

experiments with hydrobromic acid (Analyses 8, 10, 11, 12) the concentration of the solutions during precipitation was made from one-half to one-third that previously used. These experiments yielded results concordant with those of the earlier chlorides as well as with Experiment 9 in which the chloride solution also was made more dilute before precipitation. In Analyses 10 and 12 the bromide solution was added to the silver solution.

If the correction for water in the ammonia is omitted the ratios  $\text{Ag}:\text{NH}_3$  and  $\text{NO}_3:\text{NH}_3$  become 6.33401 and 3.64073, respectively, and the atomic weight of nitrogen 14.0085.

This investigation was interrupted before it was completed. It is unfortunate that a larger number of experiments could not have been carried out. The purity of the ammonia needs further investigation, especially as regards water, although the synthetic material which we used as the starting point is unlikely to be seriously contaminated with any impurities except permanent gases and moisture. On the whole the final outcome may be looked upon as valuable corroborative evidence that the atomic weight of nitrogen is very close to 14.008. The uncertainty of the method is apparently less than 0.001 unit, which compares very favorably with that of all other methods at present available for the purpose.

If nitrogen is taken as 14.0078, the atomic weight of silver may be calculated to be 107.879, while the value for nitrogen of 14.008 gives 107.880 from the  $\text{Ag}:\text{NH}_3$  ratio and 107.879 from the  $\text{Ag}:\text{NO}_3$  ratio.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

## KINETICS OF THE POLYMERIZATION OF ETHYLENE AT PRESSURES ABOVE ONE ATMOSPHERE<sup>1</sup>

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Previous work<sup>3</sup> has indicated that the only important primary reaction of ethylene when heated in glass to 400–600° at 1 atmosphere initial pressure is one of polymerization to higher mono-olefins ( $\text{C}_n\text{H}_{2n}$ ). The point has not been conclusively demonstrated, however, as would be done if a considerable portion of the ethylene could be caused to polymerize without

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<sup>3</sup> Day, *Am. Chem. J.*, 8, 153 (1886); Bone and Coward, *J. Chem. Soc.*, 93, 1197 (1908); Hague and Wheeler, *ibid.*, 390–391 (1929); Pease, *THIS JOURNAL*, 52, 1158 (1930); Wheeler and Wood, *J. Chem. Soc.*, 1823 (1930).

the formation of appreciable quantities of by-products such as hydrogen, methane, ethane and carbon. Examination of the experimental data reveals that the polymerization reaction at 1 atmosphere is excessively slow and apparently limited, and that it is accompanied by decomposition of the product, and probably also of ethylene itself. The indications are that the polymerization reaction is fundamentally second order, whereas the decompositions are presumably first order. The former should be favored if the initial pressure is increased. It was proposed, therefore, to study the reaction at pressures somewhat higher than 1 atmosphere. A series of experiments was carried out in which ethylene was heated in a copper bomb to 350–500° at initial pressures of 2.5, 5 and 10 atmospheres. These experiments, the results of which are here reported, demonstrate that as much as 50% of the ethylene can be polymerized without the formation of more than 1 or 2% of hydrogen and methane. The importance of the polymerization reaction is, therefore, confirmed.

The apparatus consisted of a cylindrical copper bomb to which was connected (by means of copper tubing and suitable valves) a pressure gage, a tank of compressed ethylene and a mercury gasometer. The bomb was 20 cm. long with an outside diameter of 5 cm. Its walls were 5 mm. thick. Its volume was 250 cc. The copper tubing was 3.2 mm. internal diameter. The bomb was heated in an electric tube-heater. Temperature was measured with a double-junction chromel–alumel thermocouple, and was controlled by hand regulation of the heating current.

The bomb was flushed out five times with ethylene before and after each run. In starting a run, ethylene was allowed to flow through the bomb. The outlet was closed, and the pressure was allowed to rise to the value desired, the starting time being taken at the mid-point of filling. After some definite time interval was completed, the gases were released into the mercury gasometer. The gas was then passed through a trap at 0° to condense liquid products. A sample was analyzed for higher olefins by absorption in ordinary concentrated sulfuric acid; for ethylene by absorption in dilute bromine water; and for hydrogen plus saturated gaseous hydrocarbons by difference. The total volume of off-gas was then measured. The percentage of ethylene reacting was calculated from the volume in the off-gas, and the volume required to fill the bomb. This was compared with the amounts of higher olefin, and of hydrogen plus hydrocarbons formed.

