

[CONTRIBUTION FROM THE CATHOLIC UNIVERSITY OF AMERICA]

## The Mechanism of the Homogeneous Thermal Reaction between Ethylene and Deuterium<sup>1</sup>

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The reaction  $C_2H_4 + D_2$  has been studied and the initial rates of formation of the products have been measured at a series of temperatures. Initially  $CH_2=CHD$  is formed predominantly accompanied by smaller quantities of  $HD$  and  $C_2H_5D$  and still smaller quantities of  $C_2H_6$ ,  $C_2H_4D_2$  and  $H_2$ . The results are interpreted in the basis of a free radical mechanism.

The earliest detailed quantitative kinetic studies<sup>3</sup> of the  $C_2H_4 + H_2$  reaction indicated that it is homogeneous and second order with an activation energy of 43.15 kcal. The measurements were made in a Pyrex vessel and the speed of the reaction was obtained by pressure-time measurements. Chemical analysis indicated that when the hydrogen was in excess, ethylene polymerization could be neglected.

In later work,<sup>4</sup> following a similar procedure, a study was made of the relative rates of combination of hydrogen and deuterium with ethylene. It was found that light hydrogen reacts two and a half times as fast as the heavy isotope. The authors considered the possibility that the reaction proceeds through a free radical chain mechanism<sup>5</sup> but concluded that the evidence favored the view that a bimolecular association occurred.

In this paper we have made a rather detailed study of the  $C_2H_4 + D_2$  reaction and have obtained, by mass spectrometric analysis, the initial rates of disappearance of both the ethylene and deuterium and the initial rates of formation of the various products over a range of temperatures.

### Experimental

The apparatus and the mass spectrometer used in this investigation are the same as reported previously.<sup>6</sup> The ethylene was Matheson C.P. grade, 99.5% pure  $C_2H_4$ ; the deuterium was supplied by Stuart Oxygen<sup>7</sup> with a minimum purity of 99.5%  $D_2$ . Equimolar mixtures of  $C_2H_4$  and  $D_2$  were prepared and heated in the quartz reaction vessel at a constant temperature in the range of 570 to 660°. This investigation was restricted as far as possible to the initial stages of the reaction. The extent of the interaction of  $C_2H_4$  and  $D_2$  was determined manometrically, on the basis of the pressure decrease during the reaction, and mass spectrometrically, on the basis of the product analysis. The reaction mixture was drawn off completely at different stages of reaction at each temperature and divided into three portions, (1), (2) and (3) for mass spectrometer analysis. These samples contained unreacted  $C_2H_4$  and  $D_2$ ,  $CH_2=CHD$ ,  $HD$ ,  $C_2H_5D$ ,  $H_2$ ,  $C_2H_4D_2$  and  $C_2H_6$  present with  $C_2H_2D_2$ ,  $C_2D_3H$ ,  $C_2H_3D_3$ ,  $C_2D_4H_2$ ,  $CH_4$ ,  $CH_3D$  and  $CD_3H$  some or all of which were formed depending on the extent of reaction.

Portion (1) was left untreated and the spectrum from mass 2 to 36 was obtained for the entire sample at the usual nominal 60-volt electron potential. The spectra for several samples were run at mass 70 and indicated that the formation of propanes and butanes was much less than 1% under the conditions of our experiments.

The method of Stevenson and Wagner<sup>8</sup> was then employed for the detection of the ethylenes in the presence of ethane. Since the appearance potentials for the molecule ion,  $C_2H_6^+$ , and the ion fragment,  $C_2H_4^+$ , in the spectrum of ethane are 1.1 to 1.4 e.v. greater than the appearance potential for the molecule ion,  $C_2H_4^+$ , in the spectrum of  $C_2H_4$ , we reduced the electron energy to a value such that ethane was not ionized and only the molecule ions of the ethylenes were produced; we obtained the spectrum for the isotopic ethylenes in (1) at this low potential. We did not calibrate the galvanometer set-up on the mass spectrometer in order to determine the absolute value of this electron energy but we were able to reproduce it within  $\pm 0.01$  volt from experiment to experiment. This method has been employed previously<sup>9</sup> and provides a powerful means of obtaining the relative concentrations of the isotopic ethylenes.

