234. *The Thermal Combination of Ethylene and Bromine at Glass Surfaces. Part I. General Kinetics of the Reaction at* 16°.

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In the course of some unpublished work upon the thermal interaction of bromine and vinyl bromide vapours at a glass surface, it has been observed that the rate of reaction decreases with rise of temperature. The kinetics of this reaction are complicated (at ordinary temperatures) by the fact that the reaction product separates out upon the walls of the containing vessel as a liquid film, through which the reactants have to pass in order to reach the catalysing glass; and it seemed possible that the temperature effect might be due to a diminution in the solubility of the reactants in the product with rising temperature. It was thought that this possibility might be tested by a comparison with the bromine–ethylene reaction, in which the formation of a liquid film of reaction product can be avoided. The latter has been shown previously to be a surface reaction at 0° (Stewart and Edlund, *J. Amer. Chem. Soc.*, 1923, **45**, 1014), proceeding at a rate which varies with the polar nature of the surface (Norrish, J., 1923, **123**, 3006). In both investigations the reaction was made to take place in the presence of large amounts of air and, under these conditions, the process was found to be of the second order. The rate was increased by the presence of moisture. It has generally been supposed (compare, *e.g.*, Schwab, " Die Katalyse," Berlin, 1931, p. 159) that bromine and ethylene are both adsorbed to a slight extent on the walls, where they interact in a simple bimolecular surface reaction. However, no data have been recorded for the temperature coefficient of the bromine–ethylene reaction and the kinetics have hitherto been investigated only over a rather restricted pressure range.

New experiments have therefore been performed over extended pressure, temperature, and surface conditions, and Part I describes the kinetics at ordinary temperatures and at pressures low enough to ensure that no part of the product condenses as a liquid during the reaction. It may be stated at once that the rate of reaction decreases with rising temperature and that the simple theory mentioned above does not account for all the facts. Part II (following paper) is concerned with the part played by water in the bromine–ethylene reaction; the effects of (*a*) higher temperatures, and (*b*) the separation of a liquid film will be dealt with later.

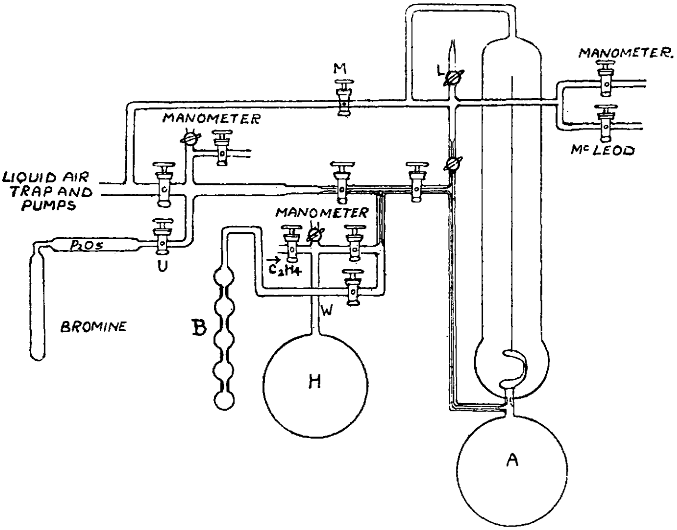
EXPERIMENTAL.

Materials.—Bromine. Kahlbaum's bromine "for analysis" was shaken with dilute potassium hydroxide solution (Scott, J., 1913, **103**, 847), separated from the aqueous layer, and dried by standing for 3 days with phosphoric oxide. It was then distilled, and the middle fraction was again distilled, once from potassium bromide and twice from phosphoric oxide, pure Kahlbaum materials being used in all cases. The product was finally collected in the bromine store tube of the apparatus, where the vapour was in permanent contact with phosphoric oxide. Finally, the bromine was repeatedly frozen with liquid air and pumped out with a Hyvac pump until permanent gas could no longer be detected, its pressure then being less than 10^{-3} mm. (compare Smits and Swart, J., 1929, 2724, for a discussion of the effectiveness of this procedure for removing permanent gas).

