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## The Decomposition of Ethyl Bromide and the Collision Theory of First-Order Reactions\*

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The reaction  $C_2H_5Br \rightarrow C_2H_4 + HBr$  has been studied in the neighborhood of  $400^\circ$  with special reference to the effect of the wall surface and the addition of bromine. Earlier experimental facts are summarized and shown to be in agreement with the hypothesis that the primary step is the production of  $C_2H_5$  and  $Br$ , followed by chemical reactions which do not involve a long chain. The low pressure effects are explained on the basis of wall effects. The decrease in the value of the first-order rate constant at low pressures can be explained in this reaction and in the decomposition of nitrogen pentoxide without the aid of the collision theory. It is suggested that other examples which have been regarded as confirmations of the collision theory may find similar explanations. It may be necessary to revise the quantitative aspects of the collision theory to allow for a decrease in  $k$  at lower pressures than have been heretofore considered.

ETHYL bromide decomposes in the gas phase at about  $400^\circ$  according to a first-order rate equation and gives ethylene and hydrobromic acid with less than five percent of other gases. The chemical analysis of the products and the influence of pressure and foreign gases have been reported earlier.<sup>1-3</sup> In the present work special attention has been paid to the determination of the activation energy and the effect of surface walls, in order to determine more definitely the mechanism by which decomposition occurs and to test the applicability of the collision hypothesis and the hypothesis of free radicals.

### EXPERIMENTAL PROCEDURE

The ethyl bromide was prepared from hydrobromic acid and alcohol. The constancy of its freezing point throughout the entire freezing of the liquid showed that the purification was adequate. The decomposition rates checked with those obtained with ethyl bromide prepared by Professor Timmermans in Brussels and distributed by the National Bureau of Standards. Several glass bulbs of about 0.5 cc capacity were filled with the degassed liquid in an all-glass chamber. The removal of dissolved oxygen and other gases was accomplished by successive freezing, evacuation and melting, continuing until no

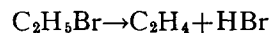
discharge could be obtained with a Tesla coil. The bulbs were sealed and later broken with magnetic hammers when introducing the ethyl bromide into the heated reaction chamber.

The 250-cc spherical flask of Pyrex was provided with a diaphragm and electrical contact for measuring pressures while submerged in a stirred lead thermostat kept constant to  $0.1^\circ$ . A long lever permitted adjustment of the zero point of the diaphragm without removing the vessel from the bath. The all-glass apparatus was cleaned with fuming nitric acid, rinsed and heated while a stream of oxygen passed through to oxidize organic material. Before introducing the ethyl bromide, the whole system was evacuated to  $10^{-5}$  or  $10^{-6}$  cm with a mercury pump while heating.

The special feature of the present technique was a series of capillary gates, the tips of which were broken by rotating a lever in a ground glass joint. The capillary tubes were then sealed off when the entering ethyl bromide had reached the desired pressure. Eight successive experiments could thus be made, each with a new filling, without removing the vessel and without admitting air. In this way it was possible to determine the progressive effect of the products of the reaction on the catalytic behavior of the walls.

### EXPERIMENTAL RESULTS

The influence of the walls is seen in Fig. 1 where the pressure increase due to the reaction



\* Presented at the symposium on "Kinetics of Homogeneous Gas Reactions." See page 725.

<sup>1</sup> E. T. Lessig, *J. Phys. Chem.* **36**, 2335 (1932).

<sup>2</sup> E. L. Vernon and F. Daniels, *J. Am. Chem. Soc.* **55**, 922 (1933).

<sup>3</sup> P. Fugassi and F. Daniels, *J. Am. Chem. Soc.* **60**, 771 (1938).

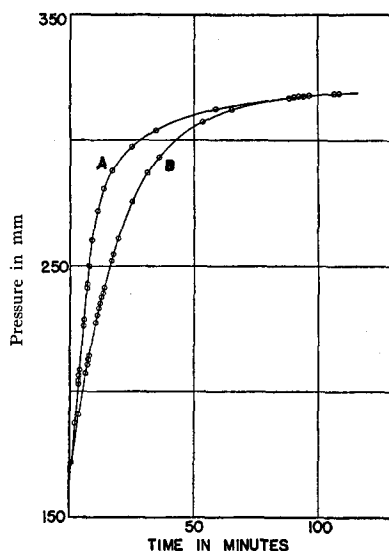


FIG. 1. Decomposition of ethyl bromide at 400°. *A* with cleaned Pyrex walls; *B* with coated Pyrex walls.

is clearly shown for a cleaned flask at *A* and an aged flask at *B*. In the latter experiment the walls were allowed to become coated with the carbonaceous film that is produced by the decomposition of the ethyl bromide.

The specific reaction rate was determined from the slope of the line obtained by plotting  $\log(2p_i - p_t)$  against time where  $p_i$  is the initial pressure of ethyl bromide and  $p_t$  is the total pressure of gases at time  $t$ . Justification of this formula and the chemical analyses of the products have been given before.<sup>1-3</sup> Hundreds of these graphs have been plotted and in nearly all cases a straight line can be passed satisfactorily through all the points out to about one-third completion. A first-order reaction is thus established. The formula cannot apply throughout the whole course of the reaction because the final pressure is appreciably less than twice the initial pressure, probably on account of the condensation of products on the walls.

