$TiClO_4^{++}$ and that this is followed by a rapid reaction between the addition compound and trivalent titanium. It may be noted that the results of the present research, as well as those of Bredig and Michel, could be interpreted by assuming the slow production of quinquivalent titanium to be the first stage in the reaction. There is no independent experimental evidence either for the addition compounds referred to above or for the existence of quinquivalent titanium. The fact, however, that ionic reactions of metathesis and of addition are usually rapid makes it more probable that the slow step in ionic reactions is commonly due to valence changes.

Summary

The rate of the reaction between iodine and trivalent titanium has been measured and found to be directly proportional to the concentrations of trivalent titanium and triiodide ion and inversely proportional to the concentrations of hydrogen ion and iodide ion. Taking into account the triiodide-iodine equilibrium and the probable hydrolysis of trivalent titanium salts, this is shown to correspond to a slow reaction between iodine and $TiOH^{++}$. This fact is not in agreement with the formation of hypo-iodous acid as an intermediate compound. The results could be explained by assuming the slow formation from $Ti(OH)^{++}$ and iodine of an addition product which in turn reacts rapidly with more $Ti(OH)^{++}$ to give the final products of the reaction. A mechanism is also suggested which involves the existence of quinquevalent titanium.

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THE RATE OF THE REACTION BETWEEN ETHYLENE AND CHLORINE

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Previous Work

The rate of the reaction between gaseous ethylene and gaseous bromine, diluted with air, was determined by Stewart and Edlund.[1] They found a second-order reaction taking place exclusively on the walls of the glass vessel containing the gaseous mixture and showed that the pressure of water vapor had a marked effect on the rate of the reaction. Norrish[2] studied the same reaction in a glass vessel and in glass vessels coated with paraffin wax, stearic acid and cetyl alcohol. The relative rates of the four reactions were approximately as follows: paraffin 1, cetyl alcohol 9,

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[1] Stewart and Edlund, This Journal, **45**, 1014 (1923).

[2] Norrish, *J. Chem. Soc.*, **123**, 3006 (1923).

dry glass 17,[3] stearic acid 29. He observed in the case of the paraffin-coated vessel an induction period of about one minute's duration. The start of the reaction after this period seemed to be sharp and normal, and he drew the conclusion that *no* reaction took place on the paraffin surface but that after the induction period the reaction "may be a result of diffusion of the reactants through cracks in the wax to the underlying glass surface."[4] Stewart and Edlund found that the specific reaction rate constants were closely proportional to the surface-volume ratio of the containing vessel, and since it is hardly possible that from 3 to 5% of the glass in Norrish's experiment was not covered by paraffin, we must conclude that the reaction did take place at a measurable rate at the paraffin surface. Diffusion through even a thin layer of paraffin would be too slow to account for the effect. The observation that cracks in the paraffin were marked by the presence of bromine dissolved in ethylene bromide indicates that the reaction, for the most part, did take place locally, started, perhaps, at a point where glass was actually exposed or, better, where a crack in the paraffin offered a relatively large surface. At this point ethylene bromide separated as a liquid almost immediately, and the reaction from then on was catalyzed by the presence of liquid ethylene bromide. This phenomenon has been repeatedly observed in the case of ethylene and chlorine, namely, that at a point where ethylene chloride separates when the reacting gases are flowing through a tube, the reaction is rapid enough to warm the tube and the sphere of reaction, as marked by the condensing liquid and heat, will extend along the tube against the direction of flow of the gases. Presumably liquid ethylene bromide and ethylene chloride are non-polar liquids and by forming on the glass surface should inhibit rather than accelerate the reaction.

Although the comparative polarity of surfaces undoubtedly has an influence on the reaction between ethylene and bromine or chlorine, the basic cause of the influence is still in question. The results of Norrish could be explained by assuming that the different types of surface influenced greatly the deposition of liquid ethylene bromide. About 90% of the total ethylene bromide formed in his reaction separated as liquid during the reaction. If this formed a uniform film over the surface a rapid reaction could be expected. If it formed in droplets a slower reaction could be expected, assuming that the rate on the uncovered surface was slow compared with the rate on the surface of the droplet. If the liquid separated only with points where the glass was exposed or the surface broken and did not spread

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[3] Stewart and Edlund dried their reaction vessels at room temperature in a stream of air dried by phosphorus pentoxide. The reaction vessels of Norrish were apparently dried to the same extent. In both cases the gases were dried by phosphorus pentoxide. Stewart and Edlund found that the introduction of 1.5 mm. of mercury pressure of water vapor increased the reaction rate about two- to three-fold.

[4] Ref. 2, p. 3015.

rapidly, the phenomenon observed by Norrish would be expected. It is obvious that a paraffined surface catalyzes the reaction less than does a dry glass surface, but the difference between the effect of paraffin, cetyl alcohol and stearic acid could easily be due to mechanical differences in the surface. A stearic acid surface is greatly different in appearance from the surfaces of paraffin or cetyl alcohol. It is more obviously crystalline, and could readily contain throughout the mass the cracks that in paraffin seem so efficient as catalysts. Moreover, ethylene bromide more readily "wets" a stearic acid or cetyl alcohol surface than it does a paraffin surface so that if a reaction sphere started, due to any cause, it might be expected to extend its effective area rapidly by the spreading of the film of ethylene bromide.

The observed induction period in the case of the paraffined wall may be due to the existence of a very slow reaction up to the time when the gas phase becomes saturated with respect to ethylene bromide. As the liquid separates, the reaction is catalyzed greatly and unless the extension of the effective catalytic area is very slow an apparently normal reaction will follow. The flow method used in filling the reaction vessel with the reacting gases offered an opportunity in the case of a fast reaction for the walls to become covered with ethylene bromide before the initial reading was taken, and in the case of the slow reaction the gas phase was probably very nearly saturated. In fact, the induction period observed may have been due simply to supersaturation of the gaseous ethylene bromide. The numerous uncertainties involved make it desirable to re-test the effect of these catalysts under such conditions that ethylene bromide does not separate as a liquid. Work along this line is under way in this Laboratory.

Discussion of Results

The present paper deals with the reaction between ethylene and chlorine gases, mixed with dry air. The reaction is much slower than the reaction between ethylene and bromine. The specific reaction rate calculated for a bimolecular reaction between gaseous ethylene and gaseous chlorine, mixed with dry air, and contained in dry glass vessels at about 17°, is about $K'' = 1 \times 10^{-4}$ to 3×10^{-4} for a 2cm. tube, and about $K'' = 3 \times 10^{-5}$ to 5×10^{-5} for a 2000cc. bulb. Calculated for a 2cm. tube, the corresponding specific reaction rate for ethylene and bromine at 0° is about $K'' = 4 \times 10^{-3}$. The ratio of the surface-volume ratios for a 2cm. tube and a 2000cc. bulb is about 5. The average values of the specific reaction rate constants for the two containers are about 20×10^{-5} and 4×10^{-5}, respectively. The reaction between ethylene and chlorine is purely a wall reaction, the rate of which is proportional to the surface-volume ratio of the containing vessel. The rate of the reaction is assumed to be proportional to the partial pressures of ethylene and chlorine, respectively.

Only a few of the preliminary experiments are recorded here. There is evidence that the reaction may be, to some extent, autocatalytic. In some of the plots obtained, analogous to those given in Fig. 2, there was a noticeable and unaccountable dip in the curve, extending over the first ten to twenty minutes of the reaction. In some cases no actual dip occurred. This phenomenon was marked in the first experiment (not given) and in later experiments where an oil manometer was used to increase the accuracy of the readings. In any given experiment there was no certain trend in the values of the specific-rate constant that could not be accounted for by experimental error and yet, as in Expt. II, the rate of the reaction in the 2cm. tube was often faster for the second sample than for the first, although the same original gas mixture was involved, and the only difference in the two lay in the fact that the products of reaction from the first sample were perhaps incompletely evacuated from the reaction chamber before admitting the second sample. Correspondingly, in Expt. III the rate of the reaction in the large bulb for the first 75 minutes seemed to be less than for the succeeding 100 minutes. These inconsistencies make it probable that the reaction is more susceptible to surface conditions than the faster reaction between ethylene and bromine.

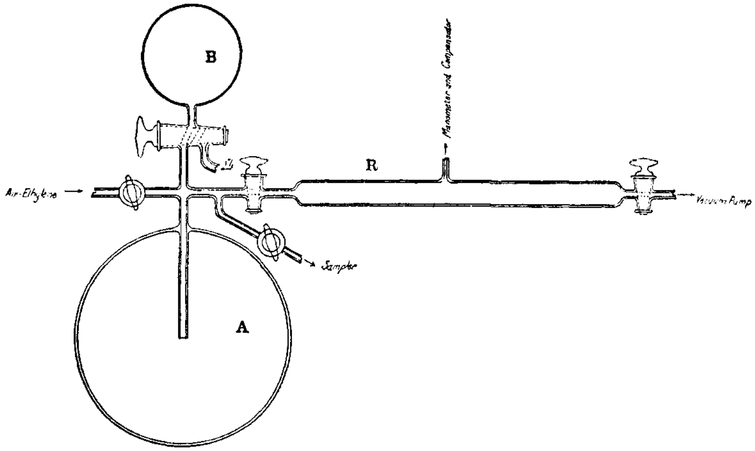

Fig. 1.

