CCCLXII.—*The Surface Reactions between Ethylene and the Halogens.*

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IT has been shown by Norrish (J., 1923, **123**, 3006) and Stewart and Edlund (*J. Amer. Chem. Soc.*, 1923, **45**, 1014) that the reaction $C_2H_4 + Br_2 \longrightarrow C_2H_4Br_2$ does not take place in the gas phase, but on the surface of the containing vessel. The nature of the surface determines the speed of the reaction, the catalytic efficiency decreasing in the order stearic acid>glass>cetyl alcohol>paraffin wax. The presence of a film of water accelerates the reaction. The addition of chlorine to ethylene is a surface reaction of the same type (Norrish and Jones, J., 1926, 55; Stewart and Fowler, *J. Amer. Chem. Soc.*, 1926, **48**, 1187; Stewart and Smith, *ibid.*, 1929, **51**, 3082), although at room temperature the reaction is complicated by the formation of the substitution products $C_2H_3Cl_3$ and $C_2H_2Cl_4$ (Bahr and Zieler, *Z. angew. Chem.*, 1930, **43**, 233). At – 20°, the addition reaction predominates. The much slower reaction between ethylene and iodine differs from the above reactions in that it is reversible under ordinary conditions; at equilibrium there is an appreciable concentration of free ethylene and iodine. This equilibrium has been studied by Mooney and Ludlam (*Proc. Roy. Soc. Edin.*, 1929, **49**, 160) for the reaction in the gaseous phase and by Polissar (*J. Amer. Chem. Soc.*, 1930, **52**, 956) for that in carbon tetrachloride solution.

Mooney and Ludlam measured the velocity of both the formation and the decomposition of the di-iodide, in presence of solid iodine and di-iodide. Velocity coefficients were calculated on the assumption that the reaction was homogeneous, in which case the rate of change of pressure would be given by

$$dp/dt = k_1 P_{C_2H_4I_2} - k_2 P_{C_2H_4} \times P_{I_2},$$

where $P_{C_2H_4I_2}$ and P_{I_2} are constant in presence of the solids. The values of k_2 obtained were not constant but showed a drift with time; they also depended on the previous history of the reaction system, *e.g.*, the temperature to which it had been heated; this affected the amount of ethylene adsorbed. This result suggested that the reaction is not homogeneous, but takes place on the surface of ethylene di-iodide, iodine, or the glass walls, and thus resembles the addition reactions of ethylene with the other halogens. The formation and decomposition of ethylene di-iodide in carbon tetrachloride solution (Mooney and Ludlam; Polissar, *locc. cit.*) are homogeneous reactions catalysed by iodine atoms, the rate of the reactions being given by

$$d[I_2]/dt = k_1[C_2H_4I_2][I_2]^{1/2} - k_2[C_2H_4][I_2]^{3/2}.$$

If we assume the same mechanism for the gas reaction, the values of k_1 and k_2 obtained are nearly 10^6 times greater than the values found by Polissar for the homogeneous reaction in carbon tetrachloride solution. This large discrepancy between the velocity of the reaction in solution and that of the gas reaction as found by Mooney and Ludlam, again suggests that the latter reaction is largely heterogeneous.

We have now carried out some experiments to discover the nature of this gas reaction. The results show that it is a reaction which takes place largely on the surface of the iodine crystals. Paraffin and moist glass surfaces are comparatively inactive, although a glass surface covered with a film of ethyl alcohol shows an activity approximately equal to that of iodine crystals.

EXPERIMENTAL.

Reaction between Ethylene and Iodine on Various Surfaces.—The reaction in question takes place with pressure change so that it can be most easily followed manometrically. A 500-c.c. flask was used as the reaction vessel, except in Expts. I and II, for which a litre flask was used. The iodine was introduced and the air displaced by ethylene. The flask was then connected by a ground joint to a capillary, 50 cm. long, leading to a water manometer.* The flask and joint were completely immersed in a thermostat kept at 30° ± 0·1°. The course of the reaction was followed by measuring the change of pressure at constant volume, corrections being made for barometric changes.

Variation of the nature of the surface caused large changes in the velocity of the reaction. This is illustrated in Fig. 1. The slope of curve XX gives the rate of reaction for 1 g. of iodine crystals of moderate size. For curve XVI the same weight of iodine was used, but the surface was increased by powdering the crystals, and the glass walls of the flask were coated with paraffin wax. The surface for curve V was formed by subliming small crystals on to the glass walls of the flask, while in XXIII the whole surface of the flask was moistened with alcohol and drained before introduction of the iodine.

