THE CATALYSIS OF GASEOUS REACTIONS BY CHLORINE.

By S. Bairstow.

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The catalysis of various gaseous reactions by iodine has now been fairly extensively investigated,[1] and it is of some interest to examine the catalytic influences of the other halogens. This note describes certain observations on catalysis by chlorine; from these further conclusions about the mechanism of the process may be drawn.

The decomposition of diethyl ether is catalysed by chlorine, and the ratio:

(rate with 6·7 mm. chlorine)/(rate without chlorine) for 150 mm. ether at 463° C. is about 20. The corresponding ratio for the corresponding iodine catalysis is 120, and thus chlorine is only about one-sixth as effective as iodine at this temperature. By measurement of the initial rate of reaction for different initial pressures of ether it is found that the reaction is of the first order with respect to the ether. The rate is also directly proportional to the chlorine concentration. The whole course of the reaction, however, does not conform to a definite order since the catalyst concentration changes during an experiment. This is due to the fact that some of the catalyst is used up in a chemical reaction during the decomposition, as can be shown by allowing the catalysed decomposition to attain completion and then adding a further quantity of ether. The new rate, although much greater than that of the uncatalysed decomposition, does not correspond to the full original amount of chlorine.

At all stages the reaction is much faster in presence of chlorine than in its absence, so that there is no doubt that free chlorine is present all the time.

The following conclusion is important: it was possible to argue that the catalysis by iodine involved the following definite chemical reactions:—

$$C_2H_5 . O . C_2H_5 + I_2 = C_2H_5I + HI + CH_3CHO$$
$$CH_3 . CHO + I_2 = CH_3I + HI + CO$$

followed by

$$C_2H_5I + HI = C_2H_6 + I_2$$
$$CH_3I + HI = CH_4 + I_2.$$

Now at the temperature of working, if hydrogen chloride were formed in this manner, the regeneration of chlorine would not be possible. Therefore, if catalysis by chlorine proceeded in this manner, a mixture of 10 mm. chlorine and 200 mm. of ether would show a rapid increase in pressure of 10 mm. and then the rate would fall to that of the uncatalysed reaction. Actually the whole reaction, involving a pressure

[1] See Bairstow and Hinshelwood, *Proc. Roy. Soc.*, A, 1933.

increase of about 175 mm., is catalysed right to its end. Thus the purely chemical theory is quite untenable, at least in the case of chlorine, and therefore it is improbable for the case of iodine. Since on other grounds it was regarded as unnecessary, the theory can be dismissed completely.

The action of chlorine on the decomposition of trimethylamine and of methyl ethyl ketone—two reactions which are relatively insensitive to the catalytic influence of iodine—was investigated. The object was to see whether a halogen with a higher heat of dissociation, and therefore capable of containing more vibrational energy, would be effective in cases where iodine failed. Actually the results were negative, since the effect of chlorine on trimethylamine is normal—*i.e.*, the increase in rate is about one-quarter that produced by iodine,—and the addition of as much as 60 mm. chlorine to 100 mm. methyl ethyl ketone only multiplies the rate by a factor of about three.

Trinity College,
Oxford.