235. The Thermal Combination of Ethylene and Bromine at Glass Surfaces. Part II. The Influence of Water.

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BOTH Stewart and Edlund (*J. Amer. Chem. Soc.*, 1923, **45**, 1014) and Norrish (J., 1923, **123**, 3006) observed that the reaction of ethylene and bromine at 0° was accelerated by the presence of moisture. The following results show that the same is true at higher temperatures. The experiments were conducted on a surface which gave second-order reactions with an initial bromine pressure of 8 mm. and the " standard rate " for this surface was $k_2 = 0.00144$ (compare Table III, preceding paper); but in the presence of water vapour the same surface gave invariably reactions of the first order. Expt. 168 is an example.

Expt. 168.   Ethylene = 7·59 mm.   Bromine = 7·86 mm.
Water vapour = 3·10 mm.   Temp. = 16°.

t.	p.	$p_0 - p$.	Change, %.	$k_2 \times 10^4$.	$k_1 \times 10^4$.
0	15·45				
2·90	14·44	1·01	13·3	67·1	213
7·10	13·02	2·43	32·0	83·5	245
9·50	12·24	3·21	42·3	96·7	251
15·5	10·90	4·55	60·0	119	256
19·5	10·18	5·27	69·4	142	264
25·0	9·64	5·81	76·5	157	251
33·0	8·88	6·57	86·6	222	264

Mean 0·0249.

As before, pressures are always given in mm. and time in minutes. The collected results for the influence of water vapour at 16° with this surface are given in Table I.

The concordance in the results of Expts. 163 and 172 proves the constancy of the surface conditions for the first two parts of the table. Somewhere between Expts. 172 and 179 the surface activity must have diminished somewhat; nevertheless Table I(c) indicates that, within certain limits, the value of k_1 is independent of the initial ethylene pressure, a fact which justified the procedure of calculating first-order velocity coefficients always with respect to ethylene. Other features in Table I are referred to later.

TABLE I.

(a) Variation of water pressure.				(b) Variation of initial bromine pressure.			
No.	$H_2O.$	$C_2H_4.$	$Br_2.$	$k_1 \times 10^4.$	No.	$H_2O.$	$C_2H_4.$	$Br_2.$	$k_1 \times 10^4.$

No.	$H_2O.$	$C_2H_4.$	$Br_2.$	$k_1 \times 10^4.$	No.	$H_2O.$	$C_2H_4.$	$Br_2.$	$k_1 \times 10^4.$
162	1·04	7·84	7·82	69·6	163	2·00	7·84	7·86	167
163	2·00	7·84	7·86	167	164	2·00	7·84	14·42	570
168	3·10	7·59	7·86	240	166	2·00	7·59	17·18	1120
167	4·26	7·84	7·88	459	165	2·00	7·84	22·00	3000
172	2·00	7·46	7·86	164					

(c) Variation of initial ethylene pressure.

No.	$C_2H_4.$	$Br_2.$	$k_1 \times 10^4.$	No.	$C_2H_4.$	$Br_2.$	$k_1 \times 10^4.$
177	4·77	7·86	146	175	10·90	7·84	124
178	5·35	7·86	122	174	13·95	7·86	(116—84·6)
179	8·31	7·84	116	173	19·71	7·84	(96·4—61·2)

The accelerating influence of water vapour upon the reaction, illustrated in Table I(a), is further traced to a surface action, rather than to any effect of water upon the reactants in the bulk phase, by the results given in Table II(a), which show that the characteristic effects of water (increased rate of reaction and first-order velocity coefficients) persist on the water-treated surface of Table I in runs in which no water vapour was introduced initially; and by the results in Table II(b), which show that these effects disappear when the surface is baked in such a way as to remove adsorbed water.

TABLE II.

(a) Runs at 16° on water-affected surface.

No.	$C_2H_4.$	$Br_2.$	$k_1 \times 10^4.$	No.	$C_2H_4.$	$Br_2.$	$k_1 \times 10^4.$
183	7·59	7·86	50·3	189	9·19	7·86	65·3
184	7·71	7·98	72·6	191	7·84	7·86	84·8
185	7·95	7·86	61·4				

(b) Runs at 16° with baked bulbs.

