on the reactions of the isobutyl free radical, although its unique structure makes its kinetic characterization of special interest. Since it has but one H atom per radical which by abstraction leads to olefin, one expects this radical to have an unusually low rate constant for the disproportionation reaction. Indeed Kraus and Calvert[2] estimated that the ratio of the rate constants for the disproportionation and combination

---

[1] (a) Presented at the Robert Livingston Photochemical Symposium, Minneapolis, Minn., May 9, 1967; (b) Division of Physical Chemistry, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, paper 44.

[2] J. W. Kraus and J. G. Calvert, *J. Am. Chem. Soc.*, **79**, 5291 (1957).

reactions, k_1/k_2, was very much lower for isobutyl (0.4) than that for *sec*-butyl (2.3) and *t*-butyl free radicals (4.6).

$$2C_4H_9 \longrightarrow C_4H_8 + C_4H_{10} \tag{1}$$

$$2C_4H_9 \longrightarrow C_8H_{18} \tag{2}$$

However, one must question the quantitative nature of the previous data since it is now realized that sources of butene other than reaction 1 may have been important in the dibutyl ketone photolyses at 100° employed by Kraus and Calvert. Thus radical abstraction of one of the tertiary hydrogen atoms in diisobutyl ketone may occur quite readily ($R + [(CH_3)_2CHCH_2]_2CO \rightarrow RH + (CH_3)_2CCH_2COC_4H_9$), and the decomposition of the resulting radical to form isobutylene may be important at 100° [$(CH_3)_2CCH_2COC_4H_9 \rightarrow i\text{-}C_4H_8 + COC_4H_9$]. Obviously new data derived from experiments at several temperatures are needed in order to sort out the individual reactions.

Rate data for the decomposition reaction of the isobutyl free radical (reaction 5; see below) would be most valuable. Kinetic data for (5), coupled with similar data for the *sec*-butyl radical decomposition, could provide an insight into the nature of the strong kinetic preference for the methyl radical addition to propylene to form the *sec*-butyl rather than the isobutyl free radical.

The dearth of kinetic data on the isobutyl system is probably a consequence of the difficulties involved in the unambiguous generation of the isobutyl radical in a system free from the other isomeric butyl radicals. Of course, when methyl radicals are added to propylene the *sec*-butyl radical is formed almost exclusively, and when hydrogen atoms are added to isobutylene the *t*-butyl radical is the dominant product; little isobutyl radical product forms. There is a similar complication to the preparation of the isobutyl radical by H-atom abstraction from isobutane. Again in this case the *t*-butyl radical product is highly favored.

The photochemical methods for isobutyl preparation appear to be somewhat more promising in theory. Kraus and Calvert[2] photolyzed diisobutyl ketone as an isobutyl source. However, this system is unsatisfactory for our purposes since a second primary photochemical process forming propylene is present, and a large correction would be necessitated in the treatment of the propylene rate data in order to derive estimates of the rate constant for the isobutyl radical decomposition reaction.

Considerable success has been achieved in the preparation of specific alkyl free radicals from the photolysis of the corresponding azoalkanes. In previous studies the methyl,[3] ethyl,[4] *n*-propyl,[5] isopropyl,[6] *t*-butyl,[7] and *n*-butyl[8] radicals have been prepared in this fashion. In the present study we have photolyzed 1,1′-azoisobutane at 3660 A to prepare the isobutyl free radical. The consistency of the results shows the choice of method was satisfactory.

The photochemistry of the azoalkanes is in itself very interesting. The nature of the electronic states participating in the photolysis remains uncertain. As one phase of this study, new information on the lifetime and reactions of the electronically excited 1,1′-azoisobutane molecule was determined.

Experimental Section

The 3660-A photolysis system employed in the rate studies reported here was similar to that used in previous studies from this laboratory.[8,9] Product analyses were effected using gas chromatographic methods. The fraction of products not condensed at liquid nitrogen temperature was analyzed on a $^1/_8$ in. × 6 ft chromatographic column, filled with Linde Molecular Sieve 5A, 90–100 mesh, operated at 60°, and a Gow-Mac thermal conductivity detector (JDC-301). The condensable fraction was analyzed using a capillary column, 100 ft in length, 0.02-in. diameter, coated with squalane and temperature programmed, 25–125° at 10°/min. In this case a flame ionization detector was employed. Areas of the eluted product peaks were integrated automatically from the detector signal with an electronic integrator (Infotronics, CRS-11HSB).