Experimental Method

A large bulb A, of 2110 cc. capacity, was connected by means of stopcocks to a small bulb B, of 108 cc. capacity, to a reaction tube R and to a reservoir of ethylene-air mixture under pressure. The small bulb B was filled at atmospheric pressure with pure chlorine. The large bulb A and reaction chamber R were then evacuated to a measured pressure and the stopcock between A and R closed. The chlorine in B was then allowed to expand from B into A, the stopcock between A and B was closed and A then opened to the reservoir of dry ethylene and air. The total pressure in A was built up to 12 cm. of mercury pressure in excess of atmospheric pressure. From the volume of A and B the partial pressure of chlorine in B could be calculated and, from the total pressure and percentage composition of the ethylene-air mixture, the mole fraction and partial pressure of the other constituents could be calculated. The mixing was tested by means of blank runs, using air only, and withdrawing samples for analysis. The agreement between the calculated and found values for the concentration of chlorine was within 5% and sufficiently good for the purpose, inasmuch as the initial concentration of the chlorine was to be obtained more accurately by assuming that the observed pressure drop during the reaction $C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$ at constant volume was equal to the chlorine concentration. The initial chlorine concentration was taken as equal to the total pressure drop.

The known mixture of ethylene and chlorine was allowed to expand into the evacuated reaction tube R. This tube was of Pyrex glass, closed at each end by a stopcock, and connected through a manometer to a compensating tube of corresponding dimensions. The tube was 20 cm. long and about 2 cm. in diameter, with a capacity of 64 cc. It had been cleaned with cleaning mixture, washed out with ammonia and distilled water and dried in a stream of dry air. After the reaction tube was filled with the reacting gases from A and the stopcock between A and R closed, both R and the compensator were opened to atmospheric pressure, closed again, and the zero reading of the manometer was taken. The manometer liquid at first was mercury covered on both sides with a layer of α-bromonaphthalene.

The manometer was read at convenient intervals and the pressure drop plotted against the time. From two to five minutes elapsed between the mixing of the constituents and what was taken as zero time. Of this time, only thirty seconds was required to admit the gases to the reaction tube, adjust the pressure and take the first reading of the manometer.

The bulbs A and B, the tube R and the compensator were immersed in a very large water thermostat which was thoroughly stirred. The stopcocks were greased with phosphoric acid and protected from the water by rubber thimbles and vaseline. The temperature was not regulated, but the bath was so large that the temperature rose not more than 0.5° during a run, and usually changed but 0.1° to 0.2°.

The reaction proceeded simultaneously in both A and R, but was practically complete in the small tube R when only about one-third complete in the large bulb A. At the conclusion of the first run in R, R was evacuated and refilled from A. The pressure drop of the second run in R could be used as a measure of the unreacted chlorine in A at the time when the second sample was taken. Making proper corrections for pressure changes in A, due to the filling of R, data were obtained for calculating the specific reaction rate in A as well as in R. Later, at the conclusion of the first run in R, the manometer was connected directly to A and the pressure drop due to the last two-thirds (approximately) of the reaction was measured directly.

The ethylene was always in large excess. The chlorine concentration was such as to prevent deposition of liquid ethylene chloride.

The ethylene was prepared from ethylene dibromide and zinc and purified according to the method used by Stewart and Edlund.[1] The chlorine was prepared from pure concd. hydrochloric acid and potassium permanganate, washed with permanganate solution and dried by concd. sulfuric acid.

All the experiments were conducted under water in a room illuminated by electric lights.

Experimental Results

The results of Expt. I are omitted since they were not essentially different from those of II and III. Tables I and II describe the conditions of each experiment. The first column gives the time in minutes from the first manometer reading; the second, the corresponding pressure drop in millimeters of mercury; the third, the partial pressure of chlorine, which was obtained for zero time by extrapolating the pressure drop graphically to infinite time; the fourth, the partial pressure of ethylene, which was obtained for zero time from analysis of a sample from the gas reservoir, and corrections for the dilution caused by admixture with chlorine and for the changes in the total pressure of the system. Column five gives the

TABLE I

EXPT. I OMITTED

THE RATE OF REACTION OF ETHYLENE AND CHLORINE AT 16.5°

EXPT. II

PART A. REACTION IN 2CM. TUBE

Time, min.	Pressure drop Mm. of Hg	Chlorine pres. Mm. of Hg	Ethylene pres. Mm. of Hg	$K'' \times 10^4$
0	0.0	32.0	144.6	..
5	2.5	29.5	142.1	1.13
10	4.2	27.8	140.4	0.84
15	6.0	26.0	138.6	.96
20	7.6	24.4	137.0	.92
25	9.4	22.6	135.2	1.12
50	16.5	15.5	128.1	..
55	17.7	14.3	126.9	1.26
70	21.2	10.8	123.4	..
75	22.3	9.7	122.3	1.73
100	26.3	5.7	118.3	..
105	26.8	5.2	117.8	1.56
120	28.0	4.0	116.6	..
125	28.3	3.7	116.3	1.38
∞	32.0			Av. 1.21

