XII.—*Studies of Valency. Part VII. Surface Polarity and the Reaction of Ethylene and Chlorine—The Effect of the Adsorbed Water Layer.*

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THE reaction between ethylene and bromine which occurs only at the surface of the reaction vessel (Stewart and Edlund, *J. Amer. Chem. Soc.*, 1923, **45**, 1014) has been shown by one of us to depend greatly on the nature of the surface (Norrish, J., 1923, **123**, 3006). The following figures represent the mean bimolecular velocity coefficients found for the surfaces specified in vessels of uniform dimensions: Glass, 0·0506; stearic acid, 0·0864; cetyl alcohol, 0·0266; paraffin wax, 0·0030. The low value for paraffin wax suggested that these figures might be taken as a measure of the polarity of the surfaces and that with an improvement in technique the method might be used as a general measure of surface polarity.

The present research has been undertaken to investigate the effect of moisture on the reactivity of glass and paraffin surfaces and to test a suggestion put forward in the previous paper on ethylene and bromine (*loc. cit.*), that the absolute reactivity of a paraffin surface is vanishingly small.

In these experiments we have substituted chlorine for bromine since it is more easily manipulated than the latter and admits of the pressures of the reactants being increased tenfold. Furthermore, an easier means of experimentation, which gives accurate and reproducible results, has been devised. As was expected, in view of the previous results, the reaction between ethylene and chlorine (in the absence of light) has been found to occur entirely at the surface, and to depend on the nature of the surface in the same way as the reaction of ethylene and bromine already studied. It has further been shown that whilst the rate of reaction at a paraffin wax surface is independent of the presence of water vapour, this is not so for a glass surface, the gases, in the presence of water vapour at 6 mm. pressure, uniting 1·3 times as fast as when they were dried by phosphoric acid. Further, by taking special precautions to prevent accidental exposure of the glass, it was found possible practically to suspend the reaction in a paraffin vessel, less than 0·1 of the total reactants combining in the course of 12 hours, whilst, in the case of a glass vessel of the same dimensions, the reaction was practically complete in 30—40 minutes. This indicates a reactivity for a paraffin surface some 1200 times smaller than for a glass surface of the same dimensions, whereas the earlier ethylene–bromine experiments indicated a reactivity for paraffin wax only 18 times smaller than that for glass.

FIG. 1.

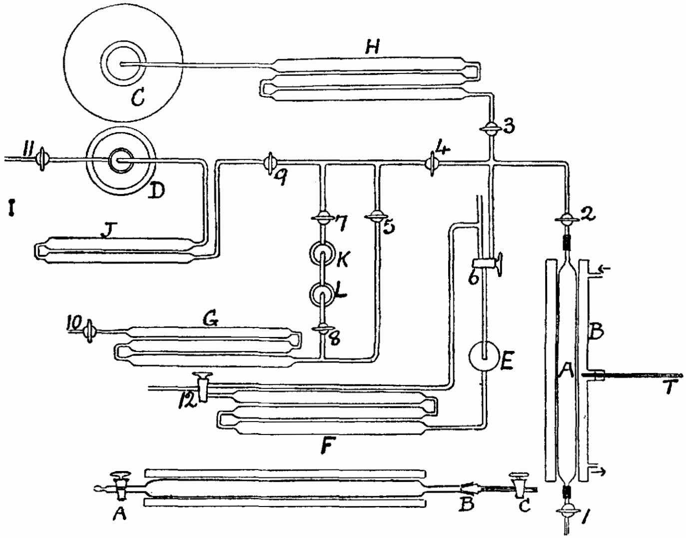

FIG. 2.

EXPERIMENTAL.

The reaction vessel (Fig. 1, A) consisted of a glass tube 35 cm. long and either 1·3 or 2·7 cm. in diameter. The tube was water-jacketed by an outer metal vessel, B, which served to screen it from light and was kept at constant temperature by a current of water circulated by a pump from a thermostat regulated to 0·1°, the temperature being indicated by a thermometer T. One end of the reaction vessel was connected *via* tap 1 and a long capillary tube to a vertical mercury manometer M; the other end was connected *via* tap 2 to the gas supply and water-pump. As it was necessary frequently to remove the reaction vessel, its connexion with taps 1 and 2 was made at first by paraffined rubber pressure tubing and later by ground glass joints. The apparatus could be evacuated *via* taps 2, 4, 9, 11, by way of the drying tubes, J, containing phosphoric oxide, and the expansion chamber, D, containing calcium chloride. Dry air could be admitted *via* the drying tubes, G, containing calcium chloride and phosphoric oxide, by way of taps 10, 5, 4, 2. Air saturated with water vapour could be admitted by way of the saturators L and K and taps 10, 8, 7, 4, 2. The saturators were so arranged that the air bubbled through the liquid in L and passed over the surface of the liquid in K. Ethylene was stored in the aspirator, C, and could be expanded into the reaction vessel by way of the calcium chloride–phosphoric oxide drying system, and taps 3 and 2. Dry chlorine was obtained *via* taps 6 and 2 from the chlorine chamber, E, which was kept continually filled by the passage of chlorine from a cylinder, through the phosphoric oxide drying system, F. The technique of the chlorine manipulation was similar to that already described by Norrish and Rideal (J., 1925, **127**, 787).