### Time lag

In the earlier work the evidence regarding the existence of a time lag was not definite. In a few of the experiments the pressure did not seem to rise until after a time longer than that required for the vessel to come to thermal equilibrium. Semenoff<sup>4</sup> commented on this fact and

<sup>4</sup>N. Semenoff, *Chemical Kinetics and Chain Reactions* (Oxford University Press, 1935), p. 450.

suggested that a chain mechanism may be involved. The experiments described here were designed especially for the study of a possible time lag and the ethyl bromide was introduced in many successive experiments while the flask remained unchanged in the thermostat. Readings could be taken in a fraction of a minute after admitting and sealing off the gas. No time lag was detected at the beginning of the experiments when the initial pressure was more than about

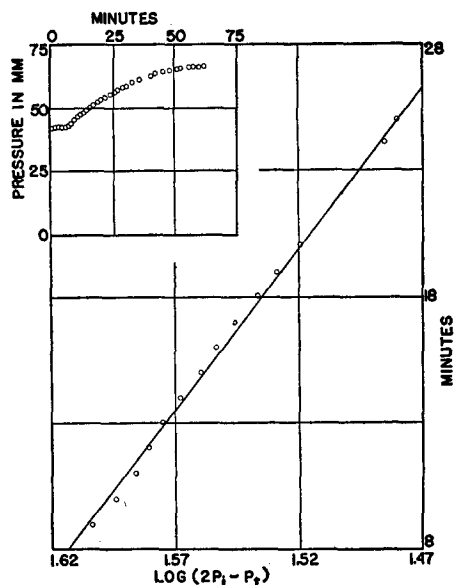


FIG. 2. Decomposition of ethyl bromide at low pressure showing time lag.

130 mm, but in all twenty-five experiments carried out in the 250-cc vessel below 100 mm there was definite evidence of a time lag. In the most extreme case studied at 400° and an initial pressure of 21 mm, the pressure remained stationary for 15 minutes and then started to rise at a measurable, normal rate. A typical experiment with a time lag is shown in Fig. 2 with pressure-time curves and with the logarithm of concentration plotted against time.

### Surface effects

In a 250-cc vessel with a surface to volume ratio of 0.9 the specific reaction rate  $k$  is two or three times as fast when the surface is freshly cleaned as when it is well coated with the carbonaceous film. In a four-liter vessel it is considerably more than twice as fast. The results of

a large number of experiments show definitely that although the reaction is catalyzed by a Pyrex surface the activation energy remains constant. However, the measurements made with coated walls are considerably more reproducible, as pointed out by Brearly, Kistiakowsky and Stauffer<sup>5</sup> in experiments on *tert*-butylchloride.

Very serious errors may be introduced in the determination of the activation energy if the surface coating is changed between determinations at different temperatures. This fact is illustrated in a series of eight determinations recorded in Table I and Fig. 3 which were carried out in the 250-cc vessel over a period of several days without removing the flask from the thermostat or admitting air.

The points are plotted on a  $\log k$  vs.  $1/T$  graph in Fig. 3 where it is seen that reproducible results are obtained after an aging period of about a day, involving experiments No. 1 and No. 2. Experiments No. 4 and No. 5 give abnormally low values of  $k$  because the initial pressures are in the low pressure region. In No. 5 there was an eight-minute time lag and in No. 4 there was a slight lag. The line drawn between experiments 7, 3 and 8, 6 is the most reliable and gives an activation energy of 53,200 which value is substantiated by many other determinations in well-coated flasks. The dotted lines giving activation energies from 20,000 to over 100,000 calories per mole show errors that might have been introduced in determining the activation energy if the measurements at the different temperatures were made while the wall was in the process of being coated. It is quite possible that errors from this changing wall effect may have crept into the measurements of the activation energy of other reactions.

TABLE I. Effect of changing surface on determination of activation energy.

EXPERIMENT	AGE	TEMPERATURE	$p_i$	$k$
1	New	390°	260 mm	0.00087 sec. <sup>-1</sup>
2	3 hours	380	110	0.00027
3	25	390	146	0.00032
4	29	380	128	0.00017
5	120	390	84	0.00029
6	120	380	182	0.00018
7	144	390	250	0.00034
8	144	380	181	0.00018

<sup>5</sup> D. Brearly, G. B. Kistiakowsky and C. H. Stauffer, J. Am. Chem. Soc. 58, 43 (1936).

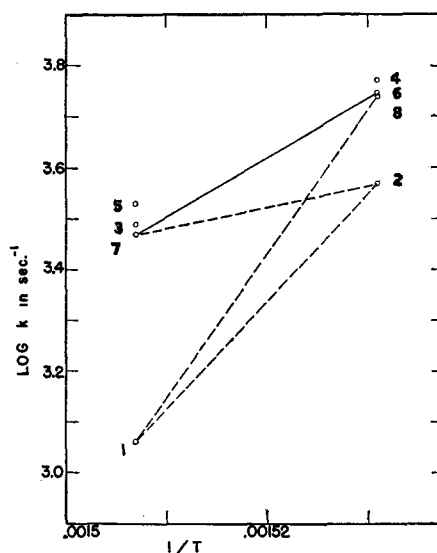


FIG. 3. Calculation of activation energy for ethyl bromide. Full line gives correct value. Broken lines give incorrect values.

