ADDITION OF ETHYL RADICALS TO ETHYLENE[1]

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ABSTRACT

The addition of ethyl radicals to ethylene has been studied in the temperature range 58° to 123° C. The radicals were produced by the mercury photosensitized decomposition of hydrogen in the presence of ethylene, and the rate of the addition reaction was measured in terms of the rate of formation of *n*-hexane by the combination of ethyl and butyl radicals. Corrections were made for the non-uniformity of radical concentrations in the reaction zone. Assuming a negligible activation energy for the combination of two ethyl radicals, the activation energy for the addition reaction is 5.5 kcal. per mole; the steric factor, relative to the square root of the steric factor for ethyl radical combination, is 5.0×10^{-5}.

Although it is generally assumed that the activation energies for the addition of free radicals to olefins are small, relatively few quantitative data are available because of the complexity of the over-all processes and the lack of suitable "reference" reactions. Raal and Danby (7, 8) have studied the addition of methyl radicals to a number of olefins using the photolysis of acetaldehyde as the source of radicals and the abstraction of H atoms from acetaldehyde by methyl radicals as the reference reaction. Mandelcorn and Steacie (6) have used the photolysis of acetone as the source of methyl radicals and the combination of methyl radicals as the reference reaction.

In the present work we have studied the rate of addition of ethyl radicals to ethylene, to form butyl radicals, by measuring the rate of formation of hexane and assuming that this substance is formed exclusively by the combination of ethyl with butyl radicals. The ethyl radicals were produced by the mercury ($^3P_1$) photosensitized decomposition of hydrogen in the presence of ethylene.

It has been established (4) that at temperatures below 200° C. the main features of the reaction can be interpreted in terms of the following mechanism:

$$\mathrm{Hg}(^3P_1) + \mathrm{H_2} = \mathrm{Hg}(^1S_0) + 2\mathrm{H} \qquad [1]$$

$$\mathrm{H} + \mathrm{C_2H_4} = \mathrm{C_2H_5} \qquad [2]$$

$$2\mathrm{C_2H_5} = \mathrm{C_4H_{10}} \qquad [3]$$

$$2\mathrm{C_2H_5} = \mathrm{C_2H_4} + \mathrm{C_2H_6}. \qquad [4]$$

At low pressures anomalous variations in the ratio of ethane to butane occur which suggest that under such conditions these compounds are not formed simply by bimolecular reactions of ethyl radicals (1, 9). At the pressures used in the present work these effects are relatively unimportant and the ratio of the rate of formation of ethane to that of butane is in good agreement with the values of k_4/k_3 obtained by other methods (9). As the pressure of ethylene is raised, small but increasing amounts of a product with a molecular weight greater than butane are found. In the present work this product was shown, by gas chromatography, to be *n*-hexane. It was assumed to be formed by the following reactions:

$$\mathrm{C_2H_5} + \mathrm{C_2H_4} = \mathrm{C_4H_9} \qquad [5]$$

$$\mathrm{C_4H_9} + \mathrm{C_2H_5} = \mathrm{C_6H_{14}}. \qquad [6]$$

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[1] *Manuscript received March 19, 1957.*
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On the assumption that all butyl radicals formed in [5] disappear by [6] it is evident that the rate of formation of hexane would be given by the expression,

$$d(C_6H_{14})/dt = k_5(C_2H_5)(C_2H_4). \quad [i]$$

Assuming, further, that butane is formed only in reaction [3], it follows that,

$$[d(C_6H_{14})/dt]/[d(C_4H_{10})/dt]^{\frac{1}{2}} = (k_5/k_3^{\frac{1}{2}})(C_2H_4). \quad [ii]$$

The errors which would arise if these two assumptions are not valid will be considered in the Discussion.

Equation [ii] applies to *local* rates. In order to utilize the measured amounts of hexane and butane formed in an experiment to evaluate $k_5/k_3^{\frac{1}{2}}$ it is necessary to apply a correction term which takes into account spatial variations in the ethyl radical concentration throughout the reaction vessel. This correction has been discussed in detail by Cvetanović and Whittle (2); it is of some importance in the present instance because of the large extinction coefficient of mercury vapor.

