THE FORMATION OF POLAR COMPOUNDS BY PHOTO-CHEMICAL REACTIONS.

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A polar compound is formed when an electropositive element reacts with an electronegative radical or element. Let us consider any hypothe the the the the the the the transformation M + N = MN in which M is the electropositive constituent This reaction may conceivably and N the electronegative constituent. take place in steps: $M = M^+ + \text{electron}$; $N + \text{electron} = N^-$; $M^+ + N^-$ = MN. The first of these reactions involves the absorption of energy. In the case of a monatomic vapour this energy could be calculated from the ionisation potential. For solid or liquid metals this energy could be calculated from the wave-length of the photoelectric threshold. The second step leads to the emission of radiation, and therefore the evolution of energy,¹ and the third step should also take place with evolution of The only step in the reaction which does not tend to take place energy. spontaneously is the first. It is a well-known fact that light of the proper wave-length will cause the emission of electrons from monatomic vapours and from solid metals. It is my purpose to discuss certain experiments which seem to indicate clearly that some photochemical reactions may take place according to the mechanism postulated.

About two years ago one of my students, Mr. H. R. Moore, investigated the reactions between oxygen and mercury and between nitrogen dioxide and mercury.² The first of these reactions leads directly to the formation of mercuric oxide. The course of the second reaction is somewhat more uncertain, but would seem to be---3

$$4Hg + 2NO_2 = 4HgO + N_2$$
 . . (1)

It is immaterial whether or not the final products of the reaction are given by this equation. The first step in the reaction would probably be the formation of mercurous or mercuric nitrite highly polar compounds. The original purpose in this investigation was to show that the mercury surface was activated after emission of electrons by the photoelectric effect. At the time our paper was published we were rather inclined to the view that this is the case, although we advanced the alternative explanation that the gas was activated in some way during our experiments. It is my intention to discuss these results more fully than has hitherto been done, as it seems to me that they elucidate the mechanism of one type of photochemical action.

Before undertaking this discussion, it would seem wise to tabulate the main points brought out in the experimental work :

 ¹See, for example, Franck, Zeitsch. für Physik, 1921, 5, 428.
² Moore and Noyes, J. Am. Chem. Soc., 1924, 46, 1367.
³ Watt's "Dictionary of Chemistry," 1894, Vol. III., p. 566.

570

THE FORMATION OF POLAR COMPOUNDS

1. The rate of reaction between mercury and nitrogen dioxide is normally quite rapid. Since the mercury surface used was small, this rate of reaction could not be satisfactorily followed by the pressure decrease. However it was possible to obtain a fairly quantitative measure of the reaction rate by observing the film of mercury. A coating is formed on it which gradually increases in thickness until wrinkles can be seen on the This point at which the film is thick enough to be easily visible surface. is very definite and the rate of the reaction is very nearly inversely proportional to the time of formation of the film up to this point. This time of formation was a function of the pressure of nitrogen dioxide (for the reaction in the dark), being longer for the lower pressures as would be expected.

2. If the mercury surface was illuminated by wave-lengths longer than the photo-electric threshold of mercury,¹ and the light turned off at the same time that nitrogen dioxide was admitted, no decrease in the time of formation of the film was noted.

3. If the mercury surface was illuminated by light of wave-length shorter than the wave-length of the photo-electric threshold the following results were obtained :

(a) If a potential was applied in such a way as to accelerate the electrons away from the surface, the time of formation depended upon this potential. With 220 volts the results were somewhat erratic and depended on whether the field was turned off with the light or not.

(b) With low accelerating voltages the shortest time of formation was noticed when about one volt was used. Since the upper electrode was of iron the contact difference of potential should be considered. This has not been accurately determined, but an average value would be about 0.6 volt. The optimum accelerating voltage would be, therefore, about 0.4_2 This optimum voltage was independent of wave-length in our volt. experiments, although the difference in kinetic energy of the electrons emitted with the wave-lengths studied would be only a few tenths of a volt and any effect of this sort might have passed unnoticed.

(c) With retarding potentials the time of formation of the film was the same as for the reaction in the dark.

4. The time of formation of the film is a function of the intensity of the light, when other conditions are maintained as nearly constant as possible.

The reaction under consideration may be considered to take place as follows :

Hg (l) + radiation = Hg⁺ (Hg, l) + e .

$$e + NO_2 = NO_2$$
 (3)
 $NO_2^- + Hg = HgNO_2 + e$ (4)

The electron is thus made available for more cycles of the same sort. In our experiments a simple calculation showed that approximately 10⁸ molecules were formed for each electron, so that it is necessary to postulate some such mechanism as that given above.

The first step is known to be brought about by the action of light. That the second step is probable is indicated by previous work.¹ There is only one serious objection to the above mechanism for this reaction. Since the negative ions formed would be in a field which tended to take them away

¹ The value of this wave-length is, it seems, still open to question. Kazda, *Physical Review*, 1923, **22**, 523, gives 2735 Å. We verified this result in a qualitative manner. Taubes. *Annalen der Physik*, 1925, **76**, 629, gives a higher value. ² Pellat. *Annales de chimie et de physique*, 1881, **24**, 5; van der Bijl, "Thermionic Varume Tube"

Vacuum Tube,'' 1920, p. 29.

571

from the mercury surface, it is difficult to conceive of any increase in The rush of reaction rate due to their combination with the mercury. incoming gas would be sufficient, however, to carry many of the ions down to the surface.