The 250-cc vessel having a surface of about 290 cm<sup>2</sup> obtained a normal coating by standing about a day in contact with the decomposition products of the ethyl bromide. After that, the rates were not changed by further aging. In the four-liter vessel (made from two 2-liter flasks) having about 1500 sq. cm of surface the normal, lower values of  $k$  were not obtained until after standing thirteen days. The pressure of gas in

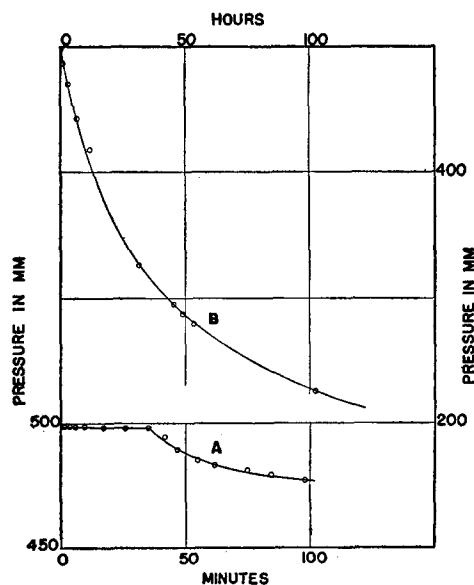


FIG. 4. Decomposition of ethylene at 390°.

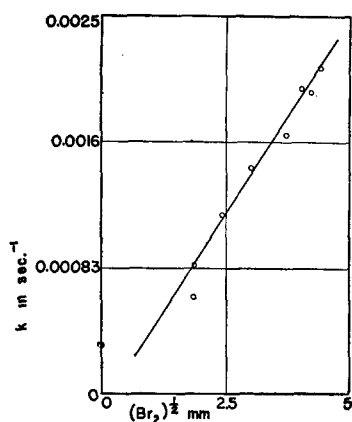


FIG. 5. Influence of bromine on the decomposition.

these experiments was somewhat lower. After the coating had become sufficiently thick the rate constants were the same in the four-liter vessel as in the coated 250-cc vessel.

The time lag is found with both fresh surfaces and coated surfaces. For example in a cleaned flask (250 cc) at 43 mm an initial time lag of six minutes was observed at 390° (Fig. 2) and after the twenty-second consecutive determination in the unopened flask, a time lag of five minutes was obtained at the same temperature with an initial pressure of 65 mm.

It was suspected that this coating on the wall was caused by the polymerization of ethylene which is formed as a product. Accordingly experiments were carried out with purified ethylene using the same vessel and same precautions. One of the resulting pressure-time curves is shown in Fig. 4 where a time lag is definitely shown. After a time lag the pressure starts to decrease and continues for a long time. This reaction has been studied by R. N. Pease.<sup>6</sup>

The film produced on the inside walls of the reaction vessel appeared to be identical with that formed in the ethyl bromide experiments. Moreover, this film produced by the polymerization of ethylene had the same influence on the rate of ethyl bromide decomposition as did the film produced from ethyl bromide itself. It was pointed out in the earlier work that the slow decrease in pressure at the end of an experiment on ethyl bromide is due to the polymerization of the product ethylene. This must account in part

at least for the fact that the final observed pressure is always less than twice the initial pressure.

The wall effect was studied further by depositing on the inner walls a heavy silver mirror and then adding bromine after heating and evacuating. A uniform film of silver bromide was produced. The first determination gave a low rate constant (about one-third) probably because the silver had not been completely converted to the bromide. Six more determinations were carried out and a normal rate constant was obtained in every case. Any effect of glass or of silver bromide is apparently destroyed by the carbonaceous film which is deposited.

It is suggested that the deposition of this carbonaceous film on glass surfaces provides a very simple means for destroying the catalytic effect of walls in other gas phase reactions and that the pyrolysis of many organic compounds could well be investigated under these conditions. The film can be easily deposited by heating ethylene above 400° but the oxygen of the air must be excluded because it causes an acceleration of the reactions and after once coming in contact with the film it cannot be easily removed.

#### Addition of bromine

Bromine is known to accelerate the decomposition of ethyl bromide<sup>1, 3</sup> and its action is important in studying the various reaction mechanisms. Bromine from which oxygen had been boiled out was introduced into a seasoned flask at 390° in amounts up to 18 mm and then ethyl bromide was introduced at 190 mm. The decomposition was accelerated but it still followed the first order with respect to ethyl bromide. The data at 390° in the 250-cc vessel are summarized in Fig. 5 where it is seen that the increase in specific reaction rate is directly proportional to the square root of the bromine concentration, a fact which suggests that bromine atoms are taking part in the reaction. The extrapolation of the line to zero concentration shows that the bromine catalyzes the reaction and suggests that the mechanism may be different.

Two determinations were made at 400° with 12 and 10 mm of bromine giving  $k$  values of 0.00188 and 0.00185, respectively. Combining these data with an interpolated value for 11 mm of bromine at 390° an activation energy of 22,000

<sup>6</sup> R. N. Pease, J. Am. Chem. Soc. **51**, 1838 (1929).

calories per mole is obtained. This value is practically half the heat of dissociation of bromine.

It is believed that bromine did not react at these temperatures to give a dibromo ethane. Mixing the products of one of the determinations with a small amount of 3-5 dinitrobenzoic acid, sodium hydroxide and alcohol gave a product ethyl 3-5 dinitrobenzoate, with a sharp melting point at 91°. If the dibromo compound had been present, the melting point would have been lowered. Furthermore, ethylene bromide would not be expected at 390° because it is unstable. Experiments with ethylene chloride gave rate constants of  $1.3 \times 10^{-3}$  and the ethylene bromide would decompose much faster. The earlier experiments<sup>3</sup> with bromine were carried out at 300° where the conditions were quite different.