Ethylene. This was prepared by the action of redistilled ethylene dibromide upon zinc dust in alcoholic suspension (Moser, "Die Reindarstellung von Gasen," Stuttgart, 1920) and freed from alcohol vapour and any traces of halogens by passage through potassium hydroxide solution and a tube cooled in carbon dioxide snow. The gas was collected over water in an aspirator, whence it was drawn as required and further purified as follows. After passage over calcium chloride and phosphoric oxide, it was frozen by a liquid-air bath and pumped free of admixed permanent gases. It was then melted and the liquid twice fractionated, the middle portion being taken each time. The final fraction was evaporated through a phosphoric oxide tube into a bulb H (Fig. 1) of 200 c.c. capacity, in which it was stored at a pressure of about 550 mm. From this bulb the gas passed directly into the reaction vessel.

Methods of Measurement.—The rate of reaction was determined by following the change in pressure in a mixture of ethylene and bromine vapour by means of a glass Bourdon gauge. The latter was generally used as a null instrument, the pressure of the reaction mixture inside the membrane being balanced against a measured air pressure in the gauge envelope, controlled by admitting air through tap L (Fig. 1) or removing air with the pump through tap M. The needle of the Bourdon gauge was read through a telescope having a scale in the eye-piece, and the pressure of air in the gauge envelope was measured to 0·01 mm. on a mercury manometer. With most of the gauges, the order of accuracy in reading the position of the needle was the same as that in reading the mercury manometer. For work at low pressures (1—2 mm.) a more sensitive gauge was calibrated for use as an absolute measuring instrument; this gave a deflexion of about 30 scale divisions in the eye piece to 1 mm. pressure change.

FIG. 1.



The reaction vessel was a glass bulb A of about 150—200 c.c. capacity connected to the inside of the gauge membrane. At the commencement of a series of runs the reaction bulb was cleaned with alcohol, chromic acid, and distilled water, and then steamed and dried, after which it was either sealed on or attached by a ground-glass joint. Before each run the apparatus was evacuated to less than 10^{-3} mm. by means of a Hyvac pump, protected from corrosive vapours by a liquid-air trap. For certain experiments an initial pressure of less than 10^{-5} mm. was attained with a diffusion pump. The pressures during the initial pumping operations were measured on a McLeod gauge.

When the apparatus had been evacuated, the pumps were shut off from the reaction system and the tap connecting the two sides of the gauge membrane was closed. Dry bromine vapour was admitted through a hollow-barrel tap U and its pressure in the reaction bulb measured. Ethylene was let in from the store bulb H, its initial pressure in the reaction system being calculated from the pressure change indicated by the manometer attached to H, which was read with a cathetometer, and the previously determined ratio of the volume of the ethylene store system to that of the reaction system. A high pressure of gas was kept in H and back-diffusion of bromine at the moment of entry of ethylene from H was imperceptible. The time of admission of the second reactant was noted, and the change of pressure in the reaction system was followed by withdrawing air from the gauge envelope so as to deflect the needle, observing the time at which it crossed the zero mark, and measuring the corresponding air pressures in the envelope.

Since the reaction is slightly photosensitive, precautions were taken to exclude light. The whole of the reaction system—bulb and gauge—and also the ethylene store bulb were contained in a water thermostat with electrical stirring. All taps were lubricated with low-vapour-pressure grease supplied by Messrs. Metropolitan Vickers and subsequently sold as Shell " Apiezon " grease. This proved to be sufficiently stable to bromine. A test of the stability of bromine vapour in the apparatus showed a pressure fall of 0·02 mm. in 150 mins. on a total bromine pressure of 8 mm.

Discussion of Results.