EXPERIMENTAL

The general procedure was similar to that used previously (3). An improved form of circulating pump was used, having a capacity of approximately 2000 cm.^{3} min.$^{-1}$ Before they entered the reaction vessel the gases were saturated with mercury vapor at 10° C. The quartz reaction vessel was 4.6 cm. in diameter and 11 cm. long; the total volume of the system, including a buffer volume, was 1910 cm.^{3}

The ethylene was Phillips Research Grade. Commercial hydrogen was purified as described previously (3). The C_6 hydrocarbons used as reference standards in the chromatography were obtained from the United States Bureau of Standards. The *n*-butane and other gases were supplied by the Ohio Chemical and Manufacturing Company.

The products were analyzed by both low temperature distillation (5) and by gas–liquid partition chromatography using a 7-ft. column containing Octoil-S supported on Celite with helium as the carrier gas. Excellent agreement was obtained between the two methods; the latter served to establish that the C_4 fraction contained only *n*-butane, and that the higher boiling fraction contained only *n*-hexane. With the high ethylene pressures and low conversions used in the present work no other olefins and no odd-numbered paraffins were found.

In order to take account of the spatial variations in the ethyl radical concentration it was necessary to determine the extinction coefficient of mercury vapor for 2537 Å. This quantity is strongly dependent on wave length, even within the narrow range of wave lengths which constitute the resonance "line" emitted by a mercury-rare gas lamp of the type used in the present experiments. As a result, for a given value of the mercury concentration (Hg) the extinction coefficient q depends on the distance L through which the light has passed as well as on the particular lamp used and its operating conditions.

Values of q were obtained in a separate series of experiments using three cells, C_1, C_2, and C_3, having internal path lengths of 0.185, 0.994, and 10.0 cm., respectively. The cells were mounted in a temperature-controlled bath containing distilled water; a parallel beam of light from the lamp entered the bath through a fused quartz window and traversed the three cells. The cross section of the beam was somewhat smaller than that of the cell windows. Each cell was filled with approximately 300 mm. of Phillips Research Grade propane and isolated with a mercury cutoff. Mercury in a side arm on each cell was allowed to reach its saturation pressure over a period of 16 hours before illumination. The period of illumination was approximately 24 hours. The non-condensable gases were removed with a liquid air trap and the hydrogen formed in each cell was measured. The average decomposition in any one experiment was of the order of 0.1%.

The arrangement of the three cells is shown schematically in Fig. 1. It was necessary to take into account the fraction of light reflected, R, and the fraction transmitted, T, at the windows W_2 and W_3. Each of these windows consisted of two glass–gas interfaces and two glass–water interfaces. For clarity the incident beam I_0 is shown entering the first cell at an angle to the perpendicular; the various transmitted and reflected beams from which appreciable absorption takes place are indicated. The amount of light transmitted through the rear window of cell C_3 was negligible under the conditions used.

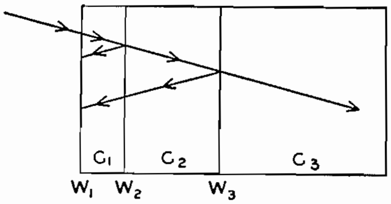

FIG. 1. Arrangement of cells used to determine the extinction coefficient of mercury vapor.