The 1,1′-azoisobutane reactant purchased from Merck Sharp and Dohme (stated purity 99%) was further purified by chromatographic separation on an Autoprep instrument equipped with a XF-1150 column operated at 140°. The purified sample showed no impurities chromatographically at the photochemical product peak regions. It was stored at −78° in a darkened sample bulb sealed to the photolysis system. The average measured molar extinction coefficient [$\epsilon = \log (I_0/I)/cl$] at 3660 A was 11.3 l./mole cm. The first absorption band is structureless, originates at about 4400 A, and extends to about 2970 A, with a broad maximum near 3665 A. A second much more intense band originates at about 2970 A and extends to the shorter wavelengths.

The light intensity was estimated in several experiments using azomethane photolysis as an actinometer. The quantum yield of nitrogen was taken as unity.[3a] Azomethane was prepared as described by Renaud and Leitch.[10]

Several dark experiments indicated that the thermal rate of decomposition of the 1,1′-azoisobutane was unimportant compared to photochemical rates at all temperatures employed.

The absorption and emission studies were done on degassed solutions of 1,1′-azoisobutane in both hexane and isopentane–3-methylpentane using a Turner absolute spectrofluorimeter, Model 210.

Results and Discussion

The rate data and the quantum yields of nitrogen formation from 1,1′-azoisobutane photolysis experiments at 3660 A and under a variety of conditions (determined by D. H. S.) are summarized in Table I. The major products for runs below 200° are nitrogen, isobutane, isobutylene, and 2,5-dimethylhexane. In runs above 200°, propylene, methane, and pentane also appear. These products and their rates may be rationalized well through consideration of the following reaction mechanism.

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

$$(i\text{-}C_4H_9)_2N_2^* + M \longrightarrow (i\text{-}C_4H_9)_2N_2 + M' \tag{A}$$

$$(i\text{-}C_4H_9)_2N_2^* \longrightarrow 2i\text{-}C_4H_9 + N_2 \tag{B}$$

$$2i\text{-}C_4H_9 \longrightarrow i\text{-}C_4H_8 + i\text{-}C_4H_{10} \tag{1}$$

$$2i\text{-}C_4H_9 \longrightarrow (CH_3)_2CHCH_2CH_2CH(CH_3)_2 \tag{2}$$

$$i\text{-}C_4H_9 + (i\text{-}C_4H_9)_2N_2 \longrightarrow i\text{-}C_4H_{10} + C_4H_8N_2C_4H_9 \tag{3}$$

$$C_4H_8N_2C_4H_9 \longrightarrow i\text{-}C_4H_8 + i\text{-}C_4H_9 + N_2 \tag{4}$$

$$i\text{-}C_4H_9 \longrightarrow CH_3 + C_3H_6 \tag{5}$$

---

(3) (a) M. H. Jones and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 1018 (1953); (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) S. Toby, *J. Am. Chem. Soc.*, **82**, 3822 (1960).

(4) (a) P. Ausloos and E. W. R. Steacie, *Bull. Soc. Chim. Belges*, **63**, 87 (1954); (b) H. Cerfontain and K. O. Kutschke, *Can. J. Chem.*, **36**, 344 (1958); (c) D. P. Dingledy and J. G. Calvert, *J. Am. Chem. Soc.*, **85**, 856 (1963).

(5) J. A. Kerr and J. G. Calvert, *ibid.*, **83**, 3391 (1961).

(6) (a) R. W. Durham and E. W. R. Steacie, *Can. J. Chem.*, **31**, 377 (1953); (b) R. H. Riem and K. O. Kutschke, *ibid.*, **38**, 2332 (1960).

(7) S. S. Thomas and J. G. Calvert, *J. Am. Chem. Soc.*, **84**, 4207 (1962).

(8) W. E. Morganroth and J. G. Calvert, *ibid.*, **88**, 5387 (1966).

(9) R. M. Smith and J. G. Calvert, *ibid.*, **78**, 2345 (1956).