No.	$C_2H_4.$	$Br_2.$	$k_2 \times 10^4.$	No.	$C_2H_4.$	$Br_2.$	$k_2 \times 10^4.$
	Surface A.				Surface G.		
192	8·08	7·86	14·2	283*	9·26	7·86	220†
193	14·37	14·16	26	287	7·80	7·86	331
	Surface C.			288	8·42	7·84	120
220*	10·74	7·86	78·7	289	9·70	7·86	‡
221	10·23	7·84	33·3	291	8·31	7·86	132
222	15·70	14·80	62—110				
223	8·29	7·86	35·6				

* Unbaked.   † $k_1.$
‡ (Temp. 360°.) No fall in pressure during 36 mins.

For the experiments in Table II(b), before each run the reaction bulb was baked out in an electric furnace for 2—5 hours at 350—400° and a pressure of rather less than 10^{-5} mm. With the surfaces A and C, 28% of the total glass surface presented to the reactants (comprising the gauge and connecting tubing) was not baked; with the surface G, less than 20% of the surface remained unbaked. According to Sherwood (*Physical Rev.*, 1918, **12**, 448; *J. Amer. Chem.*

Soc., 1918, **40**, 1645; compare Dunoyer, " Vacuum Practice," London, 1926), baking in the above manner should suffice to remove adsorbed gases (mainly water) from the glass, while leaving behind any chemically combined water. Expts. 184 and 221, taken from (*a*) and (*b*) respectively in Table II, are quoted in full to illustrate the definiteness in the assignment of first and second order.

Expt. 184.   Ethylene = 7·71 mm.   Bromine = 7·98 mm.

t.	*p.*	$p_0 - p$	Change, %.	$k_2 \times 10^4$.	$k_1 \times 10^4$.
0	15·69				
6·30	15·12	0·57	7·4	15·8	53·0
14·30	14·10	1·59	20·6	22·6	70·2
25·2	13·04	2·65	34·4	25·8	72·5
38·0	12·04	3·65	47·3	29·1	73·4
59·0	10·88	4·81	62·4	34·1	72·0
94·0	9·60	6·09	78·9	46·8	72·1
129	8·80	6·89	89·4	70·8	75·4

Mean   0·00726

Expt. 221. Baked bulb. Temperature kept at 420—430° for 25 mins. and then at 330—360° for 1 hour before run.

Ethylene = 9·61 mm.   Bromine = 7·84 mm.

t.	*p.*	$p_0 - p$	Change, %.	$k_2 \times 10^4$.
0	18·07			
4·10	17·08	0·99	12·6	33·1
8·50	16·26	1·81	23·1	33·8
14·70	15·38	2·69	34·3	32·8
24·5	14·38	3·69	47·1	32·2
33·0	13·78	4·29	54·7	31·6
41·0	13·18	4·89	62·5	33·4
66·0	12·04	6·03	77·0	36·5

Mean   0·00333

Bromine-hydration Hypothesis.—It has been shown in Part I that, provided that bromine be not present in excess, the rate of combination of ethylene and bromine can be represented in general by one or other of the equations

First order, $d[C_2H_4Br_2]/dt = k_1 \cdot [C_2H_4]$ . . . . (1)

Second order, $d[C_2H_4Br_2]/dt = k_2 \cdot [C_2H_4][Br_2]$ . . . (2)

in which concentrations are given in partial pressures. In the present paper it is shown that wetting the glass surface accelerates the reaction and favours equation (1), whilst drying it retards reaction and favours equation (2). This suggests that water participates chemically in the combination of ethylene and bromine, either by the reversible exothermal formation of a surface–bromine–water complex or, possibly, by a mechanism involving multi-body surface collisions between molecules of ethylene, bromine, and water possessing two-dimensional mobility (compare Volmer, *Trans. Faraday Soc.*, 1932, **28**, 359). The influence of water is better explained by such a hypothesis than by

one envisaging an alteration of the surface structure of the glass by the action of water (compare Frazer, Patrick, and Smith, *J. Physical Chem.*, 1927, **31**, 897) on account of the previous cleaning of the reaction bulbs with chromic acid and steam (Part I, p. 1749), and of the reversibility (*a*) of the temperature effect (Part I, Table V) and (*b*) (within limits) of the accelerating influence of water vapour (Table I).