An experimental run was carried out as follows. The vessel A was evacuated as far as possible by the water-pump, and washed out with dry air and re-evacuated several times. Finally air, either dry or moist as required, was admitted to a pressure of about 300 mm. The connecting tubes were evacuated and washed out two or three times with ethylene, and then dry ethlyene was admitted to the reaction vessel to a partial pressure of 200 mm. Finally, after the connecting tubes had been washed out as before, dry chlorine was admitted to a partial pressure of 200 mm. Stop-cocks 1 and 2 were kept closed throughout the reaction and readings of the pressure were made at intervals by momentarily putting the mercury manometer into communication with A by opening tap 1; when these precautions were taken, the mercury of the manometer was not affected by the chlorine if this gas was the last to be admitted to the system.

The bimolecular reaction coefficient used as a measure of the reactivity of a given surface was calculated by the formula

$$k = x/a(a - x)t,$$

where a is the initial pressure of ethylene or chlorine, and x the fall in pressure of either gas at time t. The value of a was fixed at 200 mm., and the value of x calculated from the fall of pressure in the reaction chamber, account being taken of the fact that the ethylene dichloride is initally formed as a gas and finally separates as a liquid when its saturation vapour pressure is reached. This vapour pressure is 55 mm. at 18°, and 60 mm. at 20° (Rex, *Z. physikal. Chem.*, 1906, **35**, 358); hence if dp represents the pressure fall at time t at 20°, then, when $dp < 60$ mm., $x = dp$, and when

$dp > 60$ mm., $x = (dp + 60)/2$. There was, in general, no noticeable change in the value of k at the moment when liquid ethylene dichloride separated, a fact which proves that the liquid exerts no appreciable catalytic activity in the reaction.

For a reaction which occurs solely at the surface, as in the present case, it may be shown that the reaction coefficient, calculated as above in terms of pressure changes, must be multiplied by the factor v/s, representing the ratio of volume to surface of the reaction vessel, in order to obtain comparable figures for different-sized vessels. In the present experiments, cylindrical tubes of uniform length were used as the reaction vessels, for which $v/s \propto d$, where d is the diameter of the tube. Thus, by taking the product kd we obtain comparable figures for surface reactivity. In Tables I and IV examples are given in full of various experiments. The further account of this work will be limited to giving figures for surface reactivity, in Tables II and III, calculated as described above from the mean reaction velocity coefficients.

TABLE I.

Effect of water vapour on the reaction of ethylene and chlorine at a glass surface.

Diameter of tube, 1·30 cm. Temp., 18°.

Experiment " Glass 10."
a, 200 mm. Water vap. press., 0.

Time (mins.).	Total pressure fall (mm.).	$k \times 10^4$.
0	0	—
2	49	8·1
4	95	7·5
6	129	7·1
8	159	7·4
10	181·5	7·2
12	199	7·3
15	220	7·3
18	234	7·2
21	245·5	7·3
25	256·5	7·0
30	266·5	6·8
		Mean 7·3

Surface reactivity (kd) = $9{\cdot}5 \times 10^{-4}$.

Experiment " Glass 11."
a, 202 mm. Water vap. press., 6·2 mm.

Time (mins.).	Total pressure fall (mm.).	$k \times 10^4$.
0	0	—
2	69	11·0
4	131	10·6
6	174	10·8
8	204	11·1
10	224·5	11·0
12	239·5	11·1
14	251	11·1
16	261·5	11·2
18	267	10·8
21	276	10·6
25	284	10·3
		Mean 10·9

Surface reactivity (kd) = $14{\cdot}2 \times 10^{-4}$.

