THE PHOTOLYSIS OF AZOETHANE¹

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ABSTRACT

The photolysis of azoethane at λ 3660 Å has been reinvestigated. The quantum yield of nitrogen formation was found to be dependent on the azoethane pressure and the temperature, indicating collisional deactivation of excited azoethane molecules.

The results confirm the mechanism proposed by Ausloos and Steacie (1). For the activation energy of the addition reaction $C_2H_5+C_2H_5N_2C_2H_5$ a value of 6.0 ± 0.3 kcal./mole has been obtained, assuming a negligible activation energy for the combination reaction of two ethyl radicals.

INTRODUCTION

The formation of nitrogen in the photooxidation of azoethane (2) was found to be greater than expected and dependent on the pressures of azoethane and oxygen, as well as on the temperature.

Weininger and Rice (3) have studied the primary process in the photolysis of azoethane and showed that the quantum yield of nitrogen formation was dependent on the azoethane pressure in a manner which is explicable in terms of an activated molecule intermediate. In their study they made the implicit assumption that the quantum yield was independent of temperature. On the other hand, Durham and Steacie (4) found the quantum yield of nitrogen formation in the photolysis of azoisopropane to be temperature dependent. This suggested that a reinvestigation of the primary process in the photolysis of azoethane would be required in order to be certain of temperature effects for the photooxidation studies.

EXPERIMENTAL

Azoethane was obtained from Merck and Company. It was distilled several times and stored behind a mercury cutoff in a blackened tube. The reaction cell, with a volume of 180 ml., was completely filled with a parallel beam of light. The total reaction cell system, including a cold finger, a magnetically driven stirrer, and connecting tubing, had a volume of 282 ml. The analytical section consisted of a solid nitrogen trap, two Ward stills, a McLeod gauge, a diffusion pump, and a combined Toepler pump and gas burette. The photolysis products were separated as follows: Nitrogen was removed at solid nitrogen temperature; C₂ hydrocarbons were separated at -165° C. and analyzed mass spectrometrically. Butane was removed at -125° C.

A Hanovia S 500 medium pressure mercury arc was used as a light source, together with a Corning filter 5860 which limited the effective radiation to the 3660 Å group of lines. Absorption measurements were made with a photocell coupled to a sensitive galvanometer. At low azoethane concentrations (<0.001 mole/l.) the absorption measurements suffered from lack of precision. In this case the light absorption was calculated from the extinction coefficient, which was estimated from the experiments at higher concentration. For the highest concentration used, about 75% of the light was absorbed. Quantum yield measurements were carried out using a potassium ferrioxalate actinometer (5, 6) according to the procedure modified by Baxendale (5). The experiments were done at room temperature in subdued light. The radiation was completely absorbed by the actinometer. For these conditions, Hatchard and Parker (6) report a quantum yield of 1.21 for the actinometer at λ 3660 Å.

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RESULTS AND DISCUSSION

Primary Processes

The light intensity was measured by placing the actinometer cell before and after the reaction cell. In the first position the intensity was found to be 1.64×10^{16} and 1.70×10^{16} quanta/second; in the second position 1.16×10^{16} and 1.00×10^{16} quanta/ second. This observed difference appreciably exceeds that accounted for by simple reflections only. Assuming identical absorption and scattering by the front and rear windows of the reaction cell to be the only cause of light loss, a transparency factor $\alpha = 0.85^{\dagger}$ per window was calculated from these data. Corrections for this and for first-order reflections from quartz-gas and pyrex-gas interfaces were made for all measurements, applying the general argument of Farkas and Melville (8) to our optical system. The data for the dependence of the nitrogen formation on temperature and azoethane concentration are given in Table I. The molar extinction coefficient *E* was calculated