#### Addition of nitric oxide

In certain chain reactions, such as the decomposition of the ethers,<sup>7</sup> nitric oxide acts as an inhibitor in small amounts. It is regarded by some as a test for one type of chain reaction. In no case was nitric oxide found to have a retarding effect on the decomposition of ethyl bromide. Even in small quantities the decomposition was accelerated slightly.

#### Reverse reaction

Several unsuccessful attempts were made to detect a reaction between hydrobromic acid and ethylene. The equilibrium constant has not been determined, but calculations show that the dissociation is nearly complete under the conditions studied. The final pressure of decomposed ethyl bromide is always less than twice the initial pressure and it was suggested<sup>2</sup> that this fact is due to the reverse reaction, but in view of the present experiments the polymerization of ethylene produced in the reaction offers a more satisfactory explanation.

#### SUMMARY OF OBSERVATIONS

The coating of the vessel walls with a carbonaceous film makes possible a greater reproducibility and a more accurate determination of the activation energy. According to the data of the present investigation, the activation energy is

<sup>3</sup> L. A. K. Staveley and C. N. Hinshelwood, J. Chem. Soc. 1568 (1937).

53,200 calories per mole. Taking this value for  $E$ , the frequency factor  $s$  in the equation  $k = se^{-E/RT}$  may be evaluated from the three different researches extending over a period of several years as shown in Table II. It is believed that the last data are the more reliable and accordingly the equation

$$k = 1.16 \times 10^{14} e^{-53,200/RT}$$

is offered as the best value for the decomposition rate of ethyl bromide. It represents the behavior out to at least one-third completion at pressures above 130 mm when the catalytic effect of the walls is repressed and oxygen is excluded. Probably it is valid beyond the one-third completion but the pressure measurements described here are not then applicable. The data of the earlier investigation,<sup>2</sup> in which oxygen was less carefully excluded, were fitted with the equation  $k = 3.85 \times 10^{14} e^{-54,800/RT}$ .

The experimental facts described here and in the preceding reports may be summarized with the statements of Table III.

#### DISCUSSION

The primary step cannot be the splitting of the molecule into  $C_2H_4Br$  and  $H$  because this would require about 90,000 calories per mole and only 53,200 calories is available as determined by the experimental measurements of the decomposition rate at different temperatures.

TABLE II. Summary of data for the decomposition rate.

	TEMPERATURE	k OBSERVED	s
Vernon	395°C	$5.92 \times 10^{-4}$	$1.53 \times 10^{14}$
	405	11.1	1.59
	420	25.0	1.50
Fugassi	395	4.10	1.05
	395	4.20	1.08
Veltman	368.5	0.78	1.04
	379.5	2.05	1.34
	380.5	2.08	1.27
	380.6	2.60	1.13
	388.5	2.93	1.10
	398.5	5.27	1.10
		Average	1.17
	380	1.80	1.14
	380	1.81	1.18
	390	3.40	1.15
		Average	1.16

TABLE III. Summary of experimental facts.

1. The reaction  $\text{C}_2\text{H}_5\text{Br} \rightarrow \text{C}_2\text{H}_4 + \text{HBr}$  proceeds conveniently in the temperature range 370 to 420° and follows the first order to at least one-third completion.
2. The data are fitted by the formula

$$k = 1.16 \times 10^{14} e^{-53,200/RT}$$

at pressures above 130 mm.

3. The decomposition rate is doubled or trebled with clean Pyrex walls and by packing with fresh glass.
4. The catalytic effect of the walls is destroyed by the carbonaceous deposit from the decomposing ethyl bromide or from pure ethylene.
5. In reaction chambers coated with this carbonaceous film, the rate constant  $k$  is independent of the size and shape of the vessel.
6. No marked difference in activation energy is observed between the cleaned and coated surfaces, but the accuracy of measurement is not sufficient to distinguish small differences.
7. At pressures below 130 mm the value of the rate constant,  $k$ , decreases as the pressure decreases.
8. Below 130 mm there is a time lag at the beginning of the experiment during which the pressure remains constant.
9. The time lag is not observed in the flow experiments when the reaction is followed by the ethylene obtained at the exit.<sup>3</sup>
10. The time lag is roughly the same with coated walls as with clean glass walls.
11. The small amount of gas (5 percent) other than ethylene consists of hydrogen, ethane, propane, butane in decreasing order of abundance.<sup>3</sup>
12. More hydrogen and ethane are obtained with the flow method.
13. Traces of oxygen accelerate the reaction.
14. Bromine accelerates the reaction and the effect is proportional to the square root of the concentration. It does not change the first-order character.
15. Traces of mercury greatly retard the reaction.
16. Nitrogen and hydrogen increase slightly the low pressure value of  $k$  and then decrease it.<sup>3</sup>
17. Nitric oxide does not retard the decomposition.
18. Decomposing ethyl bromide causes acetaldehyde to decompose at 350° where the acetaldehyde alone is stable.<sup>3</sup>

The splitting into  $\text{CH}_3$  and  $\text{CH}_2\text{Br}$  involves the breaking of the carbon-carbon bond and although there is disagreement concerning this bond energy it is undoubtedly greater than the 53,200 calories which is available. The value is generally taken as 70,000 rendering this step unlikely.