From the data of Table II, which are given in the order of experimentation, it will be seen that the surface reactivity, kd, is uniformly higher for moist gases than for dry, the mean value, calculated from the recorded figures, being $11{\cdot}3 \times 10^{-4}$ for dry gases and $14{\cdot}8 \times 10^{-4}$ for moist gases, while the ranges of surface reactivity in the two cases do not overlap. Thus the presence of about 6 mm. of

TABLE II.

Effect of water vapour on the reaction of ethylene and chlorine at a glass surface—collected data.

Diameter of tube, 1·30 cm.

Expt. No.	Temp.	Water vapour pressure.	Bimolec. reaction coeff. $k \times 10^4$.	Surface reactivity. $kd \times 10^4$.
2	18°	0	8·2	10·7
4	19	0	7·9	10·3
5	18	6·0	11·0	14·3
6	19	6·6	11·7	15·2
7	19	0	9·6	12·5
9	16	5·1	11·6	15·1
10	18	0	7·3	9·5
11	18	6·2	10·9	14·2
12	18	5·5	12·0	15·6
13	18	0	10·0	13·0
14	18	0	9·0	11·7
15	18	0	8·9	11·6
16	18	6·2	11·0	14·3

TABLE III.

Effect of water vapour on the reaction of ethylene and chlorine in a paraffin wax tube (rubber connexions).

Temperature, 20°.

Tube. No.	Diam. of tube (cm.).	Press. of water vapour (mm. Hg).	Vel. coeff. $k \times 10^4$.	Surface reactivity. $kd \times 10^4$.
1	1·3	6	0·74	0·97
		0	0·65	0·85
		0	0·71	0·92
2	2·7	6	0·17	0·45
		0	0·17	0·47
3	2·7	0	0·13	0·37
		6	0·12	0·33

water vapour in the gas phase increases the reactivity of a glass surface by about 30%.

It will be seen from the data for a given tube that the presence of water vapour has no measurable effect upon the reactivity of a paraffin wax surface. Further, the velocity coefficient does not vary in inverse ratio to the diameter of the tube as it would if the reactivities of the paraffin surfaces were uniform, and it was therefore thought that the measured reactivity was to be ascribed in part at least to the presence of the rubber connexions. In order to measure the absolute reactivity of a paraffin wax surface, the rubber connexions were replaced by ground glass joints, which together with the stop-cocks were lubricated with a grease made by melting together "nujol" and paraffin wax. The tube was constructed as shown in Fig. 2; the gases being introduced through the end A, and the end B being attached to the manometer. The paraffin wax was introduced molten into the tube, and allowed to cool with constant agitation under a vacuum, the process usually having to be repeated several times before a uniform coat was obtained. The tube fitting the ground glass joint, and communicating with the manometer, was paraffined carefully on both sides of the tap C. Great difficulty was experienced in preparing satisfactory tubes; in most cases there was some small surface of glass incompletely protected which enabled a slow reaction to proceed. After many trials, however, two cases of very low reactivity were obtained. In the better of the two, with both reactants at *ca·* 200 mm. pressure, less than 0·1 of the total reaction had occurred after 12 hours. The experimental figures are in Table IV.

TABLE IV.

Tube dimensions: length, 35 cm.; diameter, 1·3 cm.

Experiment i. Temp., 20·4°. Pressure of C_2H_4, 197 mm. Press. of Cl_2, 200 mm.			Experiment ii. Temp. 20·0°. Pressure of C_2H_4, 220 mm. Pressure of Cl_2, 182 mm.		
Time (mins).	Pressure decrease (mm.).	Bimolec. coeff. $\times 10^6$.	Time (mins.)	Pressure decrease (mm.).	Bimolec. coeff. $\times 10^6$.
0	0	—	0	0	—
16·5	3·5	5·5	124	3·9	0·88
46	8·2	4·8	227	5·5	0·64
146	18·0	3·5	358	7·0	0·53
194	21·0	3·2	449	11·0	0·65
226	25·0	3·3	825	20·0	0·60
339	35·6	3·3	955	24·4	0·72
455	45·4	3·3	1096	32·5	0·89
525	52·0	3·7	1182	42·0	0·95

To ascertain that the gases remained unreacted in the tube, in experiment ii, they were slowly withdrawn, after 20 hours, through potassium iodide solution. The quantity of unreacted chlorine (estimated by the amount of iodine set free, equiv. to 7·20 c.c. of $0{\cdot}1N$-$Na_2S_2O_3$) was in satisfactory agreement (5%) with that (7·56 c.c.) calculated from the known volume of the tube (48 c.c.) and the observed pressure changes.