Portion (2) was then cooled in liquid nitrogen and the hydrogens and methanes distilled off for analysis at the usual electron potential. Portion (3) was collected over excess bromine to remove the ethylenes according to the method which Turkevich, Schissler and Irsa<sup>10</sup> employed in their study of the catalytic interaction of ethylene and deuterium. The ethanes were distilled at  $-160^\circ$  from the dibromides and excess bromine and analyzed at the usual electron energy.

The spectrum of (1) was then resolved into the contributions of the ethylenes, ethanes, methanes and hydrogens as follows. The spectrum of (2), which was multiplied by that factor which made the ion currents of  $D_2^+$  in (1) and (2) equal, was subtracted from (1). This separated from (1) the contributions of the methanes and hydrogens. The spectrum of (3), which was multiplied by that factor which made the ion currents of  $C_2H_4D_2^+$  (or of  $C_2D_3H_3^+$  in the later stages of the reaction) in (1) and (3) equal, was subtracted from (1). This separated from (1) the contributions of the ethylenes, ethanes, methanes and hydrogens; further separation was necessary only within each class of compound. This was highly desirable. Since samples of all the isotopic compounds are not available for calibration patterns, the spectra of these compounds had to be calculated according to the method of Schissler, Thompson and Turkevich.<sup>11</sup> This calculation of spectra is not rigorous but does provide a very valuable method of approximation; as such, there is some error inherent in the method. However, in these experiments this error was accumulative only within the analysis of the ethylenes or ethanes or methanes and was not transferred. Further separation was made as follows.

**Ethylenes.**—In all cases the relative concentrations of the ethylenes as determined by the relative ion currents at masses 28 to 32, corrected for  $C_{13}$ , at low electron energy was used. The assumption was made that the sensitivities of  $C_2H_4^+$ ,  $C_2H_3D^+$ , . . . .  $C_2D_4^+$  ions due to  $C_2H_4$ ,  $C_2H_3D$ , . . . .  $C_2D_4$  were equal. This assumption is reasonable; in preliminary experiments we showed that the relative ion currents on masses 31 and 32 due to  $C_2D_3H^+$  and  $C_2D_4^+$  were equal and, thereby, probably a valid measure of the relative concentrations of  $C_2D_3H$  and  $C_2D_4$  over a wide range of electron energies from a value slightly above the appearance potential up to the usual 60 volts.

In order to determine the mole percentage of the ethylenes in the over-all sample the ion currents for each ethylene

(1) This work was supported by the United States Air Force under Contract AF-18(600)-64 monitored by the Office of Scientific Research.

(2) Weston College, Weston 93, Massachusetts.

(3) R. N. Pease, *THIS JOURNAL*, **54**, 1876 (1932).

(4) (a) R. N. Pease and A. Wheeler, *ibid.*, **54**, 1144 (1935); (b) A. Wheeler and R. N. Pease, *ibid.*, **58**, 1665 (1936).

(5) F. O. Rice and K. F. Herzfeld, *ibid.*, **56**, 284 (1934).

(6) F. O. Rice and R. E. Varnerin, *ibid.*, **76**, 324 (1954).

(7) Under authority granted by the Atomic Energy Commission, Stable Isotope Allocation #B-3878.

(8) D. P. Stevenson and C. D. Wagner, *THIS JOURNAL*, **72**, 5612 (1950).

(9) J. N. Wilson, J. W. Otvos, D. P. Stevenson and C. D. Wagner, *Ind. Eng. Chem.*, **45**, 1480 (1953).

(10) J. Turkevich, D. O. Schissler and P. Irsa, *J. Phys. Colloid Chem.*, **55**, 1078 (1951).