The primary process may be the breakdown into ethyl radicals and bromine atoms. The

energy for breaking the carbon-bromine bond is taken as 53,000 although there is some uncertainty involved when, as in this case, a free radical is formed as one of the products. The reverse reaction between free ethyl radicals and a bromine atom can involve very little activation energy so the activation energy for the reaction  $\text{C}_2\text{H}_5\text{Br} \rightarrow \text{C}_2\text{H}_5 + \text{Br}$  cannot be much larger than 53,000. From energy considerations then, this reaction is quite possible. The unimolecular decomposition directly into  $\text{C}_2\text{H}_4$  and  $\text{HBr}$  is also possible. This reaction absorbs 17,800 calories of heat, and the activation energy for the reaction  $\text{C}_2\text{H}_4 + \text{HBr}$  has been estimated by the semi-empirical method to be about 40,000 calories. The activation energy for  $\text{C}_2\text{H}_5\text{Br} \rightarrow \text{C}_2\text{H}_4 + \text{HBr}$ , then, must be about 58,000 calories and the error of calculation is sufficient for the reaction to go with 53,200 calories.

If the primary step is the formation of  $\text{C}_2\text{H}_5$  and  $\text{Br}$  several secondary reactions may result as shown in Table IV.

If the reactions (b) and (c) follow rapidly after (a), making (a) the rate determining step, most all of the facts may be satisfactorily accounted for. This results in a three-step process designated here as mechanism (I). It involves free radicals but it is not a long chain process. The concentrations of  $\text{C}_2\text{H}_4\text{Br}$  and  $\text{C}_2\text{H}_5$  must be very small, but the activation energy  $E_c$  is so low that the reaction will still be rapid.

If the decomposition of  $\text{C}_2\text{H}_4\text{Br}$  according to Eq. (d) is rapid, the liberated bromine atom will take part in the propagation of a chain by continuing alternations of reactions (b) and (d). This long chain mechanism is designated as mechanism II. Reaction (c) may be regarded as a chain breaking step for mechanism II and the relative importance of I and II is determined simply by the relative rates of reactions (c) and (d).

The straight unimolecular decomposition giving molecules instead of radicals according to reaction (g) is designated as mechanism III.

These three mechanisms and others may now be discussed with reference to the experimental facts listed in Table III.

Undoubtedly the effect of surface walls is important in explaining many of the facts but the wall phenomena are probably of secondary im-

<sup>3</sup>J. Roof and F. Daniels, unpublished.

portance. The striking fact remains that when the polar glass surfaces are covered up with the carbonaceous film and when the initial pressure is kept above 130 mm the decomposition rate is independent of the vessel, the frequency factor is  $10^{14}$  and the reaction behaves as a normal gas phase reaction.

If (a) is slow compared to (b) and (c) (as seems quite likely), and if (c) is fast compared to (d), we can explain the first-order character, the normal frequency factor and the activation energy. If diffusion to the wall is faster than (b) or (d) in the gas phase and if (d) takes place on the wall with the adsorption of ethylene up to a limiting value, we can explain the time lag at low pressures.

The adsorption of free radicals and retention of ethylene or other products on the wall would offset the expected pressure increase and give the observed time lag in the pressure measurements. After the walls become saturated with adsorbed material the normal pressure rise is obtained. Again when the pressure is increased sufficiently, diffusion to the walls is slowed down and reactions (b) and (c) are proportionally more important because reaction (d) cannot compete on the walls. A critical pressure may be expected above which the time lag in the pressure readings would not be observed. In practice such a pressure is noted at about 130 mm.

Mechanism II calls for a long chain reaction. Setting up standard rate equations and steady states it is possible to account for the first-order equation but then the over-all activation energy comes out to be very small. The time lag can be explained on the assumption that it is necessary to accumulate an equilibrium concentration of bromine atoms. The time lag and its restriction to low pressures may be explained also on the hypothesis that reaction (d) occurs on the wall and retains ethylene until the wall is saturated. In mechanism II, however, the over-all activation energy is a function of the several activation energies and there is no reason why it should take on the value 53,000 which seems to be a reasonable value for the primary step, and no reason why the composite frequency factor  $s$  should have the normal value of  $10^{14}$ .

Nearly all the experimental facts concerned with the influence of pressure, walls and added

foreign gas can be explained by either mechanism I or II. The added bromine accelerates (b) and the effect is proportional to the square root of the bromine concentration. Mercury vapor, on the other hand, reacts with bromine and retards (b). The failure of nitric oxide to inhibit the reaction may possibly be construed as evidence against a long chain by mechanism II.

Mechanism III is sufficient to explain many of the observed facts. The few percent of hydrogen and ethane and propane may be due to a condensation reaction of the product ethylene. The increased rate with fresh glass surfaces may involve adsorption and a slight reduction in the activation energy but the doubling of the decomposition rate demands such a slight change in the activa-

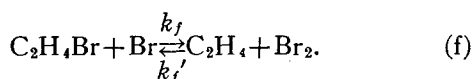
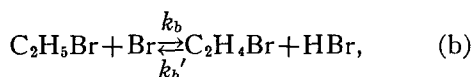
TABLE IV. Summary of reaction steps.