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

Table I. Rates of Product Formation and Quantum Yields of Nitrogen from the Photolysis of 1,1′-Azoisobutane at 3660 A

Temp, °K	P_{azo}, mm	Rates of product formation[a] moles/cc sec × 10^{12} i-C_4H_{10}	i-C_4H_8	C_8H_{18}[b]	C_3H_6	ϕ_{N_2}	i-C_4H_8/C_8H_{18}[c]
296	7.46	0.0033	..	0.013	...	...	...
368	3.28			...	...	0.12	...
368	7.07	...	...	...	....	0.045	...
368	15.72	0.63	0.090	1.62	...	...	0.056
370	10.09	0.346	0.065	1.19	...	...	0.055
373	4.53	0.0445	0.0043	0.082	...	...	0.052
379	7.46	0.0241	...	0.0107	...	...	...
383	7.82	0.42	0.059	0.79	...	0.091	0.075
383	16.42	0.957	0.091	1.37	...	...	0.066
384	4.25	0.37	...	1.38	...	0.13	...
384	5.87	0.53	0.085	1.38	...	0.10	0.062
384	6.72	0.042	0.0076	0.014	...	...	0.055
385	6.34	0.43	0.063	1.03	...	...	0.061
420	5.48	0.52	...	1.88	...	...	...
420	12.32	2.47	0.019	2.17	...	0.090	0.088
420	15.38	1.33	0.116	2.20	...	0.069	0.052
441	5.70	0.62	0.065	1.12	...	...	0.058
441	6.61	1.08	0.096	0.72	...	...	0.13
441	8.60	1.42	0.124	1.64	...	0.20	0.076
441	13.12	1.98	...	0.504	...	0.10	...
470	5.92	1.41	...	0.553	...	...	...
470	12.43	3.76	0.408	4.05	...	0.18	0.10
470	13.12	3.49	0.381	3.43	...	0.18	0.11
543[d]	5.22	...	..	5.62	0.849	...	...
561[d]	5.22	.	...	6.24	1.59	...	...
569[d]	5.22	.	...	6.03	2.33	...	...
580[d]	4.43	3.34	0.773	2.77	2.48	0.58	0.28
580[d]	6.93	4.34	0.709	1.71	1.64	0.54	0.41
591[d]	5.22	...	...	3.65	5.71	...	...
598[d]	5.51	3.33	0.851	1.39	3.80	...	0.61

[a] Dotted line for a given product indicates either that the product was not determined or that it was below the limit necessary for accurate analysis. [b] Product is 2,5-dimethylhexane. [c] In other runs, in which only isobutylene and octane were determined and which ranged in temperature from 77 to 150°, additional values of this ratio were estimated as follows: 0.095, 0.091, 0.071, 0.11, 0.069, 0.069, 0.097, 0.057, 0.067, 0.075, 0.074, 0.087, 0.075, 0.072; average of all runs at temperatures below 168° is 0.075. [d] Methane and 2-methylbutane were also products of these runs, but quantitative analysis was not made for these compounds.

$(i\text{-}C_4H_9)_2N_2^*$ represents an excited 1,1′-azoisobutane molecule as yet of undefined nature.

The Nature of the Excited Azoisobutane Molecule. The fact that the quantum yield of nitrogen is well below unity at the lower temperatures, and that this yield is raised with temperature increase and lowered with increase in pressure (see data of Table I), suggests strongly the participation of a relatively long-lived excited molecule in the 3660-A photolysis of 1,1′-azoisobutane. This is in accord with the mechanism which has been suggested for the photolysis of azoethane,[4b] azoisopropane,[6b] and 1,1′-azo-n-butane.[8] The quantum yield data can be used to test quantitatively the excited molecule mechanism I, A, B. For conditions such that reaction 4 is an unimportant source of nitrogen, the mechanism predicts that relation 6 should hold. The quantum yield data from

$$\frac{1}{\Phi_{N_2}} = \frac{1}{\phi_I} + \frac{k_A[M]}{k_B\phi_I} \qquad (6)$$

experiments at several temperatures, although not extensive, are seen to follow the form of (6) as plotted in Figure 1. The curves have been drawn making the reasonable assumption that ϕ_I equal unity. From the slopes of the lines at each temperature, estimates of k_A/k_B were determined, and the Arrhenius plot of this function is given in Figure 2. The data provide an estimate of k_A/k_B.

$$k_A/k_B \cong 10^{4.85}e^{4.8/RT}\ \text{cc/mole}$$

The value of k_A can be no larger than the collision number (3.2×10^{14} cc/mole sec); taking this value for k_A we estimate a maximum value for k_B of $\leq 4.5 \times 10^9 e^{-4.8/RT}$ sec^{-1}. This estimate agrees reasonably well with the corresponding rate constant for the decomposition of the excited 1,1′-azo-n-butane[8] where $k_B \leq 2.5 \times 10^9 e^{-3.8/RT}$ sec^{-1}.