If G_1, G_2, and G_3 are the amounts of hydrogen produced in C_1, C_2, and C_3 and α_1 and α_2 are the fractions of light transmitted in a single passage through cells C_1 and C_2 it can be shown that

$$1/\alpha_2 - R_3\alpha_2 = 1 - R_3 + T_3G_2/G_3$$

and

$$1/\alpha_1 - \alpha_1(R_2 + T_2^2R_3\alpha_2^2) = 1 - R_2 - T_2^2R_3\alpha_2^2 + (1 - \alpha_2 + R_3\alpha_2 + T_3\alpha_2 - R_3\alpha_2^2)\ T_2G_1/(G_2 + G_3).$$

The values of R and T were calculated from Fresnel's law and the known properties of the window materials. Extinction coefficients were calculated from the expression

$$\alpha = e^{-q(\mathrm{Hg})L}.$$

The mercury concentration was varied from 1.6×10^{-3} to 9.3×10^{-3} mm. by changing the bath temperature. In Fig. 2 the values of q are plotted against L', the equivalent path length for a saturation temperature of 25° C. A smooth curve can be drawn through the values for α_1 ($L' < 1.0$ cm.) and α_2 ($L' > 1.0$ cm.), indicating that adequate corrections were made for reflection and absorption by the windows.

The kinetic experiments were made with a cell 11 cm. long and a mercury saturating temperature of 10° C.; this corresponds to a path length of less than 3 cm. at 25° C. The value of q used was 15×10^{-15} cm.^{2} molecule^{-1}.

RESULTS

The production of butane and hexane was studied at four temperatures in the range 58.4° to 123.1° C. using a constant hydrogen pressure of approximately 640 mm. (at 22° C.). At each temperature the ethylene pressure was varied by a factor of about 2.5. The effect of hydrogen pressure was also studied. The results are shown in Table I.

The concentrations of hexane and butane are expressed in mm. of mercury in the

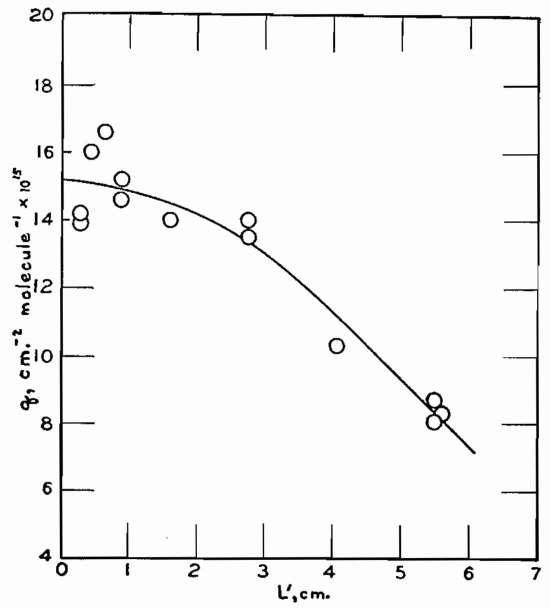

FIG. 2. Dependence of the extinction coefficient of mercury vapor on the equivalent path length for saturation at 25° C.

TABLE I

ADDITION OF ETHYL RADICALS TO ETHYLENE

T, temp., ° K.	t, time, min.	$(C_2H_4)_{av.}$, mm. at T° K.	(C_6H_{14}), mm. at 22° C.	(C_4H_{10}), mm. at 22° C.	$k_5/k_3^{\frac{1}{2}} \times 10^{12}$ (cm.^{3} molecule^{-1} sec.$^{-1}$)$^{\frac{1}{2}}$ Uncorr.	Corr.	δ
396.3	530	46.74	0.194	0.258	1.093	1.155	1.057
396.3	465	41.24	0.181	0.297	1.172	1.238	1.056
396.3	600	29.25	0.181	0.426	1.214	1.277	1.052
396.3	485	19.54	0.112	0.424	1.237	1.295	1.047
396.3*	480	19.76	0.111	0.420	1.234	1.291	1.046
396.3†	480	19.62	0.111	0.428	1.234	1.291	1.046
374.2	430	48.97	0.138	0.281	0.757	0.804	1.062
374.2	465	39.40	0.135	0.301	0.859	0.910	1.060
374.2	510	29.32	0.113	0.375	0.827	0.873	1.056
374.2	525	19.32	0.0850	0.447	0.855	0.900	1.053
354.9	460	50.38	0.113	0.387	0.471	0.500	1.062
354.9	580	39.61	0.128	0.501	0.532	0.564	1.060
354.9	431	30.20	0.0691	0.402	0.487	0.514	1.056
354.9	550	20.07	0.0728	0.498	0.618	0.652	1.055
331.6	430	48.88	0.0716	0.364	0.307	0.327	1.066
331.6	615	35.64	0.0846	0.647	0.312	0.331	1.061
331.6	555	28.56	0.0577	0.536	0.307	0.325	1.059
331.6	605	20.32	0.0442	0.567	0.308	0.326	1.058

*, † *In these two experiments the hydrogen pressure was 215 mm. and 397 mm., respectively; in all of the others it was approximately 640 mm. at 22° C.*

system (1910 cm.^{3}) at 22° C.; the concentration of ethylene is the average of the initial and final pressures in the system at the reaction temperature. Using the units given in Table I, the uncorrected values of $k_5/k_3^{\frac{1}{2}}$ given in column six were obtained from the expression

$$k_5/k_3^{\frac{1}{2}} = \frac{7.93\times10^{-12}T(\mathrm{C_6H_{14}})}{(\mathrm{C_2H_4})_{\mathrm{av.}}(\mathrm{C_4H_{10}})^{\frac{1}{2}}t^{\frac{1}{2}}}\,. \qquad \text{[iii]}$$

In column eight are given the values of the correction term δ by which the uncorrected values of $k_5/k_3^{\frac{1}{2}}$ are multiplied to obtain the corrected values in column seven.

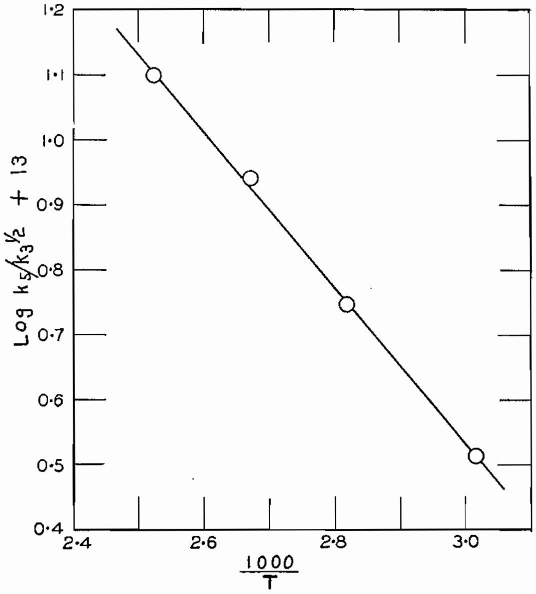

FIG. 3. Arrhenius plot for the addition of ethyl radicals to ethylene.

The quantity δ is a rather complicated function of two parameters, β and s (2). In the present instance these are given by the expressions:

$$\beta = q(\mathrm{Hg})L, \qquad \text{[iv]}$$

in which q is the extinction coefficient of mercury vapor to base e, (Hg) is the concentration of mercury vapor in the reaction vessel, and L is the length of the light path (*ca.* 11 cm.);

and
$$s = \frac{4(k_3+k_4)\,q(\mathrm{Hg})\,\phi I_0}{k_5^2(\mathrm{C_2H_4})^2}\,. \qquad \text{[v]}$$

On the assumption that $k_4/k_3 = 0.15$ (9), the quantity (k_3+k_4) in [v] can be equated to 1.15 k_3. The value of ϕI_0, the effective incident light intensity in quanta cm.$^{-2}$ sec.$^{-1}$, was calculated on the assumption that the effective number of quanta absorbed per second, $\phi I_0(1-e^{-\beta})A$, was equal to the number of molecules of hydrogen consumed per second, i.e., to the number of molecules of ethane, butane, and hexane formed per second. The average value of ϕI_0 calculated in this way was 8.2×10^{13} quanta cm.$^{-2}$ sec.$^{-1}$ ± 6.5%.