Table I summarises certain of the experiments. The rate of

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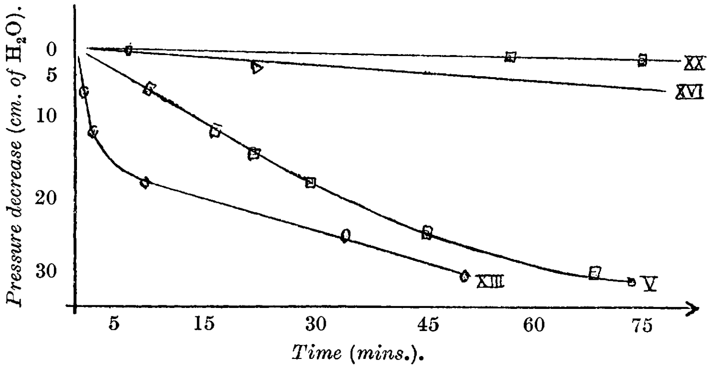
* Preliminary qualitative experiments had shown that the reaction (between ethylene and iodine) was not inhibited by drying both reactants with phosphoric oxide; it was therefore not thought necessary to take precautions to ensure constant pressure of water vapour.

change of pressure, dp/dt, in the fourth column was obtained from the slope of the initial part of the curve.

FIG. 1.



Solid iodine was present in all the experiments, and the other surfaces studied were glass, paraffin wax, ethylene di-iodide, and ethyl alcohol. The glass surface was cleaned before each experiment by immersion in chromic acid overnight, washing with distilled water, and drying in an air-blast. The paraffin surface was best obtained by melting about 5 g. of paraffin wax in the cleaned, dried flask and rotating it in every direction until it solidified in a fairly

TABLE I.

Expt. No.	Iodine surface.	Other surface.		$\frac{dp}{dt}$ (cm. of H_2O/min.).
I	6 G. powdered	Glass;	450 cm.^{2}.	0·42
II	5 G. ,,	Paraffin;	450 ,,	0·44
XVI	1 G. ,,	,,	300 ,,	0·08
XVIII	1 G. ,,	Glass + paraffin;	300 ,, 300 ,,	0·09
XIX	1 G. ,,	Glass + paraffin;	600 ,, 300 ,,	0·09
XX	1 G. crystals	Glass;	300 ,,	0·03
IV	1 G. sublimed	Glass;	300 ,,	0·5
V	,, ,,	,,	300 ,,	0·5
VI	,, ,,	,,	600 ,,	0·8
VII	,, ,,	,,	600 ,,	0·75
VIII	,, ,,	,,	900 ,,	0·9
XVI	1 G. powdered	Paraffin;	300 ,,	0·08
XXIV	,, ,,	$C_2H_4I_2$;	300 ,,	0·14
IV	1 G. sublimed	Glass;	300 ,,	0·5
V	,, ,,	,,	300 ,,	0·5
XXV	,, ,,	$C_2H_4I_2$;	300 ,,	1·2
XIV	1 G. powdered	Alcohol;	300 ,,	0·80
XV	,, ,,	,,	300 ,,	0·6
XXIII	,, ,,	,,	300 ,,	5·0

uniform layer. Whenever an increased glass surface was required it was obtained by adding a number of glass rods, of measured surface area, to the flask before filling it with ethylene. To obtain a surface of ethylene di-iodide, 5 g. of the pure crystals were melted without decomposition, and the flask was rotated as in the case of paraffin until a uniform solid layer was formed.

The following are the main features of our results. No difference is found in the behaviour of glass and paraffin surfaces. When the glass surface is increased (Expts. XVI, XVIII, XIX) there is no corresponding increase in the velocity, which suggests that neither paraffin nor glass surfaces play any considerable part in the reaction. If, however, iodine is sublimed in small crystals on to an increasingly large glass surface (Expts. IV—VIII), which effectively increases the iodine surface, there is a corresponding increase in the speed of the reaction. If powdered iodine is used, the speed is about ten times less than that observed when the iodine surface is increased by sublimation. The speed can be reduced still further by using large crystals instead of powdered iodine (Fig. 1, Expt. XX). It is evident that under the conditions of our experiments the reaction between ethylene and iodine takes place almost entirely at the surface of solid iodine, and that glass or paraffin surfaces are of secondary importance. A surface of ethylene di-iodide crystals seems to be more active than glass or paraffin, but very much less active than an iodine surface. The results obtained with the alcohol surface are very irregular, but it is obvious from a comparison of Expts. XIV, XV, and XXIII with Expt. XVI that the presence of alcohol greatly accelerates the reaction. It is significant that Semenow's method of preparing the di-iodide (*Jahresber.*, 1864, 483) involves passing ethylene over iodine crystals covered with alcohol.

The graphs obtained by plotting pressure against time are fairly straight lines for experiments with powdered iodine or large crystals, but in those with iodine sublimed as small crystals on to the walls there is a gradual falling off in speed. This is probably due to gradual decrease of the iodine surface owing to the disappearance of the smallest crystals. The deceleration is not due to the back reaction (decomposition of ethylene di-iodide), for the reaction was never followed very far towards equilibrium. At 30° the pressure of ethylene in equilibrium with iodine and ethylene di-iodide is 18 mm. of mercury : in our experiments it was never below 700 mm.

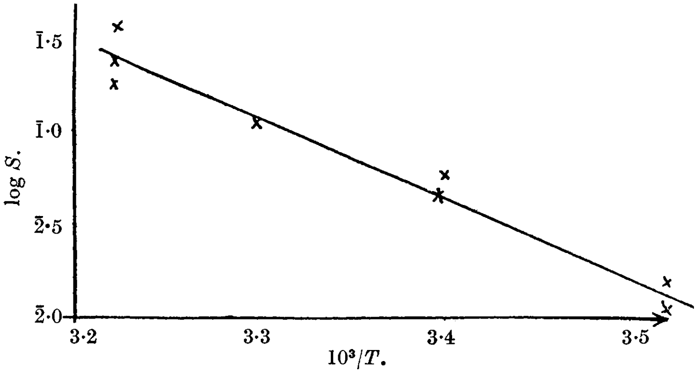
The Reaction on a Glass Surface.—Although we have no measurements for the rate of the reaction on a glass surface alone, we can at least give an upper limit for this value. It is of interest to compare this upper limit with the published figures for the reactions C_2H_4 +

$Cl_2 \longrightarrow C_2H_4Cl_2$ and $C_2H_4 + Br_2 \longrightarrow C_2H_4Br_2$ on wet glass surfaces. The course of these reactions can be represented by

$$- d[C_2H_4]/dt = k[C_2H_4][X_2] \quad . \quad . \quad . \quad . \quad (1)$$

where $X_2 = Cl_2$ or Br_2. Assuming that it is similarly bimolecular, we have calculated velocity coefficients for the reaction between ethylene and iodine on the glass surface: $- d[C_2H_4]/dt = 0{\cdot}022$ (mm. Hg/min.) on the surface of 1 g. of iodine crystals + 300 sq. cm. of glass at 30° (Expt. XX). The rate of the reaction on the glass surface alone is certainly much less than this, but we shall take this value for the upper limit. Substituting in (1) the values $[C_2H_4] =$ 760 mm., and $[I_2] = 0{\cdot}5$ mm., we obtain $k_{I_2} = 0{\cdot}022/0{\cdot}5 \times 760 = 5{\cdot}8 \times 10^{-5}$. The velocity coefficient k_{Cl_2} for $C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$ (Norrish and Jones, *loc. cit.*) is approximately 10^{-3} at 18°.

FIG. 2.



Values for k_{Br_2} at 0° are 10^{-2} (Stewart and Edlund) and 5×10^{-2} (Norrish). The reactivity of the halogens towards ethylene on a glass surface therefore increases in the order $I_2 < Cl_2 < Br_2$.*

Temperature Coefficient.—The most important result of the above experiments is that the reaction takes place almost entirely on the iodine surface. A second series of experiments has been carried out on measured iodine surfaces. The most uniform crystals of iodine were selected, and the surface area of a weighed portion of them found approximately by fitting them as closely together as possible on a sheet of graph paper. Twice the area covered by the iodine gave a first approximation to the surface area of the crystals. Values were obtained for the rate of the reaction per sq. cm. of iodine surface at temperatures 11°, 21°, 30°, and 37·3°. From these values the

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* In a recent paper Boer (*Z. physikal. Chem.*, 1931, *B*, **13**, 134) has shown that the adsorption of iodine on glass is practically negligible. This accounts for the low catalytic activity of a glass surface in our experiments.

" apparent " heat of activation of the reaction was calculated. The results are given in Table II, and in Fig. 2 the logarithm of S, the ratio rate/area, is plotted against the reciprocal of the absolute temperature. The points lie on a line, which is reasonably straight in view of the approximate nature of the experiments. From the slope of this curve the " apparent " heat of activation was found to be 19·8 ± 3 kg.-cals.

TABLE II.

Expt. No.	Temp.	Area, cm.^{2}.	Rate (cm. H_2O/hr.).	Rate/area.
XXVIII	11·15°	14	0·22	0·015
XXIX	11·10	16	0·18	0·011
XXX	21·1	14	0·83	0·059
XXXI	21·4	16	0·72	0·045
XXVI	30·1	17	1·88	0·11
XXXIII	37·3	17	3·1	0·18
XXXIV	37·3	18	6·7	0·37
XXXV	37·3	94	23·4	0·25

Mechanism of the Reaction.—There are two possible mechanisms for the reaction : it takes place either (1) in a layer of ethylene adsorbed on the iodine surface, or (2) between gaseous ethylene molecules and solid iodine at the moment of impact. The latter mechanism being assumed, and postulating that all the energy of activation is supplied by the kinetic energy of the ethylene molecules, the energy of activation can be calculated from the formula $\log_e Z/Z_0 = -E/RT$, where Z_0 and Z are the numbers of molecules respectively striking the surface and reacting. For example, in Expt. XXX, $Z/Z_0 = 8{\cdot}2 \times 10^{-10}$, which leads to the value $E = 12{\cdot}2$ kg.-cals. This is definitely lower than the value of E calculated from the temperature coefficient, *viz.*, 19·8 ± 3 kg.-cals. If it is assumed that n internal degrees of freedom of the ethylene molecule (and also the energy of the iodine molecules in the crystal) contribute towards the heat of activation,

$$\frac{Z}{Z_0} = \frac{e^{-E/RT}(E/RT)^{\frac{1}{2}n-1}}{\underline{|\tfrac{1}{2}n-1}}$$

(Hinshelwood, " Kinetics of Chemical Change in Gaseous Systems," 2nd Ed.). To bring the value of E up to the lower limit calculated from the temperature coefficient, it is necessary to assume $n > 19$. To raise E to the mean value, 19·8 kg.-cals., one must assume 50 degrees of freedom. The molecular heat of ethylene is 11·3 cals. and the atomic heat of solid iodine is 6·6 cals., which indicate 11 and 7 active degrees of freedom respectively. The total, $n = 18$, is scarcely sufficient to raise the value of E to the neighbourhood of that calculated from the temperature coefficient. We may therefore conclude that the first mechanism is more probable, *i.e.*, that the reaction takes place in the layer of ethylene adsorbed on the surface of the iodine crystals. In order to maintain the equilibrium $C_2H_4 + I_2 \rightleftharpoons C_2H_4I_2$, the decomposition of the adsorbed di-iodide must also be catalysed by the iodine surface.

It is difficult to say whether the reaction on the iodine surface is a simple addition reaction or whether it goes *via* iodine atoms and the free radical C_2H_4I, as has been shown to hold for the homogeneous reaction in solution (Schumacher, *J. Amer. Chem. Soc.*, 1930, **52**, 3132; Schumacher and Wiig, *Z. physikal. Chem.*, 1930, *B*, **11**, 45).

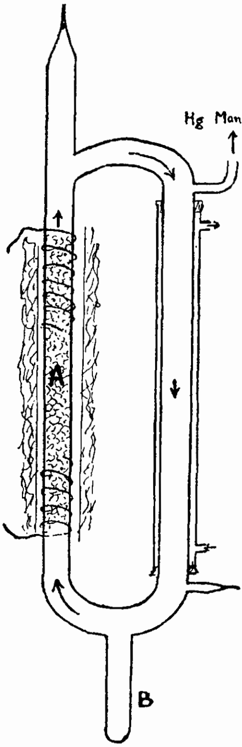
We have made some measurements to test the relation between reaction rate and ethylene pressure. The reaction vessel containing, in these cases, 5 g. of iodine crystals, was connected to a mercury manometer, evacuated, and filled with ethylene at the pressure required. The figures given below show that, for a constant iodine surface, the rate is proportional to the ethylene pressure.

Expt. No.	$P_{C_2H_4}$ (mm. Hg).	dP/dt (mm./hr.).	$(dP/dt)/P$.
XXXVIII (*a*)	740	10·1	0·014
(*b*)	260	3·0	0·012
XXXIX (*a*)	750	10·5	0·014
(*b*)	320	5·2	0·016

The reaction is therefore expressed kinetically by the equation $dP_{C_2H_4}/dt = k.S.P_{C_2H_4}$, where S is the area of the iodine surface. This resembles the kinetics of the reactions between chlorine or bromine and ethylene on a glass surface, where the rate is equal to $k(G.P_{Cl_2}).P_{C_2H_4}$ and $k(G.P_{Br_2}).P_{C_2H_4}$, where G is the area of the glass surface.

Reaction between Ethylene and Cyanogen.—Since many of the properties of cyanogen are similar to those of the halogens, some experiments were conducted to find out if ethylene will combine with cyanogen at a surface as it does with chlorine, bromine, and iodine. In the first experiment, which gave entirely negative results, equal volumes of ethylene and cyanogen were introduced into a 500-c.c. flask, loosely packed with glass wool, and kept at 150°. Even after six weeks, no pressure decrease was observed, except a few mm. attributed to the formation of paracyanogen. The glass wool, which had turned slightly brown, was extracted with alcohol, but no trace of ethylene dicyanide (succinonitrile) could be found in the extract. This might have been due, as in the case of iodine, to poor adsorption of cyanogen on glass. Silica gel was used in the second experiment to get better adsorption of cyanogen. The apparatus is shown in Fig. 3. The catalyst, *A*, was electrically heated to 110°. By cooling the opposite limb below room temperature by a stream of water at 10°, a convection current was set up which kept the gases continuously circulating over the silica gel catalyst. After 4 weeks the gases were frozen out into tube B, with liquid air. When the tube was allowed to become warm, the ethylene boiled off, leaving crystals of cyanogen, which in turn melted and evaporated. A white crystalline solid was left behind. This substance did not melt, but sublimed slowly at room temperature and rapidly at 60°. It was finally shown to be ammonium carbonate. The silica gel, which had turned dark brown, was extracted with water. The solution obtained had a brilliant violet fluorescence which became green and less intense on addition of a drop of sodium hydroxide solution. The substance responsible for this fluorescence is almost certainly azulmic acid, $C_4H_5ON_5$, which is formed by the interaction of cyanogen and aqueous ammonia (Beilstein, "Organische Chemie," Vol. II, p. 553, 4th Edn.). The solution was evaporated to dryness and the residue examined for succinonitrile or its hydrolysis product, ammonium succinate, by heating with zinc and testing for pyrrole with a shaving of red pine moistened with hydrochloric acid.* A very slight reddening of the pine shaving was observed. This, however, is probably to be attributed to azulmic acid rather than to a trace of a succinic acid derivative. It is clear that the reaction $C_2H_4 + (CN)_2 = C_2H_4(CN)_2$ does not take place to any appreciable extent on a glass surface at room temperature or on silica gel at 110°.

FIG. 3.



Ethylene and the Cyanogen Halides.—If there is any reaction between ethylene and the cyanogen halides (CN·Cl, CN·Br, CN·I), three different kinds of reaction product are possible, *viz.*, $C_2H_4X_2$, $C_2H_4(CN)X$, and $C_2H_4(CN)_2$, where X = Cl, Br, or I. In our experiments at 37°, no reaction was observed between the chloride or bromide and ethylene, but with the iodide a slow reaction, which pro-

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* In order to obtain satisfactory results with the pine-shaving test, it was found necessary to purify the zinc dust by heating it in a Rose crucible in a stream of hydrogen. If this precaution were not taken, the zinc dust contained sufficient nitrogenous matter to give a positive test. Using the purified zinc dust, it was possible to detect the presence of as little as 0·01 mg. of ammonium succinate. If oxalic acid is present, the test is much less sensitive because the red coloration is bleached by the vapours given off.

ceeded without pressure change, took place. The products, identified by their m. p.'s, were ethylene di-iodide and cyanogen. It is improbable that this is a direct reaction according to the equation

$$2CN{\cdot}I + C_2H_4 \longrightarrow C_2H_4I_2 + (CN)_2;$$

it is more likely that an equilibrium exists : $(CN)_2 + I_2 \rightleftharpoons 2CNI$. The ethylene present in the system will remove the free iodine until the cyanogen iodide is completely decomposed.

Summary.

1. The reaction between ethylene and iodine has been shown to be a surface reaction. It thus falls into line with the corresponding reactions between ethylene and the other halogens.
2. The reaction takes place almost entirely on the surface of solid iodine.
3. Glass and paraffin walls are equally unimportant as catalysts.
4. The rate of the reaction is proportional to the pressure of ethylene.
5. The heat of activation of the reaction, calculated from the temperature coefficient, is 19·8 ± 3 kg.-cals.
6. The reaction probably takes place in the layer of ethylene adsorbed on the surface of the solid iodine.
7. No reaction takes place between ethylene and cyanogen or its chloride or bromide at the temperatures studied. The reaction between ethylene and cyanogen iodide at 37° leads to the formation of cyanogen and ethylene di-iodide.

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