It is instructive to compare k_B with the theoretical rate constant for radiative decay of the excited singlet state of 1,1-azoisobutane. An integration of the ϵ *vs.* $1/\lambda$ data for the compound suggests $k_C \cong 1.3 \times 10^5$ sec^{-1}.

$$(i\text{-}C_4H_9)_2N_2\ (S_1) \longrightarrow h\nu' + (i\text{-}C_4H_9)_2N_2\ (S_0) \qquad (C)$$

At 20° our experimental data suggest that the excited azoisobutane molecule decomposes with a rate constant $k_B \leq 1.4 \times 10^6$ sec^{-1}. The data predict that, if the excited singlet state is the reactant in reactions A and B, then fluorescence should be observable in the 1,1′-azoisobutane photolysis. In this work an extensive search for emission from azoisobutane was made by one of us (S. S. C.) using hexane solutions of the compound in experiments at room temperature and very viscous solutions in isopentane-3-methylpentane at −180°. No emission was detected. The sensitivity of the measuring instrument was such that the emission yield of azoisobutane must be less than 1×10^{-4}. These observations are in accord with the results reported for other azoalkanes. Rebbert and Ausloos[11] concluded that azoalkanes do not fluoresce or phosphoresce when irradiated at any wavelengths at which they absorb. Only the fluorescence of the bicyclic azo compounds has been observed by Steel and Thomas.[12] It is interesting to note that in this case where fluorescence is observable that the measured lifetime of the excited singlet state, 0.33×10^{-6} sec for 2,3-diazabicyclo[2.2.2]oct-2-ene, is very close to that calculated (0.6×10^{-6} sec) from the integrated molar absorption coefficient *vs.* $1/\lambda$ plot and the measured ϕ_f (0.20). This agreement lends additional credence to the estimate of k_C made above for 1,1′-azoisobutane; this fact and the k_B estimate made in this work suggest that the excited singlet state is not responsible for reactions A and B.

Further work on the nature of the excited state responsible for reactions A and B is now in progress and will be reported soon in a subsequent paper.

The Ratio of Rates of the Disproportionation to the Combination Reactions of the Isobutyl Free Radical. An inspection of the data presented in the last column of Table I and footnote c of that table shows a reasonably constant value for the isobutyl to octane ratios for experiments at, or below, 168°. The data at higher temperatures show an increasing magnitude of the ratio. Furthermore in the 3660-A photolyses of azoisobutane with added oxygen gas, the octane yield was insignificant. Thus intramolecular formation of the octane in a possible primary act must be an unimpor-

---

(11) R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, **87**, 1847 (1965).

(12) C. Steel and T. F. Thomas, *Chem. Commun.*, 900 (1966).

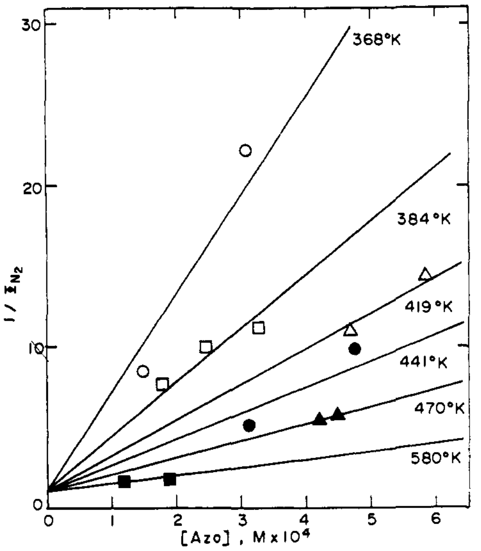

Figure 1. Plot of function 6 *vs.* the azoisobutane concentration for quantum yield data from the 3660-A photolysis of 1,1′-azoisobutane vapor at various temperatures.