Course of the Reaction.—Throughout these experiments, pressures are expressed in mm. of mercury and time in minutes.

Let p_0 be the total initial pressure in the reaction system, p the pressure at time t, x the pressure of either reactant used up at time t, and P the vapour pressure of ethylene dibromide. Then, if the reaction follows the equation

$$C_2H_4 + Br_2 = C_2H_4Br_2 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

we have $x = p_0 - p$ if $p_0 - p$ is less than P,

or $x = (p_0 - p + P)/2$ if $p_0 - p$ is greater than P.

The vapour pressure P (in mm.) of ethylene dibromide at absolute temperature $T°$ is given by the following equation over the range 10—150° C (" International Critical Tables," Vol. III, p. 216) :

$$\log_{10} P = - 0{\cdot}05223 \times 38{,}082/T + 7{\cdot}792 \quad . \quad . \quad . \quad (2)$$

whence $P = 8{\cdot}13$ mm. at 16° C. Consequently it is necessary at this temperature to keep the pressure of one reactant at 8 mm. or less in order to avoid the separation of liquid ethylene dibromide.

The validity of equation (1) can be tested by observing the total fall in pressure when reaction is complete. Table I gives some results for the end-point of the reaction with various initial proportions of ethylene and bromine.

The results of Table I fall into two categories: (A) When the reactants are present in equivalent proportion, or when ethylene is in excess, the final fall in pressure approximates to that for a simple addition reaction; (B) when excess of bromine is present addition is accompanied or succeeded by some other reaction occurring with diminution in pressure. A substitution reaction seems to be excluded, since attempts, both qualitative and quantitative, to detect the formation of hydrogen bromide by freezing out the reaction products in a bulb (B, Fig. 1), which was subsequently opened under a solution of potassium iodide and iodate, have hitherto given negative results. Control experiments with added hydrogen bromide proved the validity of the method of testing. The absence of a substitution reaction is rather in accord with general preparative experience, according to which marked substitution takes place in the reaction between ethylene and chlorine, but not in that between ethylene and bromine (Bahr and Zieler, *Z. angew. Chem.*, 1930, **43**, 233; compare Stewart and Smith, *J. Amer. Chem. Soc.*, 1929, **51**, 3082; 1930, **52**, 2869).

TABLE I.

					Final pressure-fall.	
No.	Temp.	C_2H_4.	Br_2.	Reaction order.	Calc.	Obs.
(A) 163	16°	7·84	7·86	1st	7·84	7·88
97	12	53	52	—*	96·5	93
98	0	53	52	—*	106	104
141	16	51·5	7·64	2nd	7·64	8·06
(B) 213	16	6·99	7·86	Zero	6·99	7·75
252	16	8·54	14·83	1st	8·95	11·14
204	16	8·83	23·92	1st	9·53	13·37
133	16	9·60	43·60	—†	11·07	17·50

* Reactions retarded by condensing products.

† Reaction too rapid for determination of order.

It is known that neither substitution nor polymerisation ordinarily occurs with ethylene at the temperatures employed and, moreover, it has been found that neither ethylene nor bromine separately reacts appreciably with ethylene dibromide vapour in the dark at 16°; also that ethylene and hydrogen bromide do not react in a glass bulb at 16° over a period of 50 minutes, and that the presence of hydrogen bromide does not increase the speed of the bromine–ethylene reaction, as shown below:

No.	C_2H_4.	Br_2.	HBr.	k_1.
245	8·54	7·86	—	0·0140
248	8·00	7·86	2·22	0·0145
249	7·90	7·86	4·96	0·0130

The occurrence of a supplementary reaction, with high bromine pressures, in the present experiments therefore seems to point to the production of some excited molecular species during the bromine–ethylene reaction under these conditions. If this is so, a polymerisation either of ethylene or of a primary brominated product (such as a radical C_2H_4Br) seems a possibility. Emeléus and Taylor (*J. Amer. Chem. Soc.*, 1931, **53**, 562, 3370) have found that ethylene undergoes induced polymerisation at room temperature during the photochemical reaction with ammonia. Attempts to collect and analyse the bromination products of ethylene have hitherto given inconclusive results owing to the very small amounts available with the experimental conditions employed. Traces of non-volatile products were observed.