If union with ethylene requires the participation of water, the negative temperature coefficient of the process may be accounted for by the diminution of the surface concentration of hydrated bromine with rising temperature.

The identity in the numerical values of the temperature coefficient in the presence and absence of water vapour, found in Part I, may be fortuitous, but if correct, it supports the view that water is concerned in the reaction at " normal " glass surfaces, which doubtless hold adsorbed water. For additional support, reference may be made to the kinetics of the addition of bromine to olefinic compounds in solution in chloroform and carbon tetrachloride. The rates of such reactions have been found to be susceptible to the presence of traces of moisture (Sudborough and Thomas, J., 1910, **97**, 715, 2450; D. M. Williams and James, J., 1928, 343), and Davis (*J. Amer. Chem. Soc.*, 1928, **50**, 2769) finds that bromine and ethylene react extremely slowly in dry carbon tetrachloride; the reaction is accelerated by moisture and the rate of reaction decreases with rise of temperature from 0° to 25°. This behaviour is ascribed to the reversible formation of a bromine hydrate which is supposed to be the reactive component.

The initial speed of the gaseous bromine–ethylene reaction does not appear to depend upon the time elapsing between the introduction of bromine into the reaction vessel and the subsequent admission of ethylene; nor is it affected by previous exposure of the surface to a high bromine pressure. The hydration of bromine is not, therefore, the rate-determining step.

The Variability of the Reaction Order.—The influence of water in bringing about first-order reactions is interpreted as meaning that the transition from second to first order occurs when the surface concentration of hydrated bromine becomes so high that the chance of a surface collision between an ethylene molecule and a hydrated bromine molecule is independent of the gaseous bromine pressure. This supposition is consistent with the following further facts.

(*a*) Even in the presence of water vapour, the first-order equation, whilst holding in a reaction with a 40% excess initial ethylene pressure (175, Table I,*c*), breaks down if ethylene is initially present in 80% excess (174, 173).

(b) A reversible transition from equation (1) to equation (2) can be brought about on all surfaces, without special wetting or drying, if the conditions are properly chosen. For example, on surface D (Expts. 226—253), the reaction appeared to be always first order; at the " standard " initial pressures of 7·9 mm. the unimolecular law fits very well—compare Expt. 227 in Part I. But a reaction of the second order is observed if the initial pressures of the reactants are reduced to 2 mm. (see Expt. 233).

Expt. 233*. Ethylene = Bromine = 1·83 mm. Temp. 16°.

t.	p.	$p_0 - p.$	Change, %.	$k_2 \times 10^5.$	$k_1 \times 10^5.$
0	3·66				
8	3·58	0·08	4·4	312	239
17	3·50	0·16	8·7	318	232
25	3·43	0·23	12·6	314	232
40	3·32	0·34	18·6	311	223
70	3·14	0·52	28·4	310	207
104	2·99	0·67	36·6	303	190
172	2·74	0·92	50·3	321	176
226	2·59	1·07	58·5	340	169
280	2·49	1·17	64·0	345	158
320	2·41	1·25	68·3	(368)	158

Mean 0·00319

* In this experiment the Bourdon gauge was used as an absolute measuring instrument.

The conditions bringing about the transition from second to first order are a relatively high initial bromine pressure or a lowered temperature. Increasing the initial ethylene pressure to a high value does *not* alone induce a transition.

(c) In Expt. 193 on a baked surface (Table II, b), the reaction was of second order with relatively high reactant pressures, which gave the first-order law on the same surface before baking, even without deliberate wetting.