I (THREE-STEP REACTION)		
$\text{C}_2\text{H}_5\text{Br} \xrightleftharpoons[k'_a]{k_a} \text{C}_2\text{H}_5 + \text{Br}$	(a)	
$\text{C}_2\text{H}_5\text{Br} + \text{Br} \xrightleftharpoons[k'_b]{k_b} \text{C}_2\text{H}_4\text{Br} + \text{HBr}$	(b)	
$\text{C}_2\text{H}_4\text{Br} + \text{C}_2\text{H}_5 \xrightleftharpoons[k'_c]{k_c} \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5\text{Br}$	(c)	
II (LONG CHAIN)		
$\text{C}_2\text{H}_5\text{Br} \xrightleftharpoons[k'_a]{k_a} \text{C}_2\text{H}_5 + \text{Br}$	(a)	
$\text{C}_2\text{H}_5\text{Br} + \text{Br} \xrightleftharpoons[k'_b]{k_b} \text{C}_2\text{H}_4\text{Br} + \text{HBr}$	(b)	
$\text{C}_2\text{H}_4\text{Br} \xrightleftharpoons[k'_d]{k_d} \text{C}_2\text{H}_4 + \text{Br}$	(d)	
<i>Chain stopping mechanisms</i>		
$2 \text{Br} \xrightleftharpoons[k_e]{k'_e} \text{Br}_2$	(e)	
$\text{C}_2\text{H}_5\text{Br} + \text{Br} \xrightleftharpoons[k'_b]{k_b} \text{C}_2\text{H}_4\text{Br} + \text{HBr}$	(b)	
$\text{C}_2\text{H}_4\text{Br} + \text{C}_2\text{H}_5 \xrightleftharpoons[k'_c]{k_c} \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5\text{Br}$	(c)	
$\text{C}_2\text{H}_4\text{Br} + \text{Br} \xrightleftharpoons[k'_f]{k_f} \text{C}_2\text{H}_4 + \text{Br}_2$	(f)	
$\text{C}_2\text{H}_5, \text{C}_2\text{H}_4\text{Br}, \text{Br} + \text{wall} \xrightleftharpoons[k_o]{k_o} \text{C}_2\text{H}_4, \text{CH}_4, \text{H}_2, \text{HBr}, \text{C}_3\text{H}_8, \text{etc.}$	(g)	
III (SINGLE STEP)		
$\text{C}_2\text{H}_5\text{Br} \xrightleftharpoons[k'_h]{k_h} \text{C}_2\text{H}_4 + \text{HBr}$	(h)	



tion energy that it cannot be detected with certainty, particularly in view of the lack of consistency obtained with the cleaned glass surfaces. However, the time lag and the marked influence of bromine and traces of oxygen cannot be explained by this mechanism.

The bromine catalyzed reaction can be explained as follows:



The rate of change of each of the substances  $\text{C}_2\text{H}_5\text{Br}$ ,  $\text{Br}$ ,  $\text{C}_2\text{H}_4\text{Br}$ ,  $\text{Br}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{HBr}$  and  $\text{C}_2\text{H}_5$  can be expressed in terms of these equations, giving an over-all equation for the rate of change of pressure  $dp/dt$  as follows:

$$\frac{dp}{dt} = k_b \left( \frac{2k_e}{k_e'} c_{\text{Br}_2} \right)^{\frac{1}{2}} c_{\text{C}_2\text{H}_5\text{Br}}.$$

Here it is assumed that either  $k_b'$  or the concentration of  $\text{HBr}$  is sufficiently small so that the reverse reaction of (b) may be neglected.

The first-order character of the bromine catalyzed reaction can be explained in this way.

The activation energy for this bromine-catalyzed reaction is low (about 22,000 calories) and one might expect a very rapid reaction. However, the experimental facts of Fig. 5 show that at pressures of a few millimeters of bromine it is only about ten times as fast as the uncatalyzed reaction.

It is thus possible to explain the fact that reaction (a) is still the slow, rate determining step in the uncatalyzed reaction. It is possible to explain also the fact that the free radicals have time to diffuse to the walls at low pressures before reacting.

#### THE COLLISION HYPOTHESIS

One of the achievements of the collision hypothesis of chemical reactions has been the explanation of first-order gas reactions and the prediction that the specific rate constants will

decrease at low pressures.<sup>9-11</sup> The quantitative prediction of the pressure range in which this decrease should occur and the apparent checks with experimental data in several reactions were largely responsible for its ready acceptance.<sup>12-15</sup> Two reactions have been intensively studied in this laboratory for the purpose of checking current theories, and in both cases the data were accepted as supporting the collision hypothesis. The specific decomposition rate of ethyl bromide decreased as the pressure was decreased below 100 mm in agreement with the hypothesis. The fact that nitrogen pentoxide gave a decreasing value of  $k$  at pressures below 0.01 mm was regarded as a check even though it was necessary to stretch all the constants to the limit of reasonable values.<sup>16</sup> However, doubt has been expressed<sup>17</sup> that the experimental data of these reactions, and possibly others, necessarily support the quantitative predictions of the collision hypothesis.

In view of the experiments described in the present communication, it seems clear that the decrease in the value of  $k$  for ethyl bromide at pressures below 130 mm is due not to the failure of collisions to maintain a steady state of activated molecules as predicted by the collision hypothesis, but that it is due to the fact that the surface effect becomes appreciable when the time required for diffusion to the walls is short. In the case of nitrogen pentoxide, also, recent experiments seem to confirm the prediction<sup>17</sup> that the decrease in  $k$  is explainable on the basis of simple chemical reactions. At ordinary pressure nitric oxide, produced by the decomposition of nitrogen pentoxide, reacts with another molecule of nitrogen pentoxide so rapidly that the first step, the unimolecular decomposition, of the nitrogen pentoxide is the rate-determining step. However,

<sup>9</sup> J. A. Christiansen, *Reaktionskinetiske Studies* (Copenhagen, 1921).

<sup>10</sup> F. A. Lindemann, *Trans. Faraday Soc.* **17**, 599 (1922).

<sup>11</sup> W. H. Rodebush, *J. Am. Chem. Soc.* **45**, 606 (1923).