We may explain, satisfactorily I hope, all of the phenomena observed, by means of the above mechanism for the reaction. Let us consider first the question of the optimum accelerating voltage. This optimum voltage is considerably below the ionisation or resonance potential of any gas so far studied, so that we may rule out ionisation or resonance by collision. If a beam of light is incident on a metallic surface, the maximum velocity of the emergent electrons (expressed in volts) may be calculated by the wellknown Einstein equation-

$$V = \frac{h}{e}(v - v_0)$$
 (5)

Electrons will be given off by the surface and the surrounding glass walls will eventually be charged up to a negative potential V. Electrons subsequently emitted will return to the surface and since many of the electrons leave the surface with practically zero kinetic energy, the actual density of the electrons in the space above the mercury will be small. As the potential of the surroundings (including the glass walls and an electrode placed above the surface) is made to approach that of the mercury, more electrons will leave the surface and the number of electrons in the space above the mercury will be maximum when there is no potiential gradient. Since the glass walls had doubtless acquired a negative charge in our experiments, an apparent accelerating potential of about 0.4 volt was required to produce this maximum electron density. It is possible to show mathematically, without making too many doubtful assumptions, that a curve similar to that actually observed should be obtained if it is assumed that the reaction occasioned by the electrons is independent of the normal dark reaction and that the fraction of the total reaction caused by the electrons is given by the expression $\frac{t_n - t_1}{t_n}$ in which t_n is the time of formation of the film for the

dark reaction and t_1 is the time of formation of the film after the action of light.

An increase in the apparent accelerating potential beyond the o'4 volt necessary to obtain the maximum emission of electrons from the surface would cause a decrease in the number of electrons actually present in the space between the electrodes. Here again it is possible to show that the type of curve actually obtained is similar to that required by theory. Α high accelerating potential should cause the reaction rate to approach the reaction rate in the dark for two reasons: (1) The density of the electrons in the space above the mercury would be smaller at the time the nitrogen dioxide was admitted; (2) the negative nitrogen dioxide ions would have less chance of reaching the mercury surface. There may be, in addition, a third factor. If the large number of molecules reacting per electron is to be ascribed to the re-emission of the electron after the formation of each molecule of mercurous nitrite, then these electrons would be taken away by the action of the electric field and the reaction would tend to follow Einstein's law of photochemical equivalence closely. A similar effect may occur with slight retarding potentials and would partially account for the rapid decrease in reaction rate with retarding voltages. The electrons re-emited would be driven into the mercury by such potentials and would no longer be available to continue the chain reaction.

¹ Gibson and Noyes, J. Am. Chem. Soc., 1921, 43, 1255.

THE FORMATION OF POLAR COMPOUNDS 572

There still remains to be considered the activation of the mercury surface. It is apparently not necessary to postulate such an activation in order to account satisfactorily for the phenomena observed. Any such activation would be of extremely short duration. Emission of electrons from the surface might leave small regions in which there is a positive charge, but this charge should rapidly be distributed throughout the whole body of the mercury. If a metal consists of a system of positive mercury ions, mercury atoms and electrons in equilibrium, then the emission of the electrons should temporarily, at least, lead to an increase in the concentration of positive mercury ions. These positive ions could react with nitrogen dioxide at the same time taking up an electron to complete the quota necessary for the molecule formed. This mechanism for the reaction would not account satisfactorily for the effect of accelerating or retarding fields and moreover would lead to the prediction of an increased reaction rate if the mercury could be given a high positive charge without the action of light. This experiment was tried without success, although the potential used (220 volts) may not have been sufficient to give the same deficiency in electrons in the surface as is obtained with the photoelectric effect.

The results we have just discussed would indicate that a reaction leading to the formation of a polar compound may be accelerated by light of such wave-length that electrons are emitted from the electro-positive constituent and made available for absorption by the electro-negative constituent. Reactions of this type are in general exothermal in character and do not obey Einstein's law of photochemical equivalence.

There has been much discussion in the literature as to whether all reactions are not accompanied by ionisation, or are not, at least, ionic in character. Haber and Just¹ found that electrons were emitted during the course of reactions between certain metals and gases. Other observers have reported negative results, but some very careful work by Brewer² has shown that ions are produced during the five reactions he studied (nitric oxide with oxygen, nitric oxide with ozone, nitrogen pentoxide decomposition, ozone decomposition, nitrogen dioxide decomposition). The ionisation currents he observed were proportional in every case to the number of molecules reacting. There is also an equivalence between number of ions formed and number of molecules reacting for reactions brought about by alpha particles and electrons.³ It seems impossible that light should cause the removal of electrons in most of the photochemical reactions studied, and the field of research opened up by the researches of Cario and Franck⁴ indicate clearly that ionisation is not necessary. It does seem probable, as I have already pointed out, that in the case of those reactions leading to a highly polar compound, the removal of the electron from the electropositive element by means of light may accelerate the reaction.

In conclusion the writer wishes to express his appreciation to Mr. Louis Kassel for aid in preparing this paper.

¹Haber and Just, Annalen der Physik, 1909, 30, 411; 1911, 36, 308; Zeitschr. für Elektrochemie, 1914, 20, 320. ² Brewer, J. Am. Chem. Soc., 1924, 46, 1403. ³ See, for example, Lind, The Chemical Effects of Alpha Particles and Electrons,

1921. ⁴ Cario and Franck, Zeitschr. für Physik, 1922, 11, 161.