In view of the uncertainty regarding the nature of the secondary reaction, the experiments described in this and the following paper have been confined, in the main, to reactant ratios similar to those of Table I (A), with which the simple addition reaction predominates.

Order of Reaction.—As mentioned earlier, previous workers have found the bromine–ethylene reaction to be of the second order at 0°, in the presence of air. The earlier experiments in the present series also gave bimolecular reactions, but it was soon found that the order was not necessarily the same in different glass bulbs and reactions of order 0, 1, and 2 have been observed with different surfaces, as shown below, the symbols k_0, k_1, and k_2 being the corresponding velocity coefficients.

Expt. 116. $C_2H_4 = Br_2 = 11·50$ mm. Temp. 16°.

t.	p.	$p_0 - p$.	Change, %.	$k_2 \times 10^4$.
0	23·00	—	—	—
2·00	22·34	0·66	5·7	26
7·40	21·96	1·04	9·0	12
14·30	21·16	1·84	16·0	12
23·8	20·50	2·50	21·7	10
40·4	19·38	3·62	31·5	10
65·2	18·08	4·92	42·8	10
113	16·42	6·58	58·1	10
136	15·92	7·08	61·5	10
163	15·18	7·82	68·0	11
214	14·42	8·58	72·7	11
258	13·76	9·24	75·5	10

Expt. 124. $C_2H_4 = Br_2 = 8·00$ mm.

0	16·00	—	—	—
11·50	15·34	0·66	8·3	9·8
29·0	14·04	1·96	24·5	14·0
49·0	13·02	2·98	37·3	15·1
93·0	11·48	4·52	56·5	13·1
143	10·54	5·46	68·3	18·8

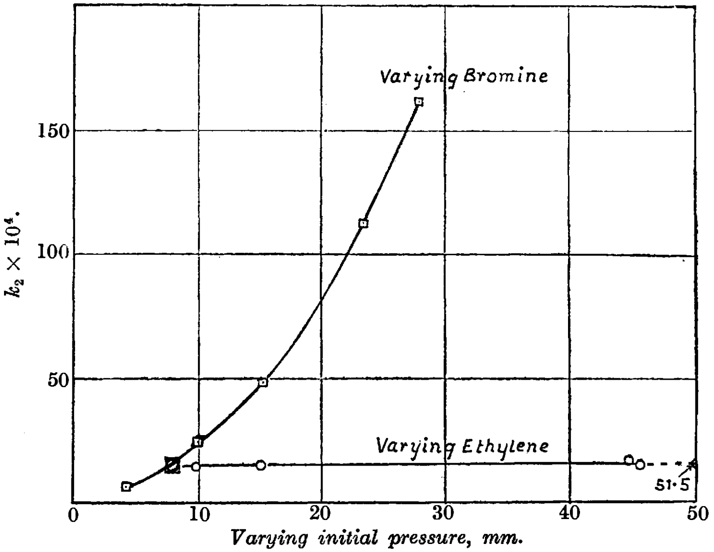
Expt. 227. $C_2H_4 = 7·44$ mm. $Br_2 = 7·90$ mm. Temp. 16°.

t.	p.	$p_0 - p$.	Change, %.	$k_1 \times 10^4$.
0	15·34	—	—	—
0·78	14·90	0·44	5·9	340
3·40	14·14	1·20	16·1	225
4·63	13·78	1·56	21·0	221
6·07	13·30	2·04	27·4	229
8·05	12·76	2·58	34·7	229
0·65	12·16	3·18	42·8	227
13·30	11·72	3·62	48·6	218
16·55	11·10	4·24	57·0	222
22·12	10·40	4·94	66·4	214
26·20	10·00	5·34	71·8	210
32·55	9·50	5·84	78·5	205
41·40	8·88	6·46	86·9	213

Zero-order runs were observed with one surface only (Table IV, *d*); the conditions for their occurrence have not yet been fully investigated.