tant source of octane in this system. The isobutylene and octane rate data seem best interpreted in terms of reactions 1–4. The relatively constant ratio of isobutylene to octane at the lower temperatures suggests that the dominant sources of these compounds for these conditions are reactions 1 and 2, respectively. At higher temperatures an additional source of isobutylene can be derived from reactions 3 and 4. With this assumed mechanism all the data for runs below 168° give an estimate for k_1/k_2 of $\cong 0.075 \pm 0.007$. The error limits shown are the 95% confidence limits calculated assuming only random errors in the determinations. Recently Terry and Futrell[13] estimated independently that $k_1/k_2 \cong 0.078$ from the photolysis of 1,1′-azoisobutane at room temperature and relatively high light intensity. The good agreement between these two independent studies is gratifying and lends some additional confidence to the present estimate of k_1/k_2. The higher value estimated years ago by Kraus and Calvert[2] (0.4) probably resulted from additional sources of isobutylene besides reaction 1 in the diisobutyl ketone photolysis at 100° as discussed in the introductory section.

If one compares the present estimate of k_1/k_2 for the isobutyl radical (0.075) with that derived recently for the similar ratio for *n*-butyl free radical (0.14),[8] he observes the proportionality of these ratios to the number of H atoms per radical which by abstraction can lead to olefin product. This is the trend expected if the rates of the combination reactions for the *n*-butyl and isobutyl free radicals are near the same, since the probability of the formation of the transition state responsible for the disproportionation reaction would be roughly proportional to the number of H atoms per radical which by abstraction lead to olefin. Although the near equality of the combination rate constants may exist for the isobutyl and *n*-butyl radicals, it cannot hold for the entire butyl series as Kraus and Calvert's data originally suggested. If these conditions were true, we would predict incorrectly that the rate constant ratios analogous to k_1/k_2 for *t*-butyl and *sec*-butyl would be 0.65 and 0.36, respectively, much below the best presently available estimates of these quantities (2.2–4.6 and 0.94–2.3, respectively).[14]

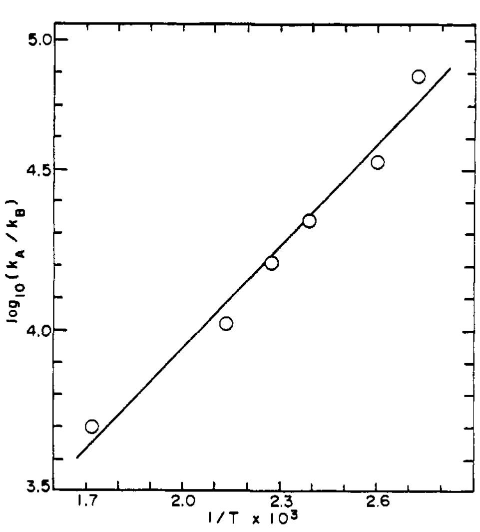

Figure 2. An Arrhenius plot of the slopes from the data of Figure 1 and from which the estimate of k_A/k_B was derived.

If the rate constant for the disproportionation reaction per H atom is the same for all the butyl radicals, then the rate constant for the combination reaction of the branched radicals, *sec*-butyl and *t*-butyl, must be a factor of 3 to 6 times smaller than that for the *n*-butyl and isobutyl radicals. There are no direct comparative data on the combination rate constants which allow a test of this hypothesis at present.

The H-Atom Abstraction Reaction of the Isobutyl Free Radical. The rate data for isobutane and octane can be used to derive an estimate of the H-atom abstraction reaction by isobutyl radicals (reaction 3). If one makes the reasonable assumption that isobutane and octane are formed only in reactions 1, 2, and 3, then the rate function 7 should hold. The terms in the

$$k_3/k_2^{1/2} = \frac{(R_{C_4H_{10}})_{total} - (R_{C_4H_{10}})_1}{R_{C_8H_{18}}^{1/2}[(i\text{-}C_4H_9)_2N_2]} \qquad (7)$$

numerator of (7) refer to the total isobutane rate and the rate of isobutane formed in reaction 1, respectively. The latter term can be estimated through the function $(R_{C_4H_{10}})_1 = R_{C_8H_{18}}(k_1/k_2) \cong 0.075R_{C_8H_{18}}$.