The reactivity of the tube in experiment ii was much lower than that in experiment i, a fact which suggests that this residual activity was entirely due to the accidental exposure of glass surface.

Reactivity of a Stearic Acid Surface.—As data for comparison with the experimental results of the ethylene–bromine reaction (*loc. cit.*), figures were obtained for the reactivity of a stearic acid surface, a tube of 2·7 cm. diameter being used. The tube was coated with stearic acid under the conditions described above for paraffin wax and the initial pressure of each reactant was fixed at 200 mm. The constancy of the velocity coefficients was good, there being no variation from the mean values greater than 5%. In two experiments the mean values were $4{\cdot}52 \times 10^{-4}$ and $4{\cdot}20 \times 10^{-4}$.

In Table V is a comparison of the relative surface reactivities measured by the ethylene–chlorine and by the ethylene–bromine reactions. These are referred to the reactivity of glass, taken as unity, by computing the ratios of the reactivities of the given surfaces to that of glass, the reactivity being measured, in the way described above, as the product of the bimolecular reaction coefficient and the diameter of the tube.

TABLE V.

Comparative surface reactivities by two methods.

Surface	Glass; gas dry.	Glass; gas wet.	Stearic acid; gas dry.	Paraffin wax with rubber.	Paraffin wax, optimum.
C_2H_4–Br_2	1·0	—	1·7	0·06	—
C_2H_4–Cl_2	1·0	1·3	1·06	0·076	0·0008

It will be seen that the results of the earlier work have been confirmed, while the prediction that the non-polar surface of paraffin wax is entirely unreactive has been practically demonstrated.

The results described above, when considered with reference to the adsorbed water layer which is known to exist at the surface of glass, would seem to have an important bearing on any explanation of the suspension of reactions by extreme drying. The adsorbed water layer, under " dry " conditions, is probably but one molecule thick, but tends to pile up as the vapour pressure is increased towards saturation point (McHaffie and Lenher, J., 1925, **127**, 1559). Hence, if we assume that the water layer is the polar catalyst in the case of the glass surfaces, we can explain the increased reactivity of moist gases as due to the more complete saturation of the surface water film. When the surface is covered with paraffin wax, it seems reasonable to assume that the water layer cannot form, in agreement with the fact that water shows no tendency to wet paraffin wax. There is thus no reaction, either with dry or with wet gases, a fact which shows also that no volume reaction sets in, in the presence of water vapour. It seems highly probable that we are here imitating the effects of Baker: by the extreme drying of his systems we may suppose that he was removing the water from the walls, while by using walls composed of a substance upon which water cannot condense we achieve the same result, even in the presence of moist gases. Finally, if a polar group such as carboxyl or hydroxyl be introduced into the paraffin molecule, we can imitate the effect of the water layer on glass; thus with walls composed of stearic acid, or cetyl alcohol, the surface becomes once more reactive.

If we inquire further as to the mechanism of the present reaction, there is little evidence to guide us. It seems probable, however, that the presence of water on the surface might cause a greater modification of the dielectric constant in the immediate vicinity of the surface than can be brought about by a single molecule in the ternary complex [$A{\cdot}H_2O{\cdot}B$], so that the whole reaction takes place through the medium of the adsorption layer, even in the presence of water vapour. It seems significant also that all the polar catalysts so far obtained contain oxygen, and we might regard their function as the formation of a complex with the chlorine molecule, through the medium of quadrivalent oxygen $\left(e.g.,\ \begin{smallmatrix}H\\H\end{smallmatrix}\!>\!O\!<\!\begin{smallmatrix}Cl\\Cl\end{smallmatrix}\right)$ which, under the influence of the surface forces, is more dissociable than the chlorine molecule itself.

Summary.

A study has been made of the reaction between ethylene and chlorine, each at an initial partial pressure of 200 mm., at the surface of glass, paraffin wax, and stearic acid. By taking special precautions, a paraffin wax-surface was prepared showing a reactivity some 1200 times smaller than that of glass and about 70 times less than that previously found for a paraffin wax surface in the experiments on the union of ethylene and bromine. It has been shown that water vapour present at a partial pressure of 6 mm. increases the reactivity of the glass surface by 30%, whilst it has no effect on the paraffin wax surface. These results are discussed from the point of view of surface polarity and in the light of our knowledge of the adsorbed water film existing at the surface of many solid substances.

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