Equations of " intermediate " order such as those representing heterogeneous reactions in which one reactant is moderately heavily adsorbed have been tested graphically with the experimental results, and found to offer no advantage over the simple first- or second-order formulæ.

FIG. 2.



Catalysis by the Walls of the Reaction Vessel.—The glass retaining walls play a dominant part in the bromine–ethylene reaction at 16°. The evidence for this statement is as follows. (*a*) The speed and order of reaction in a given bulb may be altered by treating the glass surface by heat or with water. With one bulb, the rate of reaction increased in the course of a few runs from an initial low value to a constant value which was retained for 7 weeks. After leaving the bulb idle for 25 days, it was found that the activity had diminished to one-half, but the previous value was recovered after three runs.

(*b*) Norrish (*loc. cit.*) discovered that there was very little combination of ethylene and bromine at 0° in a vessel with walls of paraffin wax, indicating that the reaction did not occur spontaneously in the bulk phase.* It is unlikely that a spontaneous

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* Norrish's experiments prove that the reaction must be *initiated* at a polar surface; but they do not exclude the possibility of chains starting at the surface and spreading into the gas.

bulk reaction, imperceptible at 0°, becomes appreciable at 16°, since the reaction speed decreases with rising temperature over a wide range.

(*c*) It has been shown that the rate of reaction is raised by increasing the area of glass exposed to the reactants; but the variations in the surface activity of different specimens of glass make it difficult to connect the reaction speed quantitatively with the surface/volume ratio of the containing vessel. Table II shows the results of some experiments in which the extent of surface S presented to the reactants was increased by introducing pieces of glass tubing of known area. The time of half reaction t is taken as a measure of the rate, since the order of the reaction was changed from 2 to 0 by the introduction of the tubing. In the table, V is a measure of the volume of the reaction system and r ($= V/tS$) is a measure of the specific surface reactivity.

TABLE II.

Temp. 16°.

No.	S.	C_2H_4.	Br_2.	t.	$V/tS = r$.	r_1/r_2.
216	446	7·53	7·86	8·6	3·5	0·9
207	233	7·43	7·86	14·4	4·1	
214	446	13·98	14·70	2·2	13·4	1·2
206	233	14·07	14·68	5·1	11·5	
215	446	7·81	23·94	0·8	38	1·6
204	233	8·83	23·92	2·4	24	
257	442	8·70	7·86	(k_2 = 0·00237)		1·1
258	219	7·04	7·86	(k_2 = 0·00107)		

In Expts. 257 and 258 of Table II, with different glass throughout, the reactions were of second order both with and without added tubing. The quantity r_1/r_2, *i.e.*, the ratio of the specific surface activities of the two reaction systems, should always be equal to unity if the rate of reaction were strictly proportional to the surface/volume ratio of the containing vessel. It is approximately unity for the lower pressures of reactants, but at the higher bromine pressures, the rate of reaction is enhanced by increase of glass area to a higher degree than simple proportionality, and this effect has been confirmed in later experiments in which a 100-cm. length of glass tubing cut into 2-cm. pieces was present in the reaction bulb. Pieces of the tubing were moved in successive experiments.

Variation of the Initial Ethylene Pressure.—With fixed surface conditions a constant catalytic activity was retained over long periods of time. On one surface the value of k_2 obtained with "standard" pressures of ethylene and bromine of about 8 mm. was used as a "normal" value from which to determine the effects of varying conditions of pressure, temperature, and presence of foreign gases. After each change of conditions a "standard" run was performed in order to test the catalytic constancy of the surface. Table III illustrates the degree of reproducibility of such standard runs, and also provides a proof that the rate of reaction is truly proportional to the ethylene pressure, since the magnitude of k_2 is independent of the initial pressure of ethylene.