In Figure 3 is given an Arrhenius plot of function 7 derived in this fashion from the data of Table I. Although some of the points show considerable scatter, the great share of the data fit well the expected functional form of (7). The least-squares line derived from all the data provides an estimate of $k_3/k_2^{1/2}$.

$$k_3/k_2^{1/2} \cong 6.73 \times 10^3 e^{-6.7/RT} \text{ (cc/mole sec)}^{1/2}$$

Taking $k_2 = 2.2 \times 10^{13}$ cc/mole sec, the rate of association of the methyl radical,[15] k_3, can be estimated.

$$k_3 \cong 3.2 \times 10^{10} e^{-6.7/RT} \text{ cc/mole sec}$$

Compare this estimate for isobutyl with that for other

---

[13] J. O. Terry and J. H. Futrell, private communication to the authors: ref 1b, paper 43.

[14] (a) S. W. Benson and W. B. DeMore, *Ann. Rev. Phys. Chem.*, 16, 387 (1965); (b) J. G. Calvert, *ibid.*, 11, 41 (1960).

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

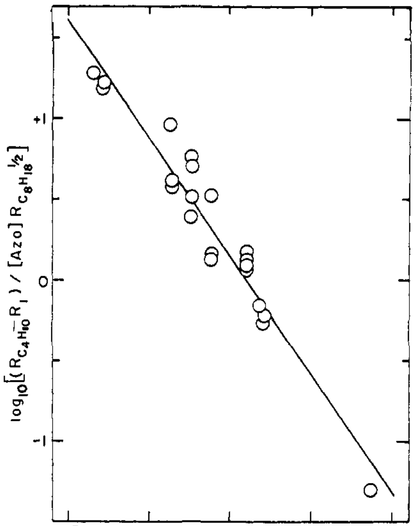

Figure 3. An Arrhenius plot of function 7 from which an estimate of $k_3/k_2^{1/2}$ was derived.

alkyl free-radical reactions of H-atom abstraction involving the azoalkanes in Table II. There is an obvious correlation of the rate constant data when the nature of the H atom abstracted is noted in each case. The alkyl radicals, ethyl, *n*-propyl, and *n*-butyl, abstract a secondary H atom, while the isopropyl and isobutyl radicals abstract a tertiary H atom in each of the reactions compared in Table II. The activation energy and preexponential factors for compounds in each of the individual series are very similar. It is evident that both isobutyl and isopropyl abstract a tertiary H atom with almost equal facility at any given temperature (equal *A* and *E* factors).

Table II. Rate Constant Factors for the Reactions $R + RN{=}NR \rightarrow RH + RN{=}NR(-H)$

R	E_a, kcal/mole	Log *A*, cc/mole sec	Ref
CH_3	7.6	11.0	3a
	6.9	10.5	3d
	7.3	10.7	3b
	8.4	11.5	3c
C_2H_5	7.5	10.9	4a
	8.0	11.3	4b
n-C_3H_7	7.9	11.3	5
n-C_4H_9	7.1	11.2	8
i-C_3H_7	6.5	10.4	6a
	6.7	10.5	6b
i-C_4H_9	6.7	10.5	This work

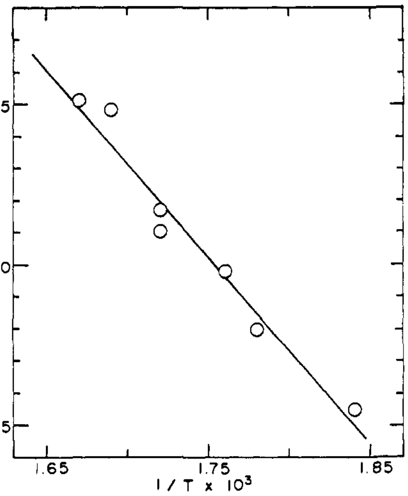

Figure 4. An Arrhenius plot of function 8 from which an estimate of $k_5/k_2^{1/2}$ was derived; the line drawn is the least-squares fit with equal weighting of all the data.