Table I (*Concluded*)

Part B. Reaction in 2cm. Tube, Filled at Conclusion of Part A

Time, min.,	Pressure drop Mm. of Hg	Chlorine pres. Mm. of Hg	Ethylene pres. Mm. of Hg	$K'' \times 10^4$
0	0.0	18.0	132.3	..
10	5.0	13.0	127.3	2.51
20	7.5	10.5	124.8	1.70
40	11.7	6.3	120.6	..
50	13.2	4.8	119.1	2.27
70	15.0	3.0	117.3	..
80	15.7	2.3	116.6	2.25
∞	18.0			Av. 2.18

Part C. Reaction in 2110cc. Bulb. Reaction Concurrent with Part A

Using the extrapolated pressure drop of Part B as a measure of the unused chlorine in Bulb A at the time t = 131 minutes, and making proper correction for changes in pressure due to the manipulation of the system, $K''_{0\text{-}131} = 3.1 \times 10^{-5}$.

Table II

The Rate of Reaction of Ethylene and Chlorine at 17.5°

Expt. III

Part A. Reaction in 2cm. Tube

Time, min.	Pressure drop Mm. of Hg	Chlorine pres. Mm. of Hg	Ethylene pres. Mm. of Hg	$K'' \times 10^4$
0	0.0	32.0	144.6	..
5	5.7	26.3	138.9	2.77
10	9.9	22.1	134.7	2.54
15	13.5	18.5	131.1	2.68
20	16.6	15.4	128.0	2.83
25	19.5	12.5	125.1	3.30
30	22.1	9.9	122.5	3.77
40	25.5	6.5	119.1	..
45	26.9	5.1	117.7	4.10
60	29.1	2.9	115.5	..
65	29.5	2.5	115.1	2.57
∞	32			Av. 3.07

Part B. Reaction in 2110cc. Bulb, at Conclusion of Part A

				$K'' \times 10^4$
0	0.0	20.0	132.3	..
5	0.8	19.2	131.5	6.3
10	1.5	18.5	130.8	5.66
15	2.18	17.8	130.1	5.92
50	6.6	13.4	125.7	..
55	7.2	12.8	125.1	7.3
100	12.0	8.0	120.3	..
105	12.4	7.6	119.9	8.4
∞	20.0	..		Av. 6.7

Part C. Reaction in 2110cc. Bulb. Concurrent with Part A

Time 0—75 minutes, $K'' = 4.2 \times 10^{-5}$.

specific reaction rate calculated by intervals for a second-order reaction. The ethylene was in large excess, hence the constancy of K'' cannot be taken as proof of a second-order reaction. The results of previous work warrant the assumption, however, and the values of K'' serve as a means of comparison of the results in the different experiments.

Fig. 2 contains for each experiment the pressure drop in millimeters of mercury plotted against the time. A given Roman numeral denotes a given gas mixture, the letters A and B denote different parts or samples of that mixture.

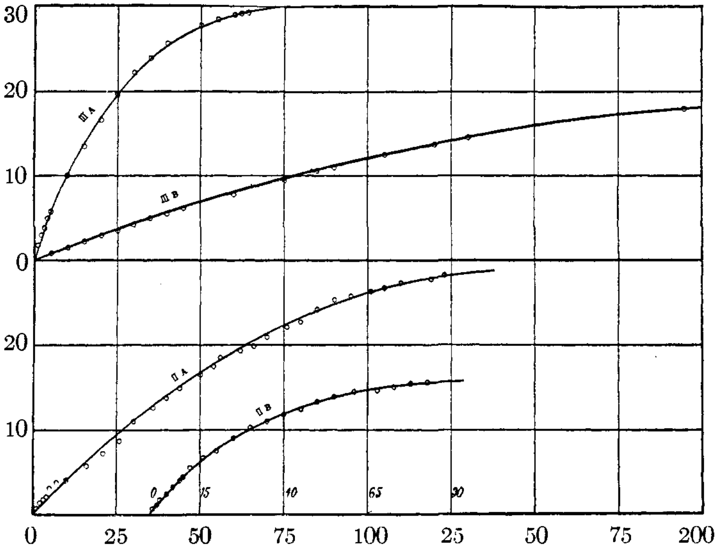

Fig. 2.

Summary

The rate of the reaction between gaseous chlorine and gaseous ethylene, mixed with dry air and contained in glass vessels, has been determined. The reaction is a purely surface reaction, and at 17° is approximately one-tenth as rapid as is the reaction between ethylene and bromine at 0°. Some inconsistencies in the reaction have been noted.

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