(11) D. O. Schissler, S. O. Thompson and J. Turkevich, *Disc. Faraday Soc.*, **10**, 46 (1951).

in the 60 volt spectrum of (1) had to be resolved. The ethylene patterns were calculated<sup>11</sup> from our own pattern for C<sub>2</sub>H<sub>4</sub>, corrected for C<sup>13</sup>. The factors compensating for the relative probabilities of the rupture of the C-D and C-H bonds were calculated from the ethylene spectra of Dibeler and Mohler<sup>12</sup> so as to give the best fit on the highest masses. Spectra for all the ethylenes calculated from the C<sub>2</sub>H<sub>4</sub> spectrum of Dibeler and Mohler agreed within  $\pm 2.6\%$  of their experimental patterns in the mass range of 26 to 32; this error was not reduced as much as possible because the best fit on the highest masses was desired. It was assumed that the sensitivities of the parent masses of the ethylenes were equal. The relative concentrations of the ethylenes obtained by this method agreed within  $\pm 2$  to 3% of the analyses at low electron energy; residue ion currents on masses 26 and 27 were less than 5% of the original.

TABLE I

## PARTIAL PRESSURES OF REACTANTS AND PRODUCTS

Three representative analyses of the twenty-two made are listed below. These three analyses represent experiments at 616° and different times of reaction. The partial pressures were obtained from the mole percentages of each constituent in the different fractions for three runs containing initially 100 mm. C<sub>2</sub>H<sub>4</sub> and 100 mm. D<sub>2</sub>.

Fractions, mm.			
C <sub>2</sub> H <sub>4</sub>	85.6	74.2	53.9
C <sub>2</sub> H <sub>3</sub> D	8.7	14.8	20.3
C <sub>2</sub> H <sub>2</sub> D <sub>2</sub>	1.5	2.2	3.8
C <sub>2</sub> D <sub>3</sub> H		1.7	2.1
D <sub>2</sub>	87.2	74.5	66.3
HD	4.5	7.2	11.7
H <sub>2</sub>	1.1	2.8	5.2
C <sub>2</sub> H <sub>6</sub>	0.2	1.5	2.3
C <sub>2</sub> H <sub>5</sub> D	3.9	6.6	9.5
C <sub>2</sub> H <sub>4</sub> D <sub>2</sub>	0.5	1.4	3.1
C <sub>2</sub> H <sub>3</sub> D <sub>3</sub>	0.3	0.2	0.6
CH <sub>4</sub>	0.3	0.4	0.6
CH <sub>3</sub> D	0.5	1.3	3.3
CH <sub>2</sub> D <sub>2</sub>			0.4
Atom % carbon <sup>a</sup>	25.2	25.4	24.6
Atom % hydrogen <sup>a</sup>	50.3	50.8	50.2
Atom % deuterium <sup>a</sup>	24.5	23.8	25.2

<sup>a</sup> Note that the original mixture of C<sub>2</sub>H<sub>4</sub> + D<sub>2</sub> contained 25 atom % of carbon, 25 atom % of deuterium and 50 atom % of hydrogen. These weight balances demonstrate the over-all accuracy of the analyses.

experimental pattern of Schissler, Thompson and Turkevich.<sup>11</sup> In no experiment was there more than 0.1% of an ethane in which there was more than three deuterium atoms. The relative sensitivities of the isotopic ethanes as reported in the literature were used. The residual ion currents in the 26 to 29 mass range were 5% or less of the original.

**Methanes.**—The methane patterns were calculated<sup>11</sup> from the CH<sub>4</sub> pattern, corrected for C<sup>13</sup>. It was assumed that the sensitivities of the molecule ions of the methanes were equal; the accuracy of the method was about the same as in the case of the ethylenes and ethanes.

**Hydrogens.**—The ion current at mass 2 was corrected for D<sup>+</sup> from D<sub>2</sub> and HD. The contributions of the methanes to masses 2, 3 and 4 were found to be 1 to 2% of the parent methane mass; we neglected these contributions since there was such a small concentration of methane present. The relative concentrations of H<sub>2</sub>, HD and D<sub>2</sub> were determined on the basis of the ion currents at masses 2, 3 and 4.

The relative sensitivities of C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub>, H<sub>2</sub> and D<sub>2</sub> were determined by calibration of standard samples.