The reaction is believed to be homogeneous as carried out, although no direct tests of the effect of increased copper surface were made. The conclusion is based on the fact that the rates are comparable with those obtained in empty pyrex glass reaction vessels, the surface of which has been shown to have a small though definite repressive action. Thus, at 500° and 1 atmosphere in glass, it was found that 14% of the ethylene reacted in twelve minutes and 19% reacted in twenty-four minutes. In the copper bomb, at 500° and 2.56 atm. pressure, 41% reacted in fifteen minutes. This is about the expected relation if the reaction is second order (as it appears to be). Further, there was no evidence of a "drift" in the results such as might have occurred if a gradual change in the surface of the bomb due to carbonization were affecting the reaction rate.

## Results

Results of the experiments appear in Table I. For each experiment there are given the temperature, the initial pressure of ethylene in atmospheres

TABLE I  
 ETHYLENE UNDER PRESSURE AT 350-500°

Expt.	Temp., °C.	Init. press. C <sub>2</sub> H <sub>4</sub> , atm.	Time, hours	For 100 cc. (S. T. P.) C <sub>2</sub> H <sub>4</sub> reacted, cc.	Gaseous C <sub>n</sub> H <sub>2n</sub> Formed, cc.	H <sub>2</sub> + H. C.	$k_2$ , fraction per hour at 1 atm.
13	350	9.85	8	30.7	4.5	0	0.0056
14	375	4.83	4	23.7	7.0	0	.0161
1		9.72	1	13.8	2.9	0	.0165
12		9.80	4	37.0	8.4	0.1	.0150
15	400	4.94	2	31.7	10.5	0.3	.0470
10		9.85	1	26.9	4.0	1.6	.0374
11		9.85	2	47.9	11.6	1.0	.0467
17	425	4.90	0.5	20.3	10.8	0	.104
5		4.95	1	33.4	11.4	0.7	.101
16		4.97	2	61.5	17.3	3.0	.161
4		10.03	0.25	17.8	4.4	0.2	.086
3		9.70	0.5	34.3	6.3	0.7	.108
2		9.54	1	57.9	10.7	2.7	.144
18	450	2.52	0.5	27.0	11.3	0.3	.294
6		2.56	1	46.1	15.7	3.7	.334
8		4.95	0.25	23.1	6.1	1.5	.243
7		4.97	0.5	39.8	10.5	1.1	.266
9		9.73	0.25	42.3	11.8	1.0	.301
21	475	2.54	0.25	26.3	12.6	0.3	.457
20		2.50	0.5	48.1	16.9	2.1	.741
19		4.96	0.25	45.8	17.9	1.9	.682
22	500	2.56	0.25	41.3	15.9	3.1	1.08
23		4.87	0.25	65.1	19.8	10.9	1.53

(corrected for the nitrogen present), the time of heating in hours, and the volume in cc. (S. T. P.) of ethylene reacting, of higher gaseous olefins formed, and of hydrogen plus gaseous paraffins formed for each 100 cc. (S. T. P.) of pure ethylene introduced. The figure for ethylene is in effect the percentage of ethylene reacting. In the last column are given second order velocity constants. The numerical value of  $k_2$  is the fraction of the ethylene which would react in one hour if the pressure of that gas were maintained constant at one atmosphere, and the reaction were actually second order. The constant is based on the following. If  $p$  is the pressure of ethylene in atmospheres and  $t$  is the time in hours

$$-\frac{dp}{dt} = k_2 p^2$$

If  $x$  is fraction of ethylene converted, and  $p_0$  is initial pressure of ethylene

$$p = p_0 (1 - x)$$

Then

$$-p_0 \frac{d(1-x)}{dt} = k_2 (1-x)^2 p_0^2$$

$$-\frac{d(1-x)}{(1-x)^2} = k_2 p_0 dt$$

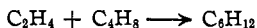
$$k_2 = \frac{1}{p_0 t} \cdot \frac{x}{1-x}$$

The results show clearly that it is possible to polymerize more than 50% of the ethylene to higher members of the  $C_nH_{2n}$  series without the formation of appreciable quantities of other products. The polymer is in part gaseous and in part liquid, the tendency being to form a greater proportion of the latter as reaction proceeds. In one or two favorable cases the yield of gaseous  $C_nH_{2n}$  was that to be expected from the reaction

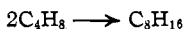


It is reasonable to conclude from this fact that butylene is the primary product of the reaction.<sup>4</sup>

This conclusion is strengthened by an analysis of the kinetics of the reaction. If the primary reaction is that shown above, and occurs as a result of a collision in the gas phase, one would expect it to be kinetically of second order. Actually it is found that the second order constant holds reasonably well when comparisons are made between corresponding conversions at different initial pressures. Nevertheless, the constants for the most part increase as the total conversion increases. This can be qualitatively accounted for by a secondary reaction between ethylene and the butylene first formed



The primary product offers an outlet for the reaction of an additional quantity of ethylene. This reaction, and the reaction



would account for the formation of the liquid products.

Bimolecular gas reactions are of special theoretical interest because it has, in general, been possible to show that the heat of activation as calculated from the temperature coefficient of the rate

$$\frac{d \ln k}{dT} = \frac{E}{RT^2}$$

can be simply interpreted as the excess of energy which two colliding molecules must possess before reaction is possible. The rate of reaction is given by the rate of collision between molecules possessing the requisite excess energy.

The case of ethylene polymerization is an exception to the rule. From the temperature coefficient of  $k_2$ , the energy of activation is calculated to be 35,000 cal.

If  $Z_{eff}$  = number of collisions per cc. per sec. between molecules possessing 35,000 cal. over the average

$n$  = number of molecules per cc.

<sup>4</sup> See Wheeler and Wood, *J. Chem. Soc.*, 1823 (1930), for confirmation.

- $\sigma$  = molecular diameter in cm.  
 $\bar{c}$  = root mean square velocity in cm. per sec.  
 then  $Z_{\text{eff.}} = \sqrt{\frac{2}{\pi}} n^2 \pi \sigma^2 \bar{c} e^{-35,000/RT}$   
 $k_2$  = fraction of molecules reacting per hour when the pressure is maintained at 1 atm.  
 $k_2 = 2.3600 \cdot Z_{\text{eff.}} / n$   
 $n$  = number of molecules per cc. at 1 atm. press.  
 $k_2 = 3600 \sqrt{\frac{2}{\pi}} n \pi \sigma^2 \bar{c} e^{-35,000/RT}$

The observed value of  $k_2$  at 425° is 0.1. The calculated value is

$$k_2 = 3600 \cdot \sqrt{\frac{2}{\pi}} \cdot 1.058 \times 10^{19} \pi (3.78 \times 10^{-8})^2 78810 e^{-35,000/4.58 \cdot 698} = 215.$$

The observed value is thus only  $1/2000$  of that calculated. If, instead of calculating  $k_2$  at 425°, we use the observed value of  $k_2$  at 425° to calculate the heat of activation, the latter comes out to be 45,650 cal. This corresponds to a temperature coefficient of 3.1 per 25°, whereas the observed value is 2.3 per 25°.

There is no question as to the existence of a wide discrepancy between the observed rate and that to be expected on the basis of the collision theory. It is true that the variation in the values of  $k_2$  at each temperature allows some latitude of choice of temperature coefficient, but even the extreme value would not be sufficiently high. The low rate of formation of product cannot be due to a reverse reaction because the discrepancy between observed and calculated rate is far too large. The reverse action would have to be more than 1000 times the faster, under which conditions no reaction whatever would be observed.

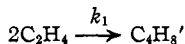
The cause of the discrepancy is undoubtedly to be sought in the type of reaction under investigation. The ethylene polymerization is an association reaction taking place in the gas phase. It is not immediately obvious how such a reaction can be of second order at all. Theoretical considerations based on the older quantum mechanics rule out the possibility that a stable product molecule can be formed as the immediate result of a collision between two active reactant molecules.<sup>5</sup> The argument is simple. The energies of the reacting molecules and the heat of reaction must be suitably represented in the product molecule. However, the translational energy of the latter with respect to that of the reactant molecules is limited by the requirements of the law of conservation of momentum, while its rotational and vibrational energy is limited by quantum restrictions. Since the energy to be accommodated in the product molecules may have any value whatsoever, the chance that it can be exactly accommodated in any particular collision under these restrictions is negligible. Hence, reaction is highly improbable. Prior to the introduction of the quantum theory there would have been no such difficulty. Now with the development of the uncertainty principle, the above argument

<sup>5</sup> See, *e. g.*, Born and Franck, *Ann.*, [4] 76, 225 (1925).

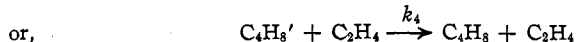
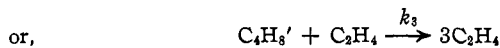
seems to lose some of its force. If, by specifying that two molecules collide, we virtually specify their positions, then their momenta become to a degree uncertain, and as a consequence there will always exist a finite though usually small probability of accommodation and therefore of successful reaction between suitably activated molecules. The average of these probabilities over all activating collisions would be given by the ratio of the reaction rate to the rate of occurrence of such collisions. In the case of ethylene polymerization, the latter has been calculated to be about 1 to 2000.

There are three alternatives to the mechanism just presented. The difficulty as to the accommodation of the energy of reactant molecules plus the heat of reaction in the product molecule may be solved by radiation of a part of the energy, or by transfer at the reaction vessel walls, or by a suitable distribution of energy between the product molecule and a third molecule which enters into the collision. Radiation by molecules of this type has not a high degree of probability. Wall reaction seems to be ruled out by the observation that a glass packing diminishes the rate somewhat. This leaves us with the possibility of termolecular collisions. The immediate objection to this latter is that it would appear to require that the reaction be of third order rather than second. However, this may not be a disadvantage since at 1 atmosphere there is some evidence of a fall in rate more rapid than would be expected of a second order reaction. Professor H. S. Taylor has suggested a mechanism which appears capable of presenting this view of the reaction. This is given below.

Assume that a quasi-molecule,  $C_4H_8$ , is formed as a result of collision between two ethylene molecules. This complex can have only an excessively short life. It may immediately resolve itself into two ethylene molecules, or it may be decomposed by collision with an ethylene molecule, or finally it may be stabilized by a collision with an ethylene molecule. We thus have



followed by



For the rates of these reactions, we write

$$+ \frac{d[C_4H_8']}{dt} = k_1[C_2H_4]^2$$

$$- \frac{d[C_4H_8']}{dt} = k_2[C_4H_8'] + k_3[C_4H_8'][C_2H_4] + k_4[C_4H_8'][C_2H_4]$$

If we assume that the concentration of  $C_4H_8'$  has a steady-state value, we can write

$$k_1[C_2H_4]^2 = k_2[C_4H_8'] + k_3[C_4H_8'][C_2H_4] + k_4[C_4H_8'][C_2H_4]$$

Whence

$$[C_4H_8'] = \frac{k_1 [C_2H_4]^2}{k_2 + k_3 [C_2H_4] + k_4 [C_2H_4]}$$

Finally

$$\begin{aligned} + \frac{d[C_4H_8]}{dt} &= k_3 [C_2H_4] [C_4H_8'] \\ &= \frac{k_1 k_3 [C_2H_4]^3}{k_2 + k_3 [C_2H_4] + k_4 [C_2H_4]} \end{aligned}$$

When the ethylene concentration is high, this reduces to

$$+ \frac{d[C_4H_8]}{dt} = \frac{k_1 k_3}{k_3 + k_4} [C_2H_4]^2$$

which is the second order form. With suitable values of the temperature coefficients of the various velocity constants involved, the experimentally observed coefficient could be fitted. At very low concentrations of ethylene, the equation becomes

$$+ \frac{d[C_4H_8]}{dt} = \frac{k_1 k_3}{k_2} [C_2H_4]^3$$

that is, the reaction is third order.

### Summary

The rate of polymerization of ethylene has been measured at 2.5, 5 and 10 atmospheres from 350 to 500°. At least 50% of the ethylene may be polymerized to gaseous and liquid mono-olefins without the formation of more than a few per cent. of hydrogen and saturated hydrocarbons.

The reaction is of second order and has an abnormally low temperature coefficient. This is discussed in the light of the fact that the reaction is of the association type.

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### NOTES

**A Note on Diffusion in Gelatin Gels.**—In a recent paper on the diffusion of non-electrolytes in gelatin gels, Friedman and Kraemer<sup>1</sup> have observed that the coefficient of diffusion is diminished by an increase in the concentration of the gel. A similar diminution was observed by Stiles and Adair,<sup>2</sup> who found that the coefficient of diffusion of sodium chloride decreased from  $0.675 \times 10^{-5}$  in a 4% gel to  $0.483 \times 10^{-5}$  in a 16% gel.

The results of Friedman and Kraemer are consistent with the formula we published, to show the relation between coefficient of diffusion and gel concentration. The formula is

$$k = a(1 - bc)$$

where  $k$  is the diffusion constant of sodium chloride in the gelatin gel,  $c$  is concentration of gelatin in percentage by weight,  $a$  is a constant = 0.74

<sup>1</sup> L. Friedman and E. O. Kraemer, *THIS JOURNAL*, **52**, 1295 (1930).

<sup>2</sup> W. Stiles and G. S. Adair, *Biochem. J.*, **15**, 621 (1921).