An Arrhenius plot of the corrected mean values of $k_5/k_3^{\frac{1}{2}}$ for each temperature is shown in Fig. 3. The least squares value of $E_5 - \frac{1}{2}E_3$ is 5.5 kcal. per mole; the steric factor ratio, $p_5/p_3^{\frac{1}{2}}$, is 5.0×10^{-5}, assuming a mean collision diameter of 4.0 Å.

DISCUSSION

It was considered worth while to evaluate the correction term δ for these experiments because of the uncertainty, arising from the large extinction coefficient, which has been associated with quantitative deductions from mercury photosensitization experiments. It was an obvious advantage, in this regard, to saturate the reagents with mercury vapor at 10° C. rather than at some higher temperature and to use a lamp with a somewhat broadened emission line.

Possible sources of error arise from the assumptions that all butyl radicals are consumed by reaction [6] and that butane is formed exclusively by reaction [3]. If the rate constants were of the same magnitude for the combination of two ethyls, an ethyl and a butyl, and for two butyls, one would expect appreciable amounts of *n*-octane to be formed at the higher ethylene concentrations, particularly at the higher temperatures. There is no evidence for this, in the form of lower values of $k_5/k_3^{\frac{1}{2}}$ under these conditions. It has already been pointed out that no compound of higher molecular weight than hexane was found by gas chromatography. Also, the uncorrected value of $E_5 - \frac{1}{2}E_3$ based on analytical data obtained by gas chromatography differed from the value based on low temperature distillation by less than 0.3 kcal. per mole.

If any of the butyl radicals formed in [5] had undergone disproportionation reactions with ethyl radicals the calculated values of $k_5/k_3^{\frac{1}{2}}$ would be in error.

$$C_4H_9 + C_2H_5 = C_4H_8 + C_2H_6 \qquad [7]$$

$$C_4H_9 + C_2H_5 = C_4H_{10} + C_2H_4 \qquad [8]$$

Assuming that any butene formed in [7] was measured as butane, it can be shown that the right hand side of equation [ii] would have to be multiplied by the term

$$[1 - (R_7 + R_8)/R_B]^{\frac{1}{2}} \,.\, R_6/(R_6 + R_7 + R_8),$$

in which R_B is the rate of formation of butane plus that of butene, and R_6, R_7, and R_8 are the rates of the corresponding reactions. It can be easily shown that if $R_7 + R_8$ were comparable in magnitude to R_6 the values of $k_5/k_3^{\frac{1}{2}}$ obtained by applying this correction would be strongly dependent on the ethylene pressures, in disagreement with the experimental results. It seems justifiable to conclude that reactions [7] and [8] can be of only minor importance.

There do not appear to be any quantitative data in the literature to compare with the present results on the addition of ethyl radicals with ethylene. However, Mandelcorn and Steacie (6) have discussed their own data and those of other workers on the addition of methyl radicals to ethylene and other unsaturated compounds. They obtained a relative rate constant, $k_{\text{addition}}/(k_{\text{combination}})^{\frac{1}{2}}$, of 11×10^{-12} at 144° C. for the addition of methyl radicals to ethylene. From our data $k_5/k_3^{\frac{1}{2}}$ would be equal to 1.8×10^{-12} at that temperature. Since there is little difference between the rate constant for the combination of two methyl radicals and that for the combination of two ethyls, it is evident that the rate constants for the addition of methyl and ethyl radicals to ethylene do not differ greatly, at least at 144° C. where the results of the three methods used by Mandelcorn and Steacie agree most closely. It is also of interest that the activation energy for the addition of ethyl radicals to ethylene obtained by us falls between the value obtained by Mandelcorn and Steacie (7.0 kcal. per mole) and the corrected value of Raal and Danby (4.6 kcal. per mole) (7, 6) for the addition of methyl radicals to ethylene.

ACKNOWLEDGMENTS

The authors are grateful to the National Research Council of Canada for supporting this research and to Mr. R. M. Atherley for his technical assistance.

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