CCCCXXIX.—*Note on the Rate of Photochemical Combination of Chlorine and Hydrogen in Glass Capillary Tubes.*

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DETERMINATIONS were recently made by Briers and Chapman (this vol., p. 1802) of the rates of photochemical union of bromine and hydrogen when the illumination of the mixture was intermittent, and it was shown that the results obtained could be interpreted by the assumption that the union of the gases is due to a catalyst formed by the light, and having an average life of an appreciable fraction of a second. As the results of the measurements of the rates of chemical change can in general be explained by more than one set of hypotheses, it is desirable that evidence, if possible of a different character, should be obtained of such long-lived catalysts in other cases of photochemical change. The experimental method adopted in the case of bromine and hydrogen cannot be applied, as already explained (*loc. cit.*), in the case of chlorine and hydrogen. However, there is another simple method of testing whether a similar theory is applicable to the photochemical union of the latter gases.

If we postulate that the union of chlorine and hydrogen is due to an unstable catalyst, and that the catalyst is destroyed when it comes into contact with glass or a film of water, then obviously if the catalyst has an appreciable life it ought to be possible to show that in light of the same intensity the rate of union of chlorine and hydrogen in capillary tubes is less than in tubes of wider diameter. The experiment has been performed and has furnished a positive result.

The determinations were made with a hermetically sealed glass apparatus of the form of a U-tube of which one limb was a capillary tube of 1 mm. internal diameter, and the other limb a tube of about 2·5 cm. diameter. The apparatus contained about 3 c.c. of water and electrolytic gas at atmospheric pressure. In purifying the water and in preparing the electrolytic gas, the usual precautions were taken to eliminate destructible inhibitors. Furthermore, as an additional precaution, the apparatus, after it had been filled and sealed, was heated at 130° for 6 hours in a bath of glycerol.

The preliminary experiments were performed in the following manner. The previously filled apparatus was placed in a horizontal position and the water removed from the capillary tube by heating it with steam. Then, in order to be certain that the capillary tube contained gas of the same composition as that in rest of the apparatus, the former was warmed and cooled many times. The apparatus was next fixed in a vertical position so that the water enclosed the gas in the capillary tube, which was then warmed so as to drive out about one-fourth of the gas it contained. The water which moved up the capillary tube on its regaining the temperature of the laboratory served as an index.

When the whole apparatus was exposed to light, so that both tubes were equally illuminated, the index in the capillary tube moved downwards, showing that the rate of combination of the gases in the wider tube was more rapid than that of the gases enclosed in the capillary. After exposure to light and before the final reading of the index was taken, the apparatus was allowed to stand at a constant temperature in the dark for 12 hours to ensure the attainment of complete equilibrium. Then, in order to estimate the proportions of hydrogen chloride formed in the wide and narrow tubes, the apparatus was completely immersed in water in an upright position, and the sealed end of the wide tube opened. The water which immediately entered the wider tube filled from one-third to one-half of its volume, showing that a considerable proportion of the gases originally contained therein had combined. The index in the capillary tube, however, only rose to its initial position, thereby showing—since the pressure of the gas in the capillary tube was initially and finally approximately the same, namely, that of the atmosphere—that only a small proportion of the gases introduced into it had united.

To measure more accurately the relative rates of combination in the two tubes, the capillary tube alone and the wider tube alone were alternately exposed to light of the same intensity. The downward movement of the index which accompanied the exposure of the wider tube to light was 40—60 times more rapid than the upward movement of the index resulting from the illumination of the capillary tube alone. Before the readings were taken, sufficient time was always allowed to elapse to ensure complete solution of the hydrogen chloride formed, and a correction was applied for the light totally reflected from the sides of the bore of the capillary tube. That the ratios of the rates of combination observed in different experiments were not constant was to be expected, since electrolytic gas contains varying small proportions of oxygen, which, being an inhibitor, would shorten the life of the catalyst.

The precautions taken to destroy destructible inhibitors appear to us to exclude the possibility that the observed effect was due to the gradual escape of such inhibitors from the surface of the glass. Moreover, the possibility that the rate of union of the chlorine and hydrogen in the capillary tube was inhibited by hydrochloric acid is excluded by well-known experiments of Bodenstein.

From the above-described phenomenon, an attempt will be made, with an apparatus designed for the purpose, to obtain an estimate of the life of the catalyst.

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