Variation of the Velocity Coefficient with Initial Bromine Pressure and Possibility of Chain Propagation.—The variation of the velocity coefficient with the initial bromine pressure (Part I, Table IV) indicates the possibility of chain propagation, which is not *a priori* unlikely in view of the occurrence of reaction chains in the *photochemical* addition of bromine to double bonds (Berthoud and Béraneck, *J. Chim. physique*, 1927, **24**, 213; Ghosh and Purkayastha, *J. Indian Chem. Soc.*, 1928, **4**, 533; *Z. physikal. Chem.*, 1930, B, **9**, 128, 154), in the photo-sensitisation by bromine of geometrical isomerisation (*e.g.*, Berthoud, *Trans. Faraday Soc.*, 1926, **21**, 554; Schmidt, *Z. physikal. Chem.*, 1928, B, **1**, 205), and in the thermal chlorine–ethylene reaction (Stewart and Smith, *J. Amer. Chem. Soc.*, 1929, **51**, 3082; 1930, **52**, 2869). The initiation of chains by hydrated halogens has been postulated in other reactions (*e.g.*, Franck and Rabinowitsch, *Z. Elektrochem.*, 1930, **36**, 794; Boden-

stein, *Trans. Faraday Soc.*, 1931, **27**, 413), and chains started at the surface might spread into the gas phase (compare Hinshelwood, *Trans. Faraday Soc.*, 1932, **28**, 184). Some additional experimental material with the bromine–ethylene reaction is most easily interpreted on this view. This evidence is only summarised here since further work is projected.

(*a*) When bromine is initially in excess a secondary reaction is induced by the addition reaction, indicating that an activated molecular species is produced at some stage [Part I, pp. 1752, 1756]. The reaction proceeds especially rapidly to completion when bromine is in excess.

(*b*) It was shown in Part I that a given increase in the area of glass exposed to the reactants is progressively more effective in accelerating the bromine–ethylene reaction as the initial bromine pressure is raised. This is understandable if a high bromine pressure favours the propagation of chains in the gas phase.

(*c*) In one instance, packing the reaction vessel with pieces of poisoned glass tubing actually reduced k_1 from 0·00624 to 0·00447. The retardation was larger than would be anticipated if the inactive tubing were merely covering up active glass.

(*d*) The presence of inert gases—air, oxygen, and nitrogen—is found to retard the combination of ethylene and bromine at 16° (Table III). This may be due to the deactivation of a chain-carrying species in the gas phase. The adsorption of the permanent gases on glass does not seem to be sufficiently great (Durau, *Z. Physik*, 1926, **37**, 419; Moles and Crespí, *Anal. Fis. Quim.*, 1929, **27**, 529; 1930, **28**, 448) to account for the observed retardation on the grounds of displacement of adsorbed reactants from the glass.

TABLE III.

No.	C_2H_4.	Br_2.	$k_1 \times 10^4$.	Inert gas.		
185	7·95	7·86	61·4	—		
186	8·20	7·86	52·4	71·8 mm.		Air
187	9·5	7·86	39·5	72·4	,,	N_2
188	9·1	7·86	41·5	73·2	,,	N_2
189	9·19	7·86	65·3	—		
190	9·2	7·86	34·2	73·5	,,	O_2
191	7·84	7·86	84·8	—		
204	8·83	23·92	1340	—		
205	8·00	24·40	874	68·4	,,	N_2
242	8·20	7·86	135	—		
243	7·49	7·86	76	21·7	,,	N_2
			$k_2 \times 10^4$.			
232	1·04	1·03	26·0	—		
234	1·86	1·03	24·5	—		
239	1·02	0·99	20·1	22·4	,,	N_2
233	1·83	1·83	31·9	—		
237	1·83	1·83	32·1	—		
235	1·79	1·79	23·3	20·6	,,	N_2

Influence of Ethylene Dibromide Vapour on the Reaction.—In the following experiments (Table IV), dry ethylene dibromide vapour at various pressures was introduced into the reaction bulb before the commencement of each run. Its presence accelerated the reaction and reduced the steepness of the negative temperature coefficient. The rates were best represented by the first-order law.