The Decomposition Reaction of the Isobutyl Free Radical. The onset of propylene and methane formation in the 1,1′-azoisobutane photolysis at temperatures of 270°, and above, must originate largely from the decomposition of the isobutyl free radical.[16] If one assumes that propylene and octane are formed in reactions 5 and 2, respectively, then the function 8 should apply. In Figure 4 an Arrhenius plot of the

$$R_{C_3H_6}/R_{C_8H_{18}}{}^{1/2} = k_5/k_2{}^{1/2} \qquad (8)$$

calculated function 8 is given as derived from the data of Table I. A least-squares treatment which includes all of the rate data with equal weight gives the line shown in Figure 4. This line suggests $k_5/k_2{}^{1/2} \cong 2.0 \times 10^4 e^{-27/RT}$ (mole/cc sec)$^{1/2}$. A more realistic method of treatment of the data to derive $k_5/k_2{}^{1/2}$ effectively excludes the least accurate point at the lowest temperature by weighting each point proportional to the measured propylene chromatographic peak height upon which the limiting accuracy of the rate data rests. This method of treatment gives

$$(k_5/k_2)^{1/2} \cong 5.0 \times 10^5 e^{-31\pm 2/RT}\ (\text{mole/cc sec})^{1/2}$$

The error limits shown represent the 95% confidence limits. Taking $k_2 = 2.2 \times 10^{13}$ cc/mole sec, an estimate of k_5 is had.

$$k_5 \cong 2.4 \times 10^{12} e^{-31\pm 2/RT}\ \text{sec}^{-1}$$

To our knowledge this is the first estimate which has been made of this important rate constant. The estimated activation energy for (5) is in reasonably good agreement with bond-strength data. The known heats of formation of propylene, methane, and isobutane can be coupled with the estimate from this work, $\Delta H_5 \cong 31 \pm 2 - E_9$, to show that $D_{CH_3-H} - D_{i\text{-}C_4H_9-H} \cong 12 \pm 2 - E_9$, where E_9 is the activation energy for the reaction

$$CH_3 + C_3H_6 \longrightarrow i\text{-}C_4H_9 \qquad (9)$$

Estimates of E_9 are not available, but a value near 8 kcal/mole would be a reasonable guess. This value coupled with the above relation suggests $D_{CH_3-H} - D_{i\text{-}C_4H_9-H} \cong 4 \pm 2$ kcal/mole, a difference which is reasonably consistent with that anticipated from thermal data.

---

(16) Another possible radical in this system which would be expected to give C_3H_8 is $\cdot CH_2CH(CH_3)CH_2N_2C_4H_9$. Since its formation involves the abstraction of a primary H atom from the parent azoisobutane, its rate of formation would be many times slower than the competitive reaction of tertiary H-atom abstraction in this compound, and it is therefore probably an unimportant source of propylene. The possible radical $(CH_3)_2CHH\dot{C}N_2C_4H_9$ might be expected to react to form $(CH_3)_2CHCH{=}N{-}N{=}CH_2$ and $(CH_3)_2CH$ radicals, but the dominant reaction of this radical for these conditions would be H-atom abstraction leading to propane formation; little or no propylene would be expected from this source.

An interesting conclusion concerning the kinetic reasons for the observed predominance of reaction 10 over 9 can be formulated from the present data for reaction 5 and the analogous published data for reaction 11. Since the pairs of forward and reverse re-

$$CH_3 + C_3H_6 \longrightarrow sec\text{-}C_4H_9 \qquad (10)$$

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

actions 10 and 11 and 5 and 9 should have the same transition states, then we would expect relation 12 to hold. Taking A_5 from the present data, A_{11} from an

$$\Delta S_5° - \Delta S_{11}° = R \ln (A_5A_{10}/A_9A_{11}) \qquad (12)$$

average of the two published estimates of this quantity (2.1×10^{15} from Calvert and Gruver[17] and 0.62×10^{15} sec^{-1} from Lin and Laidler[18]), and reasonable entropy data for the isobutyl and *sec*-butyl free radicals,[19] then from relation 12 the ratio of A_9 to A_{10} can be estimated.

$$A_9/A_{10} \cong 4.0 \times 10^{-4}$$

These results suggest that the large preference shown for the *sec*-butyl over isobutyl radical formation as methyl adds to propylene in reactions 10 and 9, respectively, is largely a consequence of the larger preexponential factor for reaction 10. The activation energy difference, $E_9 - E_{10}$, is probably small since the assumption of $E_9 \cong 8$ kcal/mole, a value near equal to that found for E_{10} by Miyoshi and Brinton (8.8 kcal/mole),[20] has been shown earlier to provide a consistency between the present kinetic data and reasonable thermal data. We are currently attempting to measure the ratio k_9/k_{10} directly to test these conclusions.

Acknowledgment. The authors are grateful for the support of this work through a research grant from the National Center for Air Pollution Control, Bureau of Disease Prevention and Environmental Control, U. S. Public Health Service, Bethesda, Md., and to Dr. Sidney W. Benson for helpful discussions of this work.

---

[17] (a) J. G. Calvert, *Chem. Rev.*, **59**, 569 (1959); (b) J. T. Gruver and J. G. Calvert, *J. Am. Chem. Soc.*, **78**, 5208 (1956); **80**, 3524 (1958).

[18] M. C. Lin and K. J. Laidler, *Can. J. Chem.*, **45**, 1315 (1967).

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

[20] M. Miyoshi and R. K. Brinton, *J. Chem. Phys.*, **36**, 3019 (1962).

Absolute Rate Constants for the Bimolecular Reaction of Radical Pairs in Solution. Benzyl and Pentyl Radicals

R. D. Burkhart

Contribution from the Department of Chemistry, University of Nevada, Reno, Nevada. *Received August 2, 1967*

Abstract: Absolute rate constants for the combination–disproportionation of pentyl radicals and for the combination of benzyl radicals have been measured in benzene at 25° in order to test the utility of the free-radical reaction between triethyl phosphite and mercaptans as a monitor for steady-state alkyl radical concentrations and to provide preliminary data with which theories of diffusion-controlled reactions might be tested for chain-like radicals in solution. The rotating sector method has been used yielding $k_{2C_5H_{11}} = 1.0 \times 10^9\ M^{-1}\ sec^{-1}$ and $k_{2C_6H_5CH_2} = 4.1 \times 10^9\ M^{-1}\ sec^{-1}$. Both experimental values are smaller than those calculated using the assumption that there is negligible difference between diffusion coefficients of the radicals and the parent hydrocarbons.

Although a number of studies have been carried out to measure absolute combination (and disproportionation) rate constants of polymeric radicals in solution, very little has been done to evaluate such rate constants for small hydrocarbon radicals; in fact, the benzyl radical, studied in relatively viscous solvents by pulsed radiolysis[1] and flash photolysis,[2] and the ethyl radical, studied by intermittent electron irradiation[3] at −177 to −140°, appear to be the only previous examples. The motivation for undertaking the present work derives from questions concerning the applicability of the theory of diffusion-controlled reactions to recombination[4] processes involving pairs of chain-like radicals in solution such as linear alkyl radicals. While it is well known that polymeric radicals recombine at smaller rates than their lower molecular weight homologs, the details of the recombination process are not well understood in spite of several theoretical and experimental investigations.[5] Data on recombination rate constants of linear alkyl radicals which are monodisperse in terms of molecular weight would be useful at least to the extent that effects of radical size could be evaluated. Indeed, the effects of most controllable factors on these reactions are virtually unexplored.

Although the studies of hydrocarbon radicals mentioned above have yielded useful information, the techniques used there are not well suited to the sort of investigation proposed here. On the one hand, high-energy electron irradiation lacks selectivity and, on the other, the spectrophotometric monitoring of alkyl radical concentrations is not feasible because of interfering absorption by most solvents. The object of

---

[1] R. L. McCarthy and A. MacLachlan, *Trans. Faraday Soc.*, **56**, 1187 (1960).

[2] G. Porter and M. W. Windsor, *Nature*, **180**, 187 (1957).

[3] R. E. Fessenden, *J. Phys. Chem.*, **68**, 1508 (1964).

[4] Although the bimolecular reaction of two pentyl radicals undoubtedly yields disproportionation as well as combination products, the term recombination will be used here to describe the radical–radical reaction irrespective of products formed.

[5] For a recent review, see A. M. North, *Quart. Rev.* (London), **20**, 421 (1966).