Twenty-two complete analyses were made and have provided the data for this study. Table I contains the data for three typical analyses and a weight balance for each case.

The initial rate of formation of each product was calculated from the initial slope of the curve obtained by plotting the concentration of the product against the time of reaction. There were two typical curves noted in these plots. In curve A, the slope at time = 0 was positive and a maximum for this curve; in curve B, the slope at time = 0 was zero and a minimum for this curve. The products C<sub>2</sub>H<sub>3</sub>D, HD, C<sub>2</sub>H<sub>5</sub>D, H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>D<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> were formed according to curve A and are called the primary products of the reaction; such products are formed from the earliest stages of the reaction and must be considered in any proposed mechanism. The products C<sub>2</sub>H<sub>2</sub>D<sub>2</sub>, C<sub>2</sub>D<sub>3</sub>H, C<sub>2</sub>H<sub>3</sub>D<sub>3</sub>, C<sub>2</sub>D<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub>, CH<sub>3</sub>D and CD<sub>3</sub>H were formed according to curve B and are called the secondary products of the reaction. The secondary products are formed by the reaction of atoms or radicals with the primary products and are not considered in our mechanism.

In Table II we show the initial rates of formation of the products and the initial rates of disappearance of the reactants, D<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>. These data were obtained from a multitude of exceedingly complicated mass spectrometric analyses and in addition, the analytical results had to be plotted and dy/dt estimated at t = 0. In Table III we show the results of a calculation at five temperatures of the amount of each substance reacting and the corresponding amount appearing in the products. The fairly good agreement for material balances shown in Table III indicates that the data in Table II are dependable.

TABLE II

## RATES OF REACTION

Initial rates of reactions C<sub>2</sub>H<sub>4</sub> and D<sub>2</sub> and initial rates of formation (molecules cc.<sup>-1</sup>, min.<sup>-1</sup> × 10<sup>16</sup>) of products in the reaction of equimolar mixtures of C<sub>2</sub>H<sub>4</sub> and D<sub>2</sub>. The concentrations are indicated as follows:

C <sub>2</sub> H <sub>4</sub>	D <sub>2</sub>	H <sub>2</sub>	C <sub>2</sub> H <sub>3</sub> D	C <sub>2</sub> H <sub>5</sub> D	C <sub>2</sub> H <sub>4</sub> D <sub>2</sub>	HD	C <sub>2</sub> H <sub>6</sub>
y <sub>1</sub>	y <sub>2</sub>	y <sub>3</sub>	y <sub>4</sub>	y <sub>5</sub>	y <sub>6</sub>	y <sub>7</sub>	y <sub>8</sub>
Initially y <sub>1</sub> = y <sub>2</sub> = 100 mm.; y <sub>3</sub> to y <sub>8</sub> initially are zero.							
Substance	Rate <sup>a</sup>	662°	643°	616°	598°	569°	E
y <sub>1</sub> C <sub>2</sub> H <sub>4</sub>	dy <sub>1</sub> /dt	-35.66	-16.94	-7.18	-4.70	-1.47	52
y <sub>2</sub> D <sub>2</sub>	dy <sub>2</sub> /dt	-19.36	-9.87	-5.68	-3.61	-1.24	44
y <sub>3</sub> H <sub>2</sub>	dy <sub>3</sub> /dt	3.47	2.18	0.75	0.33	0.09	61
y <sub>4</sub> C <sub>2</sub> H <sub>3</sub> D	dy <sub>4</sub> /dt	22.92	14.54	4.39	2.08	.88	57
y <sub>5</sub> C <sub>2</sub> H <sub>5</sub> D	dy <sub>5</sub> /dt	4.79	3.22	1.71	1.42	.57	35
y <sub>6</sub> C <sub>2</sub> H <sub>4</sub> D <sub>2</sub>	dy <sub>6</sub> /dt	1.43	1.04	0.46	0.31	.11	44
y <sub>7</sub> HD	dy <sub>7</sub> /dt	12.32	6.44	1.93	0.99	.36	61
y <sub>8</sub> C <sub>2</sub> H <sub>6</sub>	dy <sub>8</sub> /dt	0.90	0.60	0.47	0.27	.08	39

<sup>a</sup> The values of dy/dt were obtained by plotting measured values of y against t and estimating dy/dt at t = 0. Actually the values of dy/dt are not at t = 0 but at a very short time later when the stationary state concentration of radicals is established.

**Ethanes.**—The spectra for ethane-d<sub>1</sub> and ethane-d<sub>2</sub> were calculated<sup>11</sup> from our spectrum of C<sub>2</sub>H<sub>6</sub>, corrected for C<sup>13</sup>, and the spectrum of ethane-d<sub>3</sub> was approximated from the

(12) V. H. Dibeler, F. L. Mohler and M. de Hemptinne, *J. Research Natl. Bur. Standards*, **53**, 107 (1954).

## Discussion

Even a superficial inspection of the results shown in Table I indicates that any occurrence of the molecular reaction C<sub>2</sub>H<sub>4</sub> + D<sub>2</sub> → C<sub>2</sub>H<sub>4</sub>D<sub>2</sub> is inappre-

TABLE III  
REACTION OF ETHYLENE AND DEUTERIUM  
Material balance. The necessary data are taken from Table II

	662°	643°	616°	598°	569°
C <sub>2</sub> H <sub>4</sub> reacting, <sup>a</sup> mm.	35.66	16.94	7.18	4.70	1.47
H. C. produced, <sup>a</sup> mm.	30.04	19.40	7.03	4.08	1.64
D <sub>2</sub> reacting, <sup>b</sup> mm.	19.36	9.87	5.68	3.61	1.24
D <sub>2</sub> produced, <sup>b</sup> mm.	21.42	13.14	4.47	2.56	1.01
H <sub>2</sub> reacting, <sup>c</sup> mm.	71.32	33.88	14.36	9.40	2.94
H <sub>2</sub> produced, <sup>c</sup> mm.	61.54	39.14	14.90	8.94	3.48

<sup>a</sup> This is really a carbon balance. Carbon appears only in the C<sub>2</sub> hydrocarbons so that  $dy_1/dt = dy_4/dt + dy_5/dt + dy_6/dt + dy_8/dt$ . <sup>b</sup> This is a deuterium balance.  $dy_2/dt = dy_5/dt + 1/2(dy_4/dt + dy_6/dt + dy_7/dt)$ . <sup>c</sup> This is the H<sub>2</sub> balance.  $2dy_1/dt = dy_3/dt + 1.5 dy_4/dt + 2.5 dy_5/dt + 2 dy_6/dt + 0.5 dy_7/dt + 3 dy_8/dt$ .

ciable. Indeed it seems reasonable to assume that the small percentage of C<sub>2</sub>H<sub>4</sub>D<sub>2</sub> present is produced by the free radical mechanism. The following free radical scheme is proposed for the reaction between ethylene and deuterium

TABLE IV

	<i>E</i>
(1) C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>4</sub> → C <sub>2</sub> H <sub>5</sub> + C <sub>2</sub> H <sub>3</sub>	70
(2) C <sub>2</sub> H <sub>4</sub> + D <sub>2</sub> → C <sub>2</sub> H <sub>4</sub> D + D	70
(3) C <sub>2</sub> H <sub>3</sub> + D <sub>2</sub> → C <sub>2</sub> H <sub>3</sub> D + D	10
(4) D + C <sub>2</sub> H <sub>4</sub> → HD + C <sub>2</sub> H <sub>3</sub>	10
(5) D + C <sub>2</sub> H <sub>4</sub> → C <sub>2</sub> H <sub>4</sub> D	4
(6) C <sub>2</sub> H <sub>4</sub> D → C <sub>2</sub> H <sub>3</sub> D + H	40
(7) H + C <sub>2</sub> H <sub>4</sub> → C <sub>2</sub> H <sub>5</sub>	5
(8) C <sub>2</sub> H <sub>5</sub> → C <sub>2</sub> H <sub>4</sub> + H	40
(9) H + C <sub>2</sub> H <sub>4</sub> → H <sub>2</sub> + C <sub>2</sub> H <sub>3</sub>	10
(9') H + D <sub>2</sub> → HD + D	10
(10) C <sub>2</sub> H <sub>5</sub> + C <sub>2</sub> H <sub>4</sub> → C <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> H <sub>3</sub>	13
(11) C <sub>2</sub> H <sub>6</sub> + D <sub>2</sub> → C <sub>2</sub> H <sub>5</sub> D + D	13
(12) C <sub>2</sub> H <sub>4</sub> D + C <sub>2</sub> H <sub>4</sub> → C <sub>2</sub> H <sub>5</sub> D + C <sub>2</sub> H <sub>3</sub>	13
(12') C <sub>2</sub> H <sub>4</sub> D + C <sub>2</sub> H <sub>4</sub> → C <sub>2</sub> H <sub>3</sub> D + C <sub>2</sub> H <sub>5</sub>	13
(13) C <sub>2</sub> H <sub>4</sub> D + D <sub>2</sub> → C <sub>2</sub> H <sub>4</sub> D <sub>2</sub> + D	13
(14) C <sub>2</sub> H <sub>4</sub> D + C <sub>2</sub> H <sub>4</sub> D → C <sub>2</sub> H <sub>5</sub> D + C <sub>2</sub> H <sub>3</sub> D	2

Equations 1 and 2 represent the primary steps that produce free radicals; we have assumed that these intermolecular reactions have a much smaller activation energy than the dissociation of either D<sub>2</sub> or C<sub>2</sub>H<sub>4</sub> into fragments. Equations 3–13 represent reactions between radicals and one of the molecular species C<sub>2</sub>H<sub>4</sub> or D<sub>2</sub>. We have neglected all recombination of radicals except that represented by equation 14. We have also neglected reaction 12'. It has been necessary to make a number of drastic assumptions which we shall discuss at appropriate places in the following paragraphs. Since our experimental results were obtained by extrapolating to initial concentrations of reactants we are justified in neglecting all back reactions except 7.

We shall first write down the stationary state equations, the concentrations of the five radicals being indicated as

H	D	CH <sub>2</sub> =CH	C <sub>2</sub> H <sub>4</sub> D	C <sub>2</sub> H <sub>5</sub>
<i>x</i> <sub>1</sub>	<i>x</i> <sub>2</sub>	<i>x</i> <sub>3</sub>	<i>x</i> <sub>4</sub>	<i>x</i> <sub>5</sub>

The initial concentrations of C<sub>2</sub>H<sub>4</sub> and D<sub>2</sub> are equal and are each indicated by *y*. The *k*'s represent the

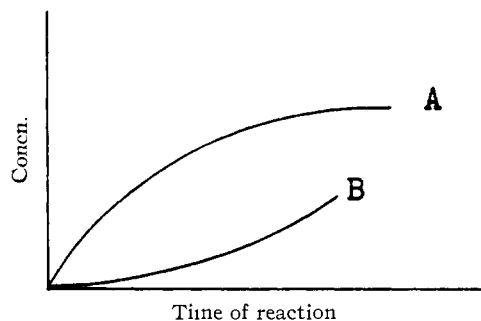


Fig. 1.

specific rate constants of the elementary reactions.

$$\frac{dx_1}{dt} = k_6x_4 - k_7x_1y + k_8x_5 - k_9x_1y - k'9x_1y = 0 \quad (I)$$

$$\frac{dx_2}{dt} = k_2y^2 + k_3x_3y - k_4x_2y - k_5x_2y + k_{11}x_5y + k_{13}x_4y + k'9x_1y = 0 \quad (II)$$

$$\frac{dx_3}{dt} = k_2y^2 - k_3x_3y + k_4x_2y + k_9x_1y + k_{10}x_5y + k_{12}x_4y = 0 \quad (III)$$

$$\frac{dx_4}{dt} = k_2y^2 + k_5x_2y - k_6x_4 - k_{12}x_4y - k_{13}x_4y - k_{14}x_4^2 = 0 \quad (IV)$$

$$\frac{dx_5}{dt} = k_1y^2 + k_7x_1y - k_8x_5 - k_{10}x_5y - k_{11}x_5y = 0 \quad (V)$$

We obtain the following values for the concentrations of the various radicals

H	$x_1 \cong \left[ \frac{2k_1k_6^2}{k_7k_{14}} \right]^{1/2}$
D	$x_2 \cong \left[ \frac{k_1k_{12}^2}{k_3^2k_{14}} \right]^{1/2} y$
CH <sub>2</sub> =CH	$x_3 \cong \left[ \frac{k_1k_4^2k_{12}^2}{k_3^2k_5^2k_{14}} \right]^{1/2} y$
C <sub>2</sub> H <sub>4</sub> D	$x_4 \cong \left[ \frac{k_1}{k_{14}} \right]^{1/2} y$
C <sub>2</sub> H <sub>5</sub>	$x_5 \cong \left[ \frac{k_1k_6^2k_8^2}{k_7^2k_3^2k_{14}} \right]^{1/2} y$

In solving for the stationary state concentrations of the radicals, we have made approximations in accordance with the assignment of *E* values and the assumption that the *A* factors for all bimolecular reactions (except 12') are equal. We neglect reaction 12' for reasons discussed in an earlier paper.<sup>13</sup>

TABLE V

CALCULATED AND OBSERVED ACTIVATION ENERGIES FOR THE RATE OF DISAPPEARANCE OF C<sub>2</sub>H<sub>4</sub> AND D<sub>2</sub> AND THE RATE OF FORMATION OF THE VARIOUS PRODUCTS IN THE REACTION C<sub>2</sub>H<sub>4</sub> + D<sub>2</sub>

			Activation energy Measured	Calcd.
CH <sub>2</sub> =CH <sub>2</sub>	<i>y</i> <sub>1</sub>	- <i>dy</i> <sub>1</sub> / <i>dt</i>	52	47
D <sub>2</sub>	<i>y</i> <sub>2</sub>	- <i>dy</i> <sub>2</sub> / <i>dt</i>	44	47
CH <sub>2</sub> =CHD	<i>y</i> <sub>3</sub>	<i>dy</i> <sub>3</sub> / <i>dt</i>	57	53
HD	<i>y</i> <sub>4</sub>	<i>dy</i> <sub>4</sub> / <i>dt</i>	61	53
C <sub>2</sub> H <sub>5</sub> D	<i>y</i> <sub>5</sub>	<i>dy</i> <sub>5</sub> / <i>dt</i>	35	47
C <sub>2</sub> H <sub>6</sub>	<i>y</i> <sub>6</sub>	<i>dy</i> <sub>6</sub> / <i>dt</i>	39	52
C <sub>2</sub> H <sub>4</sub> D <sub>2</sub>	<i>y</i> <sub>7</sub>	<i>dy</i> <sub>7</sub> / <i>dt</i>	44	47
H <sub>2</sub>	<i>y</i> <sub>8</sub>	<i>dy</i> <sub>8</sub> / <i>dt</i>	61	79

(13) F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938).

We assume that the unimolecular decompositions 6 and 8 have an  $A$  factor some  $10^4$  times greater than that for the bimolecular reactions.

By substituting the values of the  $x$ 's in the appropriate equations, we obtain the data shown in Table V. The first four substances shown in Table V are in relatively great abundance as compared with the last four; we do not have a great deal of confidence either in the measured or calculated activation energies for these last four substances. In the case of the first four substances, the agree-

ment seems reasonable in view of the experimental difficulties and the approximations made in the calculations. It is noteworthy that the theory predicts that the rate of formation of hydrogen is independent of the initial concentrations of ethylene and deuterium.

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## The Instantaneous Polymerization of Styrene by Trifluoroacetic Acid<sup>1</sup>

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Trifluoroacetic acid is a powerful initiator for carbonium ion polymerization. Styrene introduced to an excess of trifluoroacetic acid polymerizes instantaneously forming a white, friable, polymeric mass, the yield being close to 100%. On the other hand, addition of small quantities of trifluoroacetic acid to styrene yields a low molecular weight addition product (an ester). Two distinct types of termination should be considered in carbonium ion polymerization: one takes place by returning a proton from carbonium ion to the anion (gegenion), while in the other, the carbonium ion recombines with the gegenion and forms a new covalent bond. The first type of termination characterizes polymerizations initiated by complexes like  $\text{BF}_3 \cdot \text{CH}_3\text{COOH}$ , where the gegenion *cannot* form a covalent bond with the carbonium ion. These terminations are only slightly affected by the surroundings. On the other hand, the second type of termination is very susceptible to the changes of surroundings and takes place in polymerizations initiated by HCl or  $\text{CF}_3\text{COOH}$ , where the gegenion forms covalent bonds with the carbonium ions. Finally, it is pointed out that the properties of molecules in solution depend very much on the nature of the solvation shell. Thus, trifluoroacetic acid molecule in trifluoroacetic acid environment is a powerful proton donor, and its anion is highly stabilized, while the same molecule of acid in hydrocarbon surroundings is a poorer proton donor, forming an anion of low stability.

The understanding of the individual steps of an ionic polymerization is less satisfactory than of those involved in a radical polymerization, although the basic features of the former reaction are now well elucidated.<sup>3</sup> During a search for a convenient source of trifluoromethyl radicals, it was discovered that trifluoroacetic acid is a powerful initiator of carbonium ion polymerization. This was confirmed by the fact that styrene and  $\alpha$ -methylstyrene are polymerized instantaneously by this catalyst, while acrylonitrile and other monomers of similar polarity are not at all polymerized. The initiation of polymerization by trifluoroacetic acid does not require any cocatalyst, since the acid is itself a proton donor. Accordingly, it was

found that traces of water do not affect the rate of the reaction.

The polymerization of styrene by trifluoroacetic acid has been carried out in two ways. In one method, styrene is added dropwise to the stirred excess of pure trifluoroacetic acid; an instantaneous reaction takes place each drop being converted into a white, friable, polymeric mass. The results of some typical experiments are summarized in Table I. The temperature dependence of the molecular weight is found to be exponential and corresponds to a negative "activation energy" of about  $-3.0$  kcal. This relationship is illustrated by Fig. 1.

Alternatively, small amounts of trifluoroacetic acid can be added to an excess of styrene. For reasons which will be made clear later in this paper, the added trifluoroacetic acid is mixed with three volumes of ethylbenzene, and this solution is then stirred into styrene. No high molecular weight polymer is produced under these conditions, although trifluoroacetic acid is consumed rapidly. The rate of the latter reaction increases with increasing temperature, for example, in a mixture of 60 cc. of styrene and 5 cc. of trifluoroacetic acid in 15 cc. of ethylbenzene, only 24% of the acid is consumed in one hour at  $0^\circ$ , but the consumption of acid increases to about 90% in the same period of time at  $60^\circ$ . Vacuum distillation of the reacting material left an oily residue which can be easily hydrolyzed. It was shown that the acid produced in the hydrolysis together with the unconsumed acid account for the total acid added initially. These facts prove that trifluoroacetic acid adds on to sty-

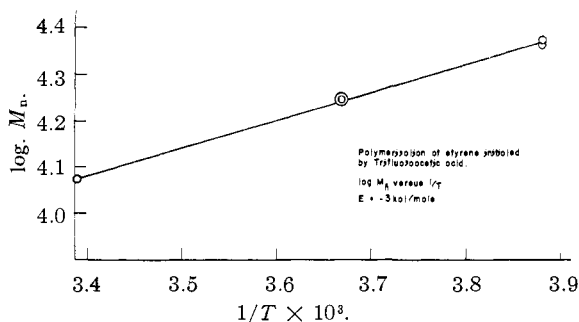


Fig. 1.

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(3) This subject is well reviewed in a recent paper by D. C. Pepper, *Quart. Revs.*, **8**, 88 (1954).