398. *The Photochemical Union of Hydrogen and Chlorine. Part VII. The Effect of Water Vapour on the Reaction at Low Pressures.*
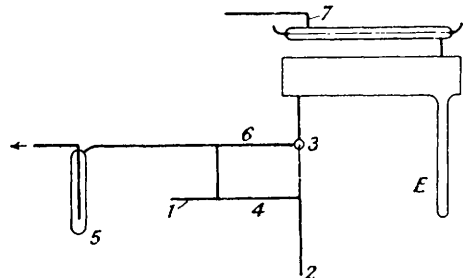
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Intensive drying of a low-pressure mixture of hydrogen and chlorine does not inhibit the reaction in light. On the contrary, the addition of small quantities of water vapour to the dried gases retarded the reaction somewhat under the conditions of experiment.

WHEN our experiments were commenced, it was generally believed, on the authority of Coehn and Jung (*Z. physikal. Chem.*, 1924, **110**, 705), that visible light was without action on a hydrogen–chlorine mixture if the aqueous vapour pressure were reduced to 10^{-7} mm., whilst at 10^{-5} mm. ready reaction took place. On the other hand, in the experiments of Bateman and Craggs (*Trans. Faraday Soc.*, 1931, **27**, 445), where the chlorine pressures, as in the present work, were controlled by suitable low-temperature refrigerants, normal reaction was observed. The refrigerant presumably also determined the pressure of water vapour in the reaction space at a value not greater than the sublimation pressure of ice at the temperature concerned, *i.e.*, at about 10^{-6} mm., 10^{-8} mm., and 10^{-9} mm. when melting carbon disulphide, methyl*cyclo*hexane and allyl chloride respectively were used. Quite apart, then, from the probability that the actual water vapour pressures would be less than those given, owing to the formation of chlorine hydrate, the results of Bateman and Craggs, amply confirmed in our own experiments, directly contradicted those of Coehn and Jung. However, although the walls of the apparatus were baked out in the preliminary evacuation, there remained the faint possibility of their slowly giving off water during the insolation, and of this distilling through the reaction space into the cooled limb. Such distillation would, of course, tend to be rapid at the low prevailing total pressures.

EXPERIMENTAL.

In order to eliminate this possibility, the matter was subjected to a more rigorous test. For this purpose, the palladium tube (7 in the figure) for the admission of hydrogen was sealed

on to the Pirani gauge, thus allowing the whole apparatus (of glass) to be evacuated with a stream of pure dry hydrogen passing through it. Such treatment is particularly effective in removing traces of adsorbed vapour from solid surfaces. The whole reaction space, including the gauge, was then baked out at 200° in an air-oven of simple construction, projecting parts being dealt with by resistance-wire electric heaters. During this treatment, hydrogen gas was passed through continually. After the temperature had been lowered and the gas stream discontinued, the gauge zero was determined, purified chlorine admitted in the usual way, and liquid air placed around E. With the exception of this cooled limb (from now onwards always immersed in either liquid air or a low-temperature refrigerant), the whole apparatus was again heated to 200°, and hydrogen passed through for 8 hours, at a mean pressure of about 1 mm. The reaction vessel was then sealed off, and the system allowed to cool. Hydrogen was removed by heating the palladium tube until the pressure had fallen within the range of the gauge, the liquid air on E replaced by melting methyl*cyclo*hexane, and insolation commenced in the ordinary way, a metal-filament lamp being used with interposition of a 5-mm. glass plate. Great care was taken when changing the temperature of E that it should not rise above the m. p. of methyl-*cyclo*hexane. Reaction took place freely at an estimated aqueous vapour pressure not exceeding 10^{-8} mm.