<sup>12</sup> C. N. Hinshelwood, *Proc. Roy. Soc. London* **A113**, 230 (1926).

<sup>13</sup> O. K. Rice and H. C. Ramsperger, *J. Am. Chem. Soc.* **49**, 1617 (1927).

<sup>14</sup> R. H. Fowler and E. K. Rideal, *Proc. Roy. Soc. London* **A113**, 570 (1927).

<sup>15</sup> L. S. Kassel, *J. Chem. Phys.* **32**, 1065 (1928); *The Kinetics of Homogeneous Gas Reactions* (The Chemical Catalog Co., New York, 1932), Chapters V and X.

<sup>16</sup> L. S. Kassel, *J. Phys. Chem.* **32**, 225 (1928).

<sup>17</sup> F. Daniels, *Chemical Kinetics* (Cornell University Press, 1938), pp. 71, 72.

it has been found recently that the reaction between nitric oxide and nitrogen pentoxide is measurably slow at one mm, and at still lower pressures it may have a rate comparable with that of the nitrogen pentoxide decomposition, thus accounting for the observed decrease in  $k$  below 0.01 mm.

In the case of ethyl bromide and nitrogen pentoxide, it is safe to state that the decrease in  $k$  observed at lower pressures is not caused by the decreased number of collisions as predicted by the collision hypothesis. It seems likely that a closer examination of other reactions will show that the decrease in  $k$  at the lower pressures can be explained in similar ways, by surface effects or competing chemical reactions which become important at low pressures. The experimental facts may not necessarily constitute a unique support of the collision hypothesis.

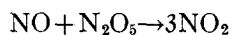
The fundamental concepts of the collision hypothesis must be correct and at some low pressure the first-order character must change to give a rate which depends on the frequency of collision but it is now suggested that this pressure is lower than heretofore believed.

If this suggestion is correct it will be necessary to re-examine the quantitative aspects of the collision hypothesis. Transfer of energy at molecular collision is probably less efficient than was formerly believed but any revision here would apply to the deactivation rate as well as to the activation rate. The simplest way to account for the maintenance of the first-order rate equation down to still lower pressures is to assume a longer life for the activated molecule. A longer life for the activated molecule may mean simply that it is more difficult to localize in the bond which is about to be broken, the energy which has been accumulated from collisions with other molecules. It is difficult to transfer energy from one mode of vibration to another when the absorbed energy is small and the motion is practically harmonic. It is difficult also when the vibration frequencies are widely different. Possibly the energy of vibrating C-H groups picked up by collision with other molecules cannot easily be transferred to the C-Br vibration.

Possibly this view can be checked with the help of photochemical studies on the rupture of complicated molecules, and on the fluorescence of infra-red radiation.

## DISCUSSION

**L. S. Kassel:** The collisional theory can account for the pressure at which nitrogen pentoxide first deviates from first order, but not so easily for the abruptness of this deviation. The slowness of the reaction



at low pressure should thus be considered a help to the theory rather than a difficulty.

The current interpretation of ethane dehydrogenation as a free radical chain, as presented for example by Rice and Herzfeld at this meeting, seems to require that the primary process is a unimolecular reaction in the second-order region.

The unimolecular character of other reactions, such as the azoalkane decompositions, is certainly at least plausible. The suggestion made by Pease in the last paragraph of his paper, that collisional activation over larger distances may prove necessary, seems uncalled for by present

facts. Even the view that no example is known, in which an observed decrease in rate is due to insufficient collisions, causes no difficulty for the present form of the theory. Such difficulty would arise only when some reaction definitely proved unimolecular was found to maintain a first-order rate at a lower pressure than the theory could account for. Such is not the case at present; it seems unnecessary for the theory to be prepared to account for nitrogen pentoxide on the assumption that a slow secondary reaction is quantitatively responsible for the entire decrease in rate down to 0.001 mm, or for other even more hypothetical situations.

**Farrington Daniels, University of Wisconsin:** One can say that the theory is in no need of revision, but I insist that one cannot state that it has been proved in the laboratory.

With reference to the nitrogen pentoxide reaction, we made measurements at 0.01 mm in the

presence of an atmosphere of nitrogen<sup>18</sup> and the specific reaction rate which we obtained falls exactly on the curve through the later low pressure data of Schumacher and Sprenger, Ramsperger and Tolman, and Linhorst and Hodges. In other words, not only does the specific reaction rate start to decrease at such a low pressure that the constants in the collision theory have to be stretched to the limit, but the addition of an inert gas does *not* restore the specific reaction rate to its high pressure value.

**O. K. Rice**, *University of North Carolina*: I wish to emphasize again my remarks on azomethane made in connection with the previous paper. I believe that it is a good example of a quasi-unimolecular reaction and that it offers considerable quantitative support to the theory.

Something should be said about the work of Koblitz and Schumacher and Schumacher and Frisch on the decomposition of  $F_2O$  and  $F_2O_2$ .  $F_2O$  acts like a quasi-unimolecular reaction which is already in the bimolecular stage; in  $F_2O_2$  the falling-off from the unimolecular rate is quite marked. Both rates are increased in the expected manner by inert gases. The collision rates are just about (as a matter of fact, apparently not quite) sufficient to maintain the reaction if everything is stretched to the limit. Schumacher assumed all classical degrees of freedom, and fairly large radii.

**J. A. Christiansen**, *Polytechnic Chemical Institute, Copenhagen*: I think that this discussion is not very useful. It seems to be a question of the experimental facts. If a chain reaction is involved one must know exactly what the chain is and how it is stopped.

**R. N. Pease**, *Princeton University*: I would like to inquire whether anything has been done in coordinating the number of "square terms." Many of us are tired of reading how many equivalent classical square terms are involved. Another thing I hold against the theory is that it has encouraged people to make measurements at very low pressures where much questionable work has been done. It is impossible to carry out chemical

analyses but the theory has given certain weight to the pressure measurements.

**E. P. Wigner**, *Princeton University*: Dr. Kassel has pointed out in his remark that the present theory of quasi-unimolecular reactions cannot predict the pressure at which the unimolecular constant begins to fall off. For some reactions, such as the  $N_2O_5$  dissociation, this occurs at a very low pressure, corresponding to a very large number of active degrees of freedom, for other reactions, such as the  $N_2O$  dissociation, at much higher pressures, corresponding to a strongly reduced number of active degrees of freedom. Without questioning the fundamental correctness of the theory, one may well understand the attitude of the experimenters who feel disappointed by the fact that the theory is so flexible that it is not amenable to proof or disproof by experiments. One would be able to make much more definite predictions on the basis of the Rice-Ramsperger-Kassel theory than is possible at present if it were possible to determine the number of active degrees of freedom on the basis of general considerations. This will necessitate a rather close study of the interactions of vibrations etc. in the dissociating molecule.

One can see rather simply that the conditions may be more complicated than we are used to think that they are. As long as we restrict ourselves to a harmonic potential, i.e., neglect the anharmonicity, it is clear that not all molecules which contain the activation energy are really activated. In fact, as long as we neglect anharmonicity, the amplitudes of the different proper vibrations must be in a definite ratio in order to enable the system to reach the activation point. Deviations from this ratio make necessary a larger energy content for the molecule to be dissociated. It follows from this that the number  $n$  in the expression  $(Q/kT)^{\frac{1}{2}n-1} \exp(-Q/kT)/(\frac{1}{2}n-1)!$  is not equal to the number of square terms in the energy expression but is in general smaller. Its exact value depends on the form of the proper vibrations with respect to the bond to be broken.

Of course, at very low pressures, the molecule will be left alone for a very long time and the anharmonic terms will bring about a redistribution of the total energy among the proper vibra-

<sup>18</sup> J. K. Hunt and F. Daniels, *J. Am. Chem. Soc.* **47**, 1602 (1925).

tions, until this corresponds to the one in which a dissociation is possible. Under extremely low pressures, therefore, the  $n$  in the above expression for the number of activated molecules is equal to the number of square terms in the energy. This corresponds, however, to extremely low pressures.

At higher pressures, only those molecules will be able to dissociate in which the total energy is approximately correctly distributed over the proper vibrations. Thus  $n$  will be very much smaller and its value depends on the properties of the proper vibrations. The result of all this is that the zone of transition between bimolecular to unimolecular reaction is very much broader than has been assumed hitherto. Under certain conditions, there may be even an intermediate zone in which the reaction is apparently unimolecular. At any rate, special properties of the dissociating molecule can play a very important role.

**O. K. Rice, *University of North Carolina*:** In a paper written in 1930 I suggested the possibility of the behavior described by Professor Wigner in his comment. But I do not believe that it is a necessary kind of behavior, and in the case of azomethane which has a reasonable value for  $n$ , I do not believe that it occurs.

**F. O. Rice, *Catholic University of America*:** What is meant by a clean surface? How did you keep the glass walls clean after the first few seconds of the reaction?

**Farrington Daniels, *University of Wisconsin*:** We cleaned the surface to start with. In successive determinations the specific reaction rate was slower but after three or four experiments, starting with 100 mm of ethyl bromide, the rate constant didn't change any more. Apparently this treatment is sufficient to cover up the active spots on the polar glass surface and give the appearance of a dark film as shown in the photograph. During the first determination or two the progressive increase in the dirtiness of the surface is certainly a complication for the determination of the decomposition rate.

**F. O. Rice, *Catholic University of America*:** Did you sensitize the reaction?

**Farrington Daniels, *University of Wisconsin*:** Yes. We mixed ethyl bromide with acetaldehyde at temperatures at which there would be no decomposition of acetaldehyde alone and found that the acetaldehyde decomposed rapidly. We took this as evidence that ethyl bromide in decomposing liberates free ethyl radicals which initiate chains in the acetaldehyde.

I do not believe that there are long chains involved in the decomposition of the ethyl bromide itself.

There is an apparent difficulty. The activation energy for the decomposition of ethyl bromide is 53,800, for methyl bromide it is probably considerably larger, and for propyl bromide it is considerably less (apparently about 36,000 though complicated by isomerization to isopropyl bromide). Each of these decompositions is thought to involve the rupture of the carbon-bromine bond in the primary step, amounting to about 53,000 calories.

**R. A. Ogg, Jr., *Stanford University*:** The difference in activation energy must be due to a difference in the behavior of the radicals and the rapid subsequent reactions which the heavier radicals can undergo.

**Farrington Daniels, *University of Wisconsin*:** For those interested in settling the controversy regarding the pressure effect on unimolecular reactions, there are at least two lines to follow. The theorists should try to make calculations regarding the movement of energy inside of complex molecules and the experimentalists must certainly get more reliable data on simple gas reactions at very low pressures. Pressure measurements which include the gross effect of several reactions and possible wall effects are not very satisfactory. New techniques and new methods of following reactions by optical or other physical or chemical methods are needed. Large scale experiments with very large tubes to minimize wall effects would be valuable.