

I THE ACTIVITY OF HYDROCHLORIC ACID IN THE PRESENCE  
OF A UNIBIVALENT SALT

II THE DISSOCIATION CONSTANT OF BROMINE CHLORIDE  
AT ROOM TEMPERATURE

III A METHOD FOR DERIVING PHOTOCHEMICAL REACTION  
MECHANISMS OF CERTAIN TYPES FROM OBSERVED REACTION RATES

Thesis by  
Philip Griffis Murdoch

In partial fulfillment of the requirements  
for the degree of Doctor of Philosophy

California Institute of Technology  
Pasadena, California

1932

For advice and direction in these investigations  
the author is indebted to Professor S. J. Bates and to  
Professor R. G. Dickinson

THE ACTIVITY OF HYDROCHLORIC ACID IN THE PRESENCE  
OF A UNIBIVALENT SALT

The effect of added salts upon the activity of hydrochloric acid has been studied by a number of investigators. All of these, except Bates and Urmston have employed chlorides for the added salts. In this investigation the influence of the added electrolyte sodium dithionite, i.e., the effects of a negative bivalent ion, was determined.

The added salt to be suitable for experiments of this nature must not react chemically with any of the essential constituents of the cell and must possess certain other properties. That is:

- (1) It should be the salt of a strong acid.
- (2) The silver salt of its acidic constituent should be soluble.
- (3) It should not be the salt of an acid such as nitric acid which acts as a (strong) oxidizing or reducing agent.
- (4) It should be quite soluble.

These conditions greatly restrict the choice of salts. However, sodium dithionite appears to fulfil the conditions in a satisfactory manner.

EXPERIMENTAL PART

The cell used consisted of three silver-silver chloride half cells and two hydrogen half cells, each containing two hydrogen electrodes, connected to the silver-silver chloride half cells through two stopcocks. Hydrogen, prepared by electrolysis of a sodium hydroxide solution, was passed through tubes containing glowing platinum wire, and admitted to the hydrogen cells by means of glass tubes which extended almost to the bottom of the electrode vessels, from which it escaped through bubblers. The elec-

trical contacts in the case of the silver-silver chloride electrodes were made by platinum wires which extended through the bottom of the electrode vessel. The stoppers of the electrode vessel were made of glass, ground to fit tightly.

The silver crystals for the silver-silver chloride electrodes were prepared by the electrolysis of 0.01 M silver nitrate solution, following the procedure of Randall and Young.<sup>1</sup>

The hydrogen electrodes were of platinum foil. The foil was first covered electrolytically with a thin coating of gold and then with a coating of platinum black. The electrodes were washed first with concentrated nitric acid, in order to eliminate any lead from the small amounts of  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  in the platinizing solution, and then with many changes of water, in which they were allowed to stand until placed in the cell. Several variations of this method were tried, as a test of its efficacy, and were found to agree within one tenth of a millivolt among themselves. Thus the effect of the use of a thick coat of platinum black, or of the omission of the gold coat, or of the use of a rough but not black platinum coat was not to change the average electromotive force reading but merely to render it a little less steady. Variation of the rate of plating of the platinum had no measurable effect.

The behaviour of the hydrogen electrodes prepared in the manner first described was quite satisfactory. As a rule they checked to 0.02 or 0.03 millivolt. Although the three silver-silver chloride electrodes were not quite so satisfactory, the largest differences were seldom greater than 0.1 millivolt. The average deviation of the final results at various series of concentrations from the smooth curve is less than 0.1 millivolt.

The cell was placed in an oil thermostat regulated to  $25^{\circ} \pm 0.05^{\circ}$ . The electromotive force was measured with a type K, Leeds and Northrup potentiometer using as standard a Weston cell that was frequently checked against a cell recently certified by the Bureau of Standards.

The sodium dithionate was purchased CP from Eimer and Amend, and purified by recrystallizing three times from water and drying at room temperature. It gave no turbidity with silver nitrate. The salt crystallizes as  $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ . The proportion of water was determined at intervals and always checked closely with the calculated value.

The hydrochloric acid was obtained by diluting the CP acid to a density of 1.1 and distilling in an all-glass still, the middle portion alone being retained. The distillate was then diluted to the desired concentration and standardized by the silver chloride gravimetric method.

All mixtures were made up by weight from stock solutions and from solid salt. All concentrations are expressed in mols per thousand grams of water.