TABLE I									
Effect	OF	TEMPERATURE	AND	PRESSURE	ON	OUANTUM	YIELD		

Temp., °C.	Azoethane conc., mole 1. ⁻¹ ×10 ³	$I_a,$ quanta second ⁻¹ $\times 10^{-16}$	$R_{N_2},$ molec. second ⁻¹ $\times 10^{-16}$	$1/\phi$	<i>E</i> , 1. mole ⁻¹ cm. ⁻¹
28	$\begin{array}{c} 7.16\\ 5.08\\ 3.57\\ 2.20\\ 1.45\\ 0.68 \end{array}$	$ \begin{array}{c} 1.10\\ 0.93\\ 0.75\\ 0.53\\ 0.380\\ 0.202 \end{array} $	$\begin{array}{c} 0.\ 648\\ 0.\ 608\\ 0.\ 533\\ 0.\ 403\\ 0.\ 305\\ 0.\ 172 \end{array}$	$ \begin{array}{r} 1.70\\ 1.53\\ 1.41\\ 1.32\\ 1.24\\ 1.17 \end{array} $	$ \begin{array}{r} 19.1 \\ 19.3 \\ 19.0 \\ 19.5 \\ 19.5 \\ 19.5 \\ 19.5 \\ \end{array} $
78	$\begin{array}{c} 6.75 \\ 4.53 \\ 2.90 \\ 1.74 \\ 0.83 \end{array}$	$\begin{array}{c} 1.10 \\ 0.91 \\ 0.68 \\ 0.449 \\ 0.248 \end{array}$	$\begin{array}{c} 0.710 \\ 0.630 \\ 0.527 \\ 0.378 \\ 0.216 \end{array}$	$\begin{array}{c} 1.55\\ 1.43\\ 1.28\\ 1.19\\ 1.15\end{array}$	$ \begin{array}{r} 19.5 \\ 20.2 \\ 20.2 \\ 19.3 \end{array} $
116	$\begin{array}{c} 6.48 \\ 4.16 \\ 2.76 \\ 1.80 \\ 0.64 \end{array}$	$\begin{array}{c} 1.01\\ 0.79\\ 0.59\\ 0.431\\ 0.185\end{array}$	$\begin{array}{c} 0.735 \\ 0.619 \\ 0.495 \\ 0.374 \\ 0.167 \end{array}$	$1.38 \\ 1.27 \\ 1.18 \\ 1.15 \\ 1.11$	$20.2 \\ 20.6 \\ 19.6 \\ 20.8$
152	$\begin{array}{c} 6.16\\ 3.86\\ 1.91\\ 1.48\\ 0.68 \end{array}$	$\begin{array}{c} 1.07 \\ 0.82 \\ 0.490 \\ 0.402 \\ 0.206 \end{array}$	$\begin{array}{c} 0.915 \\ 0.736 \\ 0.436 \\ 0.390 \\ 0.207 \end{array}$	$1.17 \\ 1.11 \\ 1.12 \\ 1.03 \\ 1.00$	20.4 20.4 20.5 20.8

from $\ln I/I_0 = -Ecd$. Fig. 1 shows the relation between the quantum yield of nitrogen formation, temperature, and pressure. The accuracy of the actinometer measurements is $\pm 10\%$. This means that the uncertainty in the $1/\phi$ scale is $\pm 10\%$. It should be recognized, however, that the uncertainty in the $1/\phi$ values relative to each other is much less than this.

The mechanism proposed by Weininger and Rice (3) represents the results satisfactorily:

$$A + h\nu \to A^*, \tag{1}$$

$$A^* \rightarrow N_2 + 2C_2 H_5, \qquad [2]$$

$$A + A^* \rightarrow 2A,$$
 [3]

 $\dagger This \ \alpha \ corresponds \ to \ 1-A \ of \ Hunt \ and \ Hill \ (7).$

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FIG. 1. Effect of pressure on reciprocal quantum yield of nitrogen formation from azoethane.

where A* represents an excited azoethane molecule. From a steady state treatment of the excited azoethane molecules, the following relation may be deduced:

$$1/\phi = 1 + (k_3/k_2) |A|, \qquad [4]$$

where ϕ represents the quantum yield of nitrogen formation and |A| the azoethane concentration.

It follows from relation [4] that a plot of $1/\phi$ against |A| should be linear at each temperature with an intercept of unity, in close agreement with the experiments. By determining the slopes of these lines, values for k_3/k_2 at each temperature were derived.

The rate constant for deactivation k_3 was calculated from collision theory assuming zero activation energy and a steric factor of unity. A value of 7.0 Å was assumed for the kinetic collision diameters of normal and excited azoethane molecules. As shown in Table II, k_2 is temperature dependent. An Arrhenius plot (Fig. 2) shows the activation energy E_2 to be 2.1 ± 0.4 kcal./mole.

	ΤA	BLE	[]			
VALUES	OF	RATE	CONSTANTS			

Temp., ° C.	$\stackrel{k_3,}{\underset{\times}{}^{\text{molec.}^{-1}\text{cm.}^3\text{second}^{-1}}}_{\times 10^{10}}$	$k_3/k_2, molec.^{-1} cm.^3 \times 10^{19}$	$k_2,$ second ⁻¹ $ imes 10^{-9}$
$28 \\ 78 \\ 116 \\ 152$	2.96 3.20 3.37 3.52	$1.35 \\ 1.13 \\ 0.88 \\ 0.515$	$2.19 \\ 2.84 \\ 3.84 \\ 6.8$

The following observations indicate that the mechanism mentioned above is oversimplified:

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temperatures nitrogen is formed not only by the primary

(a) At higher temperatures nitrogen is formed not only by the primary process, but also by thermal decomposition of the $C_2H_4N_2C_2H_5$ radical (1),

$$C_2H_4N_2C_2H_5 \rightarrow C_2H_4 + N_2 + C_2H_5.$$
 [15]

An estimate of the amount of nitrogen produced by reaction [15] was made as follows: The amount of ethylene formed by disproportionation was calculated from the amount of butane, using a value of 0.12 for the ratio of disproportionation to combination of ethyl radicals (see below, *Secondary Processes*). The deviation of this amount from the total amount of ethylene formed was assumed to be due to reaction [15] only and is consequently equal to the amount of nitrogen formed by this reaction. The percentage of nitrogen formed under our experimental conditions by reaction [15] is 0.8% of the total amount at 107° C. and 2% at 152° C. This effect is very small, even at the highest temperatures employed; hence it can be neglected for the calculation of k_2 .

(b) The intercepts of the reciprocal quantum yields of nitrogen show a small increase with a decrease in temperature.

(c) The curvature of the Arrhenius plot for k_2 probably exceeds experimental error.

(d) A fluorescence spectrogram did not indicate any fluorescence.

All these facts might well be explained by a diffusion controlled deactivation reaction of excited molecules at the wall of the reaction cell,

$$A^* + wall \rightarrow A.$$
 [5]

As the rate of disappearance of A^{*} varies exponentially with temperature and the rate of diffusion varies with the square root of the temperature, an increasing deviation from unity for the reciprocal quantum yield at zero pressure may be expected with decreasing temperature. The rate of disappearance of excited molecules for wall deactivation is given by $k|A^*|/|A|$. From a steady state treatment for excited azoethane molecules one can derive

$$1/\phi = 1 + (k_3/k_2)|\mathbf{A}| + (k/k_2)|\mathbf{A}|.$$
 [6]

Applying this equation, a corrected value for E_2 was calculated and found to be 2.4 ± 0.4 kcal./mole.

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An alternative explanation might involve the $C_2H_5N_2$ radical, which might recombine with ethyl or decompose:

$$C_2H_5N_2C_2H_5 + h\nu \to C_2H_5N_2 + C_2H_5,$$
[7]

$$C_2H_5N_2 \to C_2H_5 + N_2,$$
 [8]

$$C_2H_5N_2 + C_2H_5 \rightarrow C_2H_5N_2C_2H_5.$$
 [9]

The stability of the $C_2H_5N_2$ radical is expected to be greatest at low temperatures, and this results in a maximum decrease in quantum yield for the nitrogen formation at these temperatures. The quantum yield of nitrogen formation should be intensity dependent in the temperature range in which the lifetime of the $C_2H_5N_2$ radical is comparable to the time between collisions of C_2H_5 and $C_2H_5N_2$ radicals. The observed quantum yield, however, (Table III) is independent of the light intensity. It may therefore be concluded that the lifetime of $C_2H_5N_2$ is short compared to the time between collisions. Reaction [9] can therefore be excluded.

			TABI	LΕ	III				
Effect	OF	LIGHT	INTENSITY	ON	QUANTUM	YIELD	AT	28°	C.

Azoethane conc., mole $1.^{-1} \times 10^3$	$I_a,$ quanta second ⁻¹ $ imes 10^{-16}$	$R_{ m N_2},$ molec. second ⁻¹ $ imes 10^{-16}$	$1/\phi$
$0.75 \\ 0.75 \\ 0.75 \\ 0.75$	$\begin{array}{c} 0.242 \\ 0.0246 \\ 0.00286 \end{array}$	$\begin{array}{c} 0.215 \\ 0.0212 \\ 0.00248 \end{array}$	1.12 1.16 1.15

Internal conversion of the excited azoethane molecule to another electronic state which is incapable of dissociation (9) might be considered as a third explanation,

$$A^* \to A.$$
 [10]

From a steady state treatment of excited azoethane molecules it follows that

$$1/\phi = 1 + k_{10}/k_2 + (k_3/k_2)|\mathbf{A}|.$$
[11]

The value of k_2 increases with increasing temperature (Table II) and if k_{10} is less temperature dependent, the intercept of the plot of $1/\phi$ against |A| may be expected to decrease with increasing temperature, and to approach unity, as is, in fact, the case. Collisional deactivation has been observed in the photolysis of azoisopropane (4). For azomethane (10) the quantum yield of decomposition was found to be unity, independent of temperature and pressure. The difference in collisional deactivation for the three homologous azoalkanes is illustrated in Fig. 3. It is generally accepted (3) that, although the primary excitation in photochemical decompositions is mainly electronic, the mechanism of decomposition involves its transfer to vibrational energy and the accumulation of this energy in a particular bond. Hence the reasonable observation is made that collisional deactivation is negligible in the photolysis of azomethane, but is of considerable importance in the photolysis of the higher homologues because of their larger number of degrees of vibrational freedom.

Secondary Processes

The results of the photolysis are shown in Table IV. To avoid side reactions the

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Photolysis⁷ of Azoethane TABLE IV

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$\begin{array}{c} k_{21}/k_{12}!,\\ \text{molec.}^{-\frac{1}{2}} \text{ cm.}^{3/2}\\ \text{second}^{-\frac{1}{2}}\\ \times 10^{13}\end{array}$	$\begin{array}{c} 0.85 \\ 1.4 \end{array}$	57.7	3.4 1.0	4.5	28.2	9.6 8.4	12.0	20.9	25.8	31.3	27.8
$\begin{array}{c} R_{\mathrm{T},\mathrm{E},\mathrm{H},\prime} \\ \mathrm{molec.\ cm.^{-3}} \\ \mathrm{second}^{-1} \\ \times 10^{-13} \end{array}$	$\begin{array}{c} 0.0041 \\ 0.013 \end{array}$	$0.062 \\ 0.065$	$0.118 \\ 0.015$	0.090	0.105	0.158 0.082	0.111	0.146	0.242	0.356	0.366
$k_{14}/k_{12}^{3},$ molec. $-\frac{1}{3}$ cm. $^{3/2}$ second $-\frac{1}{3}$ $\times 10^{13}$	$1.06 \\ 0.98$	$1.07 \\ 0.92$	0.81 1.17	5.30	13.0 11.9	14.6 15.9	18.1	40.1	76.2	74.7	67.2
$\frac{c_{2}H_{0}+R}{R_{N_{2}}}$	$\begin{array}{c} 0.965 \\ 0.985 \end{array}$	$0.961 \\ 0.959$	$0.940 \\ 0.975$	0.925	0.910	0.902 0.912	0.882	0.861	0.843	0.804	0.813
R _{C2} H4 R _{C4} H10	$\begin{array}{c} 0.118 \\ 0.114 \end{array}$	$0.124 \\ 0.116$	$0.111 \\ 0.117$	0.120	$0.110 \\ 0.128$	0.133	0.116	0.139	0.250	0.250	0.251
1×10-13 R c4 H10	$\begin{array}{c} 0.0972 \\ 0.772 \end{array}$	$1.33 \\ 1.36$	$1.63 \\ 0.500$	0.915	1.19 1.14	1.07	0.595	0.547	0.467	0.500	0.561
$^{-3}$ second $^{-}$ $R_{\rm C_2 H_4}$	$\begin{array}{c} 0.0114 \\ 0.0884 \end{array}$	$0.166 \\ 0.156$	$0.181 \\ 0.0583$	0.110	$0.131 \\ 0.147$	0.143 0.0722	0.0689	0.0761	0.117	0.125	0.141
molec. cm. $R c_{2 H_6}$	$\begin{array}{c} 0.0166 \\ 0.0972 \end{array}$	$0.189 \\ 0.176$	$0.209 \\ 0.0750$	0.189	0.413 0.374	0.384 0.918	0.236	0.355	0.833	0.965	1.02
$\frac{\text{Products}}{R_{N_2}}$	$\begin{array}{c} 0.118 \\ 0.883 \end{array}$	$1.58 \\ 1.58$	$\begin{array}{c} 1.97 \\ 0.589 \end{array}$	1.20	$1.77 \\ 1.66$	1.61 0.927	0.944	1.05	1.54	1.82	1.96
Conc., azo, molec. cm. $^{-3}$ $\times 10^{-13}$	$\begin{array}{c} 0.492\\ 0.326\end{array}$	$0.605 \\ 0.641$	$0.845 \\ 0.627$	0.497	0.567	0.507 0.386	0.381	0.299	0.436	0.507	0.555
Relative intensity	9.7 98	93 90	90 35	96	x 68	68 88	88	95	89	89	- 61
Temp.,	$\frac{27}{30}$	$^{28}_{31}$	$27 \\ 29$	28	101	107 116	118	152	175	175	175

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FIG. 3. Effect of pressure on reciprocal quantum yield of nitrogen formation from the lower azoalkanes.

conversion was kept below 3%. Ausloos and Steacie (1) explained their results in the photolysis of azoethane by means of the following mechanism:

$$C_2H_5N_2C_2H_5 + h\nu \to C_2H_5N_2C_2H_5^*,$$
 [1]

$$C_{2}H_{5}N_{2}C_{2}H_{5}^{*} \rightarrow N_{2} + 2C_{2}H_{5}, \qquad [2]$$

$$2C_{2}H_{5} \rightarrow C_{4}H_{10}, \qquad [12]$$

$$C_{2}\Pi_{5} \rightarrow C_{2}\Pi_{4} + C_{2}\Pi_{6}, \qquad [13]$$

$$C_{2}\Pi_{5} + C_{2}\Pi_{5}N_{2}C_{2}\Pi_{5} \rightarrow C_{2}\Pi_{6} + C_{2}\Pi_{4}N_{2}C_{2}\Pi_{5}, \qquad [14]$$

$$C_{2}\Pi_{4}\Pi_{2}C_{2}\Pi_{5} \rightarrow C_{2}\Pi_{4} + N_{2} + C_{2}\Pi_{5}, \qquad [13]$$

$$C_{2}H_{5} + C_{2}H_{4}N_{2}C_{2}H_{5} \to C_{4}H_{8}N_{2}C_{2}H_{5},$$
[16]

$$2C_2H_4N_2C_2H_5 \to (C_2H_4N_2C_2H_5)_2.$$
[17]

Assuming ethylene, ethane, and butane to be formed only by reactions [12], [13], and [14], the following relations should be obeyed:

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$$\frac{R_{C_2H_4}}{R_{C_4H_{10}}} = \frac{k_{13}}{k_{12}},$$
[18]

$$\frac{R_{C_{2H_6}} - R_{C_{2H_4}}}{R_{C_{4H_{10}}}} = \frac{k_{14}|A|}{k_{12}^{1/2}R_{C_{4H_{10}}}^{1/2}},$$
[19]

$$\frac{R_{C_{2H_6}} + R_{C_{2H_4}}}{R_{C_{4H_{10}}}} = 2\frac{k_{13}}{k_{12}} + \frac{k_{14}[A]}{k_{12}^{1/2}R_{C_{4H_{10}}}}.$$
[20]

The ratio $R_{c_2H_4}/R_{c_4H_{10}}$ is found to be constant with a value of 0.12 ± 0.01 in the temperature range 27–118° C. This means that $E_{13}-E_{12}=0$ (cf. Shepp and Kutschke (11)). At higher temperatures an increase in the ethylene to butane ratio is observed owing to thermal decomposition of $C_2H_4N_2C_2H_5$. In Fig. 4, $(R_{C_2H_6}+R_{C_2H_4})/R_{C_4H_{10}}$ and $(R_{C_2H_6}+R_{C_2H_4})/R_{C_4H_{10}}$



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19 A.



FIG. 4. Plot of $(R_{C_{2}H_{6}}+R_{C_{2}H_{4}})/R_{C_{4}H_{10}}$ and $(R_{C_{2}H_{6}}-R_{C_{2}H_{6}})/R_{C_{4}H_{10}}$ vs. $|A|/R_{C_{4}H_{10}}^{1/2}$.



FIG. 5. Arrhenius plot of $k_{14}/k_{12}^{1/2}$.

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 $-R_{C_2H_4})/R_{C_4H_{10}}$ are plotted against $|A|/R_{C_4H_{10}}^{1/2}$ for runs at 28° C. According to relation [20] the intercept of this curve with the ordinate should be equal to $2k_{13}/k_{12}$. A value of $k_{13}/k_{12} = 0.12\pm0.01$ was obtained. Values of $k_{14}/k_{12}^{1/2}$ were calculated from relation [19]. By plotting log $k_{14}/k_{12}^{1/2}$ against 1/T (Fig. 5) a value of $E_{14}-\frac{1}{2}E_{12} = 8.0\pm0.2$ kcal./mole was obtained. This value is higher than that reported by Ausloos and Steacie, who estimated $E_{14}-\frac{1}{2}E_{12} = 7.5\pm0.1$ kcal./mole. This low value, as well as the curvature they observed in the Arrhenius plot below 70° C., may well be explained by a small impurity in their azoethane sample.

Some high ($\sim 20\%$) conversion experiments were done in order to accumulate significant quantities of heavier products for possible mass spectrometric identification; the fraction remaining after butane and higher products were removed was submitted for analysis. After subtraction of the contributions due to unreacted azoethane a large number of peaks remained between masses 28 and 150. In particular the presence of major peaks at masses 114 and 144, together with peaks corresponding to plausible fragments, suggested that ethyl butyl diimide and tetraethyl hydrazine are amongst the products. In addition, peaks at masses 56, 55, and 42, possibly corresponding to the ions $C_2H_4N_2^+$, $C_2H_3N_2^+$, and $C_2H_4N^+$ or $CH_2N_2^+$ respectively, suggested the presence of diazoethane. These ions might also arise as fragments in the spectrum of ethyl butyl diimide, however, and in the absence of pure standards the identification can be considered tentative only. Should diazoethane be a product, reaction [15a] could be suggested as a source. This is similar to the reaction thought to lead to methyl ketene in the photolysis of diethyl ketone (12),

$$C_2H_5N_2C_2H_4 \rightarrow C_2H_5 + CH_3CHN_2.$$
^[15a]

Since diazoethane is transparent at λ 3660 Å (13) no photolysis is expected even under conditions of high conversion.

The material balance $(R_{C_2H_6}+R_{C_4H_{10}})/R_{N_2}$ should be equal to unity if only reactions [2], [12], [13], [14], [15], and [16] are involved and should be greater than unity if reaction [15*a*] or [17] occurs as well. As can be seen from Table IV a value smaller than unity was observed, showing a decrease with increase in temperature. Since tetraethyl hydrazine is probably among the products, the following addition reactions between ethyl radicals and azoethane may be suggested:

$$_{2}H_{5} \rightarrow N = N \rightarrow C_{2}H_{5} + C_{2}H_{5} \rightarrow (C_{2}H_{5})_{2}N \rightarrow N \rightarrow C_{2}H_{5},$$
 [21]

$$(C_2H_5)_2N - N - C_2H_5 + C_2H_5 \rightarrow (C_2H_5)_2N - N(C_2H_5)_2.$$
 [22]

The rate of formation of tetraethyl hydrazine will be equal to $R_{T.E.H.} = R_{N_2} - R_{C_4H_{10}} - R_{C_9H_6}$ subject to the following assumptions:

(a) Reaction [21] is the rate determining step in the formation of tetraethyl hydrazine.

(b) Reaction [15], [15a], and [17] may be neglected, i.e., for every molecule of ethane formed by abstraction, a molecule of ethyl butyl diimide is formed. As pointed out before, the number of $C_2H_5N_2C_2H_4$ radicals disappearing by reaction [15] is small.

The following relation may be deduced on this basis:

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$$k_{21}/k_{12}^{1/2} = R_{T,E,H}/R_{C_4H_{10}}^{1/2}|A|.$$
[23]

By plotting log $k_{21}/k_{12}^{1/2}$ against 1/T (Fig. 6) a value of $E_{21} - \frac{1}{2}E_{12} = 6.0 \pm 0.3$ kcal./mole was obtained. A large scatter in $R_{T,E,H}$ and log $k_{21}/k_{12}^{1/2}$ may be expected at low temperatures since the material balance approaches unity under these conditions. The present value of $E_{21} - \frac{1}{2}E_{12}$ is in agreement with the activation energies for other reactions of the addition of radicals to double bonds (10, 14, 15).

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FIG. 6. Arrhenius plot of $k_{21}/k_{12}^{1/2}$.

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