An experiment was also done in which the rates of reaction in a given gas mixture, after addition of a known partial pressure of water, were compared with the rate in the " dry " gas. As in the last experiment, the reaction vessel was used with the palladium tube sealed on to the Pirani gauge (see fig.). The water was produced in a side tube 1 situated between the main apparatus and the chlorine supply, and containing 0·0021 g. of calcined cupric oxide. This, after evacuation and admission of hydrogen, was heated, and the liberated water frozen out by liquid air in another side tube 2, which was connected with the main apparatus through an internal capillary seal, 3, which could be broken by a magnetically operated, glass-covered, iron plunger. The copper oxide tube was then sealed off from the water supply at 4 after the excess of hydrogen had been pumped out. In carrying out the experiment, the apparatus was baked out as before in a hydrogen stream, and the pumps shut off. Hydrogen was admitted, the copper oxide reduced, and the water frozen out and isolated as described. Chlorine was purified as usual and collected in 5, which was immersed in liquid air. The main apparatus was again baked out, and allowed to cool in a hydrogen stream. Excess of the latter was pumped off, and the pumps shut off from the reaction vessel. The liquid air on 5 was replaced by melting carbon disulphide ($p_{Cl_2} = 1·7$ mm.), and, after a suitable interval, the apparatus sealed off at 6. The result was a baked-out reaction system containing 1·7 mm. of chlorine, but with no excess condensed out in E, into which hydrogen could be admitted at will, and water vapour up to a pressure of about 0·7 mm. (calculated from the volume of the system and the weight of cupric oxide taken), the actual figure depending on the refrigerant used on E. With liquid air on E, the gauge zero was tested, hydrogen admitted, and the palladium tube sealed off at 7.

The cell was then insolated under four different sets of conditions, viz. : (a) E in melting ethyl acetate (189·6° K.) and no water in apparatus; (b) water admitted by breaking inside seal (pressures of hydrogen and of chlorine fell slightly on account of increase in dead space)—E at 189·6° K., $p_{H_2O} = 2 \times 10^{-4}$ mm.; (c) E in melting carbon disulphide (161·4° K.)—$p_{H_2O} = 10^{-6}$ mm.; (d) E at room temperature—p_{H_2O} about 0·7 mm. The results are shown in the table.

Expt.	p_{H_2} (mm.).	Time (mins.).	Average slope.	Average p_{Cl_2}.	$\dfrac{\text{Slope}}{p_{Cl_2}}$.	Expt.	p_{H_2}. (mm.).	Time (mins.).	Average slope.	Average p_{Cl_2}.	$\dfrac{\text{Slope}}{p_{Cl_2}}$.
(a)	0·598	0				(b)	0·433	0			
	0·554	15					0·424	10	0·125	1·41	0·089
	0·496	39	0·216	1·62	0·13		0·377	48			
	0·444	60									
(c)	0·377	0	0·168	1·37	0·12	(d)	0·357	0	0·133	1·42	0·093
	0·357	14					0·347	15			

The observed rate of reaction fell off appreciably when water vapour was admitted in (b), although its pressure can have been only 2×10^{-4} mm., apart from the formation of chlorine

hydrate. It rose again, (c), when the water vapour was frozen out at a lower temperature, and decreased when p_{H_2O} was allowed to rise to its maximum figure. In column 5, it is assumed that the water condensed out in E during (b) and (c) as chlorine decahydrate, and 0·07 mm. has consequently been subtracted from what otherwise would have been the average chlorine pressure. The last column gives corrected relative slopes, the rate of reaction being assumed proportional to p_{Cl_2}.

The results show clearly that, under our conditions, water did not accelerate, but rather retarded, the action. At the low total pressures of the experiments (1·7—2·5 mm.), this effect is presumably due to the formation of an adsorbed film of water on the surface of the reaction vessel which accelerates the catalytic action of the walls on chlorine atoms. Such a result is quite different from what is observed when hydrogen atoms are involved. On the other hand, Rodebush and Klingelhoefer (*J. Amer. Chem. Soc.*, 1933, **55**, 130) have made observations which accord with ours. The main result of our work, *i.e.*, the absence of any retardation due to the intense drying of the gases, has already been briefly reported (*Nature*, 1932, **130**, 927) and is in complete agreement with the conclusions of Bernreuther and Bodenstein (*Sitzungsber. preuss. Akad. Wiss.*, 1933, 333), of Rodebush and Klingelhoefer (*loc. cit.*), and of Rollefson and Potts (*J. Amer. Chem. Soc.*, 1933, **55**, 860).