TABLE III.

Surface A. Temp. 16°.

No.	C_2H_4.	Br_2.	$k_2 \times 10^5$.	No.	C_2H_4.	Br_2.	$k_2 \times 10^5$.
122	7·50	6·96	150	152	9·80	7·70	147
124	8·00	8·00	153	131	14·89	7·58	118
130	8·12	7·78	134	137	15·00	7·64	153
142	8·00	7·86	126	136	44·75	7·62	168
143	7·87	7·92	136	132	45·63	7·72	146
145	7·76	7·76	149	141	51·50	7·64	142

Mean $k_2 = 0·00144 \pm 6·9\%$.

In all tables, the numbers of the runs in the first column give the order in which the experiments were performed.

Variation of the Initial Bromine Pressure.—The effect of varying the initial bromine pressure has been examined on a number of different glass surfaces; these are referred to as A, B, etc. On all surfaces, the velocity coefficient, whether of second, first, or zero order, rises as the initial bromine pressure is increased.

TABLE IV.

(*a*) Surface A at 16°. Second-order reaction.

No.	C_2H_4.	Br_2.	$k_2 \times 10^4$.
124	Standard run	8·00	15·3
138	7·86	4·08	6·44
125	9·84	9·82	23·3
134	8·49	15·10	48·5
145	Standard run	7·76	14·9

(*b*) Surface B at 16°. Second-order reaction.

No.	C_2H_4.	Br_2.	$k_2 \times 10^4$
203	9·10	7·84	70·0
210	11·82	7·88	62·4
211	14·68	14·06	112
206	14·07	14·68	120
208	26·70	14·82	113

(*c*) Surface D at 16°. First-order reaction.

No.	C_2H_4.	Br_2.	$k_1 \times 10^4$.
232	1·04	1·03	(12)*
233	1·83	1·83	(23)†
227	7·44	7·90	219
242	8·20	7·86	135
245	8·54	7·86	140
247	7·22	7·86	185
231	7·04	14·64	655
228	8·26	15·04	837
252	8·54	14·88	711

(*d*) Surface B_1. Reaction of zero order.

No.	C_2H_4.	Br_2.	$k_0 = (p_0 - p)/$
		At 16°.	
213	6·99	7·86	0·322
214	13·98	14·70	3·0
215	7·81	23·94	10
216	7·53	7·86	0·449
		At 25°.	
217	8·08	7·84	(0·214) ‡
219	7·81	24·00	2·4

* $k_2 = 26 \times 10^{-4}$. † $k_2 = 31·9 \times 10^{-4}$. ‡ $k_1 = 140 \times 10^{-4}$.

In all cases the velocity coefficients in Table IV refer only to that portion of the reaction in which the reaction product is not separating as a liquid. First-order velocity coefficients are calculated with respect to ethylene.

The results presented in Table III and Table IV (*a*) are shown in Fig. 2. On surface A, k_2 is proportional to the square of the initial bromine pressure, but this result does not hold for the other surfaces in Table IV. On all the surfaces, experiments were performed with still higher initial proportions of bromine to ethylene, but the reactions were then very rapid, and the secondary reaction (p. 1751) became a seriously disturbing factor. Velocity coefficients calculated from the initial stages of such experiments are included in Fig. 2.

The persistence of this variation of the velocity coefficient with the initial bromine pressure in experiments with differently purified specimens of bromine (including complete omission of drying with phosphoric oxide), has made it unlikely that the effect is due to a catalysing impurity either present in the bromine or formed by interaction of bromine with phosphoric oxide in the drying tube (Fig. 1).

It seems to be fairly clear from the results of the last two sections that, except for the one surface which gave zero-order reactions, the hypothesis that ethylene is only slightly adsorbed on the glass is justified. Further support may be derived from the figures of Crespí and Moles (*Anal. Fís. Quím.*, 1930, **28**, 448) for the adsorption of ethylene on glass at 14°, which seem to show that the glass is far from being saturated with ethylene even at 760 mm. pressure. But the assumption that bromine is simultaneously slightly adsorbed to a slight extent on the catalysing glass does not alone suffice to explain the complications of the reaction kinetics.

Temperature Coefficient of the Reaction.—The rate of the bromine–ethylene reaction decreases with rising temperature. This effect has already been recorded for zero-order reactions in Table IV (*d*) and is further illustrated, for two other surfaces, in Table V. The standard runs quoted for surface A show that the temperature effect is perfectly reversible.

If values of log k at corresponding pressures are plotted against $1/T$, a series of parallel lines is obtained, which includes the line drawn from the results with water vapour present. Using the equation $d(\ln k)/dT = L/RT^2$, and neglecting the slight effect of changing concentration for a given pressure over the small temperature range concerned, we find $-L$ to be approximately 22,000 cals. and 21,000 cals. for the absence and presence of water vapour respectively. For Surface G, $-L$ is 17,000 cals.

The apparatus in use was not suitable for exact measurements at temperatures higher than 25°; but some preliminary experiments

TABLE V.

(*a*) Surface A. Standard run at 16°, No. 122, $k_2 = 15{\cdot}0 \times 10^{-4}$.

No.	C_2H_4.	Br_2.	Temp.	$k_2 \times 10^4$.	$k_1 \times 10^4$.
126	14·48	14·92	25°	—	7·22
127	8·85	8·50	25	5·85	—
123	14·63	14·60	16	—	274
125	9·84	9·82	16	—	70·3
Read from Fig. 2		8·50	16	17·3	—
129	10·73	10·16	9	—	198
128	8·54	8·52	9	—	121
Standard run at 16°, No. 145, $k_2 = 14{\cdot}9 \times 10^{-4}$.					
(*b*) Surface A. 2·00 Mm. of water vapour present.					
169	8·28	7·90	25	—	56·3
171	7·96	7·86	25	—	56·5
163	7·84	7·86	16	—	167
172	7·46	7·86	16	—	164
(*c*) Surface G.					
282	7·90	7·86	25	—	91·7
283	9·26	7·86	16	—	220

suggest that with one surface the rate of reaction continues to decrease up to 200°.

Summary.

In confirmation of previous work at 0°, the combination of ethylene and bromine is found to be a surface reaction in a glass vessel at room temperature. The reaction appears to be predominantly simple addition of bromine to the double bond, unless bromine is initially in excess when some supplementary reaction is induced by the addition process. In the bulk of the experiments discussed in this and the following paper the conditions were such as to reduce the supplementary reaction to a minimum.

The kinetics of the reaction are not simple. It is found (*a*) that the rate of reaction decreases with rising temperature; (*b*) that the order of the reaction may be 2, 1, or, in one instance, zero, depending on the reaction vessel employed. For a given surface, lowering the temperature or raising the pressures of the reactants tends to lower the order of reaction. (*c*) For a given surface and reaction order, the magnitude of the velocity coefficient is independent of the initial ethylene pressure but rises with increasing initial bromine pressure.

The negative temperature coefficient implies that the reaction takes place in more than one stage. It does not seem probable that the variation of the adsorption of the reactants with temperature and pressure can account for the magnitude of the observed effects, for changes in reaction order due to changing adsorption on a catalyst generally require more drastic alterations of the experimental conditions (compare, *e.g.*, the ethylene–hydrogen

reaction on copper at different temperatures, Pease and Harris, *J. Amer. Chem. Soc.*, 1927, **49**, 2503). Part II presents evidence for the formation of a bromine–water complex and for chain-propagation in the bromine–ethylene reaction.

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