TABLE IV.

(a) Variation of ethylene dibromide pressure at 16°.

No.	$C_2H_4Br_2$.	C_2H_4.	Br_2.	$k_1 \times 10^4$.
148	1·14	7·86	7·86	46·3
144	2·10	7·86	7·86	76·6
146	2·30	7·75	7·86	65·8
151	2·94	8·56	7·90	122
153	3·02	7·84	7·86	181
150	3·20	7·60	7·84	171
147	4·00	7·87	7·88	175
155	4·28	8·56	7·84	197
154	5·50	7·96	7·86	271

(b) Variation of initial bromine pressure at 16°.

No.	$C_2H_4Br_2$.	C_2H_4.	Br_2.	$k_1 \times 10^4$.
149	2·20	7·84	15·36	457
156	2·20	8·69	21·74	1240

(c) Variation of temperature : Expts. 157 and 182 are at 25°.

No.	$C_2H_4Br_2$.	C_2H_4.	Br_2.	$k_1 \times 10^4$.
157	2·20	7·81	7·88	54·9
182	4·20	7·86	7·86	113

(d) Influence of water vapour at 16° : water = 2·00 mm.

No.	$C_2H_4Br_2$.	C_2H_4.	Br_2.	$k_1 \times 10^4$.
179	—	8·31	7·84	116
180	2·50	8·56	7·82	235
181	3·52	8·31	7·84	266—397

Between Expts. 144 and 146 the ethylene dibromide was dried for 2 days over phosphoric oxide and redistilled.

The accelerating influence of added ethylene dibromide vapour differs from that of water vapour in that there does not appear to be a permanent alteration of the surface condition, as is shown by the results of the following " standard runs " which were interspersed with the experiments given in Table IV.

Expt.	141	145	152	160
$k_2 \times 10^4$	14·2	14·9	14·7	16·7

It seems remarkable that the initial addition of comparatively small pressures of ethylene dibromide vapour should accelerate the reaction, since the success of the simple first- and second-order expressions in representing the rate implies that the reaction is not ordinarily autocatalytic. There was, however, in many experiments in this bulb a tendency for the velocity coefficients to rise at the end of the reaction.

When the reaction takes place on a baked surface, the products are adsorbed on the walls and, if these are not subjected to further baking, subsequent reactions proceed at an increased rate as shown :

No. of Run.	C_2H_4.	Br_2.	Temp.	$k_2 \times 10^4$.
197, Baked	8·00	7·86	16°	64·5
198, Unbaked	8·15	7·86	16	109
199, Unbaked	7·90	7·86	16	206
201, Unbaked	7·90	7·86	25	124
202, Baked	7·90	7·86	16	115

If water is removed from the surface, its place can evidently be taken by adsorbed reaction products; but the simplicity of the equation for the rate of reaction suggests that this does not ordinarily occur on " normal " glass surfaces. Stewart and Smith (*loc. cit.*) have found that the chlorine–ethylene reaction is autocatalytic on baked Pyrex surfaces. The accelerating influence of added ethylene dibromide vapour may be due to action in the gas phase. The separation of liquid ethylene dibromide during a run retards the reaction.

Summary.

(1) It is shown that water vapour accelerates the bromine–ethylene reaction, and that its influence is due, at least in part, to its participation in some action at the glass surface.

(2) The transition from a reaction of second order to one of first order is favoured by (*a*) a wet surface, (*b*) relatively high initial pressures of bromine, (*c*) low temperature.

(3) It is suggested that bromine is hydrated at the glass surface, and that ethylene reacts with the bromine–water complex. The rate of reaction becomes independent of the bulk bromine pressure when the surface concentration of hydrated bromine is relatively high.

(4) There are indications that chains may start at the glass surface and spread into the gas phase.

(5) It is shown that the introduction of ethylene dibromide vapour before the commencement of a run causes an increase in the rate of reaction.