That dissolved air has an effect upon the potential of the calomel electrode in acid solution due to a reaction between mercury, chloride ion, hydrogen ion, and oxygen has been clearly demonstrated by Randall and Young.<sup>1</sup> The similar effect on the silver-silver chloride electrode is less serious. Guntelberg<sup>2</sup> found some influence and removed oxygen from his solutions by means of nitrogen. Randall and Young, however, discovered no measurable effect upon silver-silver chloride spiral electrodes in 0.1 M hydrochloric acid.\* The change in the potential of the silver-silver chloride electrode

\*Spiral electrodes probably offer less silver surface and hence less opportunity for oxidation than do electrodes employing electrolytic silver crystals. The latter were used by Guntelberg and in this investigation.

results from the removal of chloride ion from the solution in contact with it by the reaction  $\text{Ag} + \frac{1}{4} \text{O}_2 + \text{H}^+ + \text{Cl}^- = \text{AgCl} + \frac{1}{2} \text{H}_2\text{O}$ . The change is synbat with the fractional change in chloride activity, and hence may be expected to be greatest at low chloride concentrations; likewise at high acid concentrations, as can be seen from an inspection of the equation. Thus with solutions of 0.01 M hydrochloric acid effects of the order of millivolts were observable, which were due to the effect of oxygen. With 0.05 M and 0.1 M acid, however, no observable effect of this nature was found.

The effect of possible adsorption on or reaction with the walls of the cell was tested for and proved to be inappreciable.

The measured values of the electromotive forces at 25° and the computed activity coefficients are given in the Table. The former have been corrected to one atmosphere of hydrogen; the latter have been computed from the following relation,

$$\log \frac{\alpha}{\alpha_0} = \frac{F}{2 RT} (E - E_0)$$

with the aid of the values  $\alpha_0$  and  $E_0$  for pure hydrochloric acid at the same concentration, as given by Randall and Young.<sup>1</sup>

#### DISCUSSION

During the past few years many investigations and interpretations of the properties of solutions of strong electrolytes have demonstrated that in sufficiently dilute solutions the ion attraction theory quantitatively accounts for the activity of strong electrolytes as determined from measurements of the electromotive forces of appropriate cells, of freezing point

lowerings, and of the effects of added salts upon the solubility of relatively insoluble salts.

In dilute solutions the physical basis for the ion attraction theory is relatively simple. The electrostatic forces acting between the ions are determined by the magnitude of their charges, their distribution and distances from one another, and the dielectric constant of the medium.

In a moderately concentrated solution a great many additional effects, many of them undoubtedly related to one another come into play to influence the activity coefficient. Thus the distribution of the ions will be modified in solutions in which the average effective diameter of the ions is comparable with the average distances of the ions from one another. Then at high concentrations ionization may no longer be complete. Hydration of the ions removes an appreciable part of the water from its normal state, thus changing the effective mol fraction of the ions and also the dielectric constant of the medium. In addition the dielectric constant is changed by the mere presence of a high ion concentration.

## Electromotive Forces and Activity Coefficients of HCl

$$\text{HCl} = 0.10 f \quad (\text{approx})^*$$

Added $\text{Na}_2\text{S}_2\text{O}_6$ Formality x 3	HCl formality	E.M.F.	Activity Coefficient
0	0.1036	0.3505	0.795
0.0500	0.1036	0.3521	0.771
0.1000	0.1035	0.3531	0.756
0.2000	0.1034	0.3544	0.738
0.4000	0.1031	0.3557	0.722
0.6000	0.1029	0.3564	0.714
0.8000	0.1027	0.3565	0.714
0.9000	0.1026	0.3561	0.720
1.0500	0.1023	0.3564	(0.718)
1.0500	0.1023	0.3560	0.723
1.1000	0.1023	0.3559	0.725

$$\text{HCl} = 0.05 f \quad (\text{approx})^*$$

0	0.0500	0.3861	0.830
0.0500	0.04997	0.3886	0.791
0.1500	0.04991	0.3911	0.755
0.2500	0.04985	0.3923	0.738
0.4500	0.04973	0.3931	(0.728)
0.4500	0.04973	0.3938	0.718
0.6500	0.04963	0.3944	0.711
0.8500	0.04949	0.3944	0.713
1.4291	0.04914	0.3934	0.733

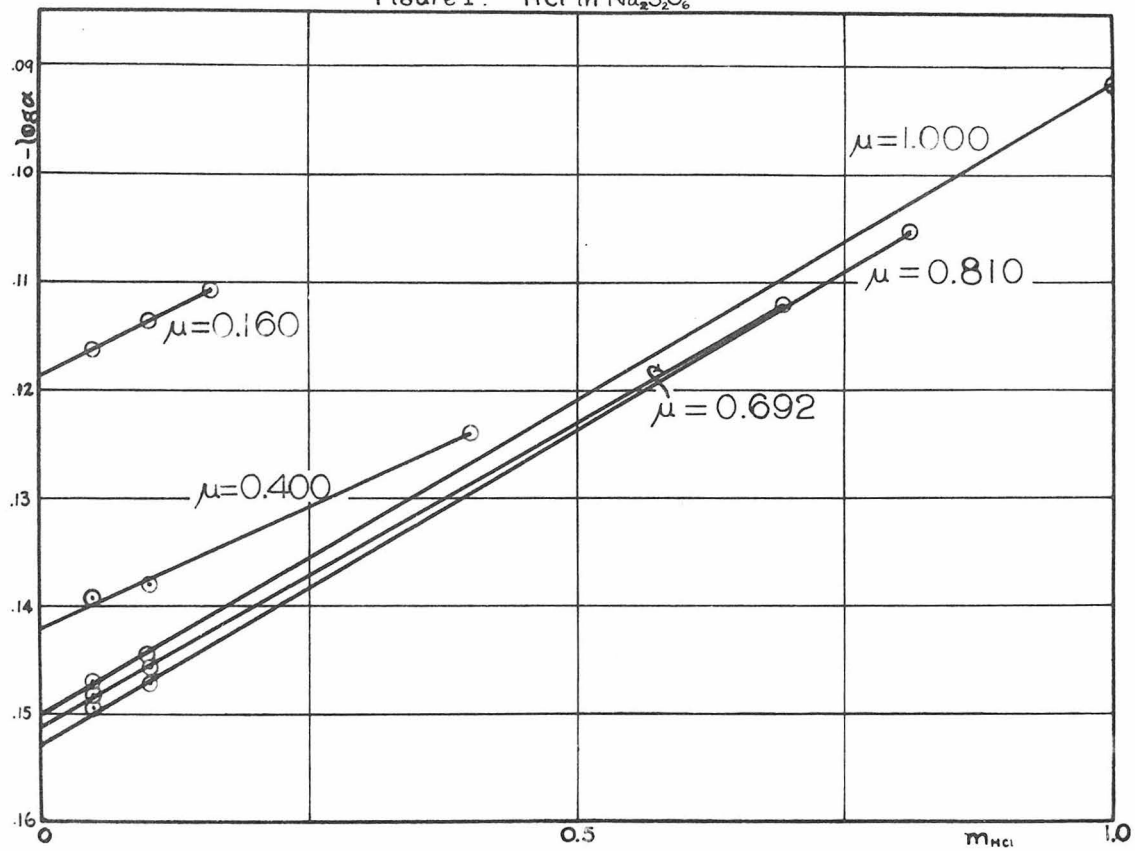
\*The changes in HCl concentration result from the water of crystallization present in the sodium dithionate.



According to the simple ion attraction theory the activity coefficient of the ions should continue to decrease with increasing ionic strength. But some of the other influences noted above cause the coefficient to be greater than that predicted by the simple theory; this increase may be called the salting-out effect. To any given ion there may be ascribed certain salting-out effects at definite concentrations because this ion has at a definite concentration a direct influence on the properties of the solution; that is, it makes a definite contribution to the thermodynamic environment. On the other hand, the ion itself tends to be salted out. Certain ions, however, are undoubtedly salted out more readily from a solution of a given thermodynamic environment than are others. The problem of the separation for analysis of these two salting-out influences (contribution and reaction to thermodynamic environment) of a given ion constituent is one which may be attacked by investigation of activities in mixed electrolytes. Thus in the case of hydrochloric acid the activity coefficient decreases in dilute solutions to a less extent than does that of almost any other electrolyte and at an ionic strength of four tenths passes through a minimum and then rapidly increases. Whether this is due chiefly to properties which the hydrogen and chloride ions impart to the solution as a whole or whether it is because these ions are especially readily salted out is not clear from data on pure hydrochloric acid alone, but can be discovered from additional information of the type mentioned.

In correlating the results of this investigation with those of others similar to it, use may be made of the following property of certain mixtures of electrolytes: In mixtures of constant ionic strength the activity coefficient  $\alpha$  of hydrochloric acid is related to the concentration

Figure 1. HCl in  $\text{Na}_2\text{S}_2\text{O}_6$



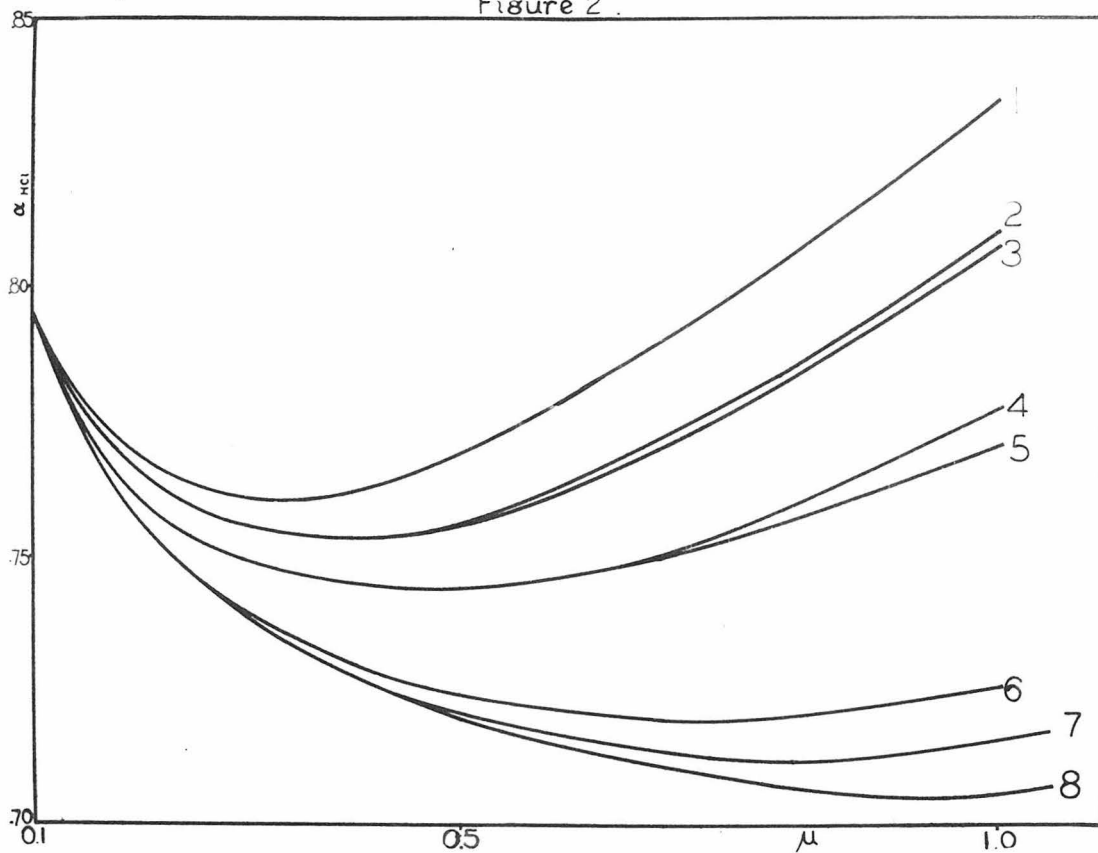
$m$  of the acid in the mixture and the activity coefficient  $\alpha_0$  of pure HCl at the same ionic strength by the equation

$$\log \alpha = \log \alpha_0 + k(\mu - m)$$

This equation has been found to hold for all the mixtures containing only univalent ions for which it has been tried. (Harned<sup>3</sup> has observed it to hold for mixtures, among others, of hydrochloric acid with lithium, sodium, or potassium chloride up to total ionic strengths of three, the highest measured.) Randall and Breckenridge,<sup>4</sup> however, found that it was not followed by mixtures containing barium chloride or lanthanum chloride, but that the similar relation in which  $m$ , the concentration of the hydrogen ion constituent, is replaced by the geometric mean molality of the hydrogen and chloride ion constituents did hold. This rule of Randall and Breckenridge (for which no derivation was given) and the one first stated are, of course, mutually exclusive except when the added electrolyte has no ion in common with those of hydrochloric acid, when the rules become identical. Such is the case with sodium dithionate; for this case plots of  $\alpha$  against  $m$  are shown in Figure 1 at various total ionic strengths. It will be seen that the above equation is closely followed.

The comparative effects of increasing amounts of various salts upon the activity coefficient of hydrochloric acid is shown in Figure 2. Here the activity coefficient of the acid, of which the concentration is maintained constant at 0.1 f., is plotted against the ionic strength for the added salts lithium chloride, sodium chloride, potassium chloride, sodium perchlorate, barium chloride, sodium dithionate and perchloric acid. The figure shows that the minimum

Figure 2.



HCl in 1, HClO<sub>4</sub>; 2, HCl; 3, LiCl; 4, NaCl;

5, NaClO<sub>4</sub>; 6, KCl; 7, Na<sub>2</sub>S<sub>2</sub>O<sub>6</sub>; 8, BaCl<sub>2</sub>.

value for the activity coefficient occurs at approximately the same ionic strength for pure hydrochloric acid and for the acid in the presence of added uniunivalent salts except for potassium chloride, which is somewhat anomalous in this respect, but that the minimum is shifted to higher ionic strengths when bivalent ions are present.

Of these salts the activity coefficients of lithium chloride, sodium chloride, potassium chloride, and barium chloride in solution alone are known. At a given ionic strength the activity coefficients decrease in the order given. Figure 2 shows that the effects of the salts on hydrochloric acid are in the same order, although no quantitative relation between the two sets of results has been discovered. This correspondence is to be expected from the ion attraction theory, or from others similar to it, since at the higher ionic strengths the properties of the solution are largely determined by the character of the added salt, and if it has a large salting-out effect on itself, i. e., if its activity coefficients are comparatively large, it would be expected to have a similar effect on others. Of course, in the mixtures which are not very dilute other influences come into play which are specific for each mixture, and may even be in a sense opposite to that which would be expected from a consideration of the properties of the unmixed component solutions. In the mixtures of Figure 2, the activity coefficient of hydrochloric acid is in each case greater than that for the pure salt at the same ionic strength (where the latter is known). This indicates that other things being the same, the hydrogen ion is probably especially readily salted out.

These results are also in accord with the fact that the activity coefficients of pure hydrochloric acid are greater than those

of other electrolytes at the same ionic strength. Hence hydrochloric acid exerts upon itself an exceptionally large salting-out influence. Whether it would do so on other substances could be found out definitely only by measuring the activity of such substances in the acid.

An inspection of Figure 2 shows that the shape of the curve with sodium dithionate is somewhat different from that with barium chloride (which is similar to the curves with calcium or strontium chloride). The former shows quite definitely a smoother, more gradually occurring rise than does the latter. Any attempt at an explanation of this phenomenon must be mere speculation; it may be surmised, however, that this is connected with the very likely phenomenon of the occurrence of pronounced "specific interactions" principally between ions having charges of opposite signs.<sup>5</sup> The influence of the bivalent ions being greater than that of the univalent ions, in all probability, the dithionate curve may indicate primarily the salting-out effect of a negative (bivalent) ion upon hydrogen ion; the barium curve may correspondingly indicate primarily the similar effect of a positive (bivalent) ion upon chloride ion.

## REFERENCES

1. Randall and Young, J. Am. Chem. Soc., 50, 989 (1928).
2. Güntelberg, Z. physik. Chem., 123, 199 (1926).
3. Harned, J. Am. Chem. Soc., 48, 326 (1926).
4. Randall and Breckenridge, J. Am. Chem. Soc., 49, 1435 (1927).
5. Bronsted, J. Am. Chem. Soc., 44, 877 (1922); 45, 2898 (1923);  
LaMer, *ibid.*, 51, 2622 (1929);  
Güntelberg, *loc. cit.*  
Guggenheim, Skand. Naturf. Report, 18 (1929).

# THE DISSOCIATION CONSTANT OF BROMINE CHLORIDE

## AT ROOM TEMPERATURE

The existence of a compound, or of compounds, between bromine and chlorine has long been suspected,<sup>1</sup> but it is only within the last few years that definite information concerning the formula and stability of such a compound has been obtained.<sup>2</sup> The evidence indicates that one, and only one, compound, of the formula BrCl, exists in appreciable proportions in the range of concentrations and temperatures studied.

Barrat and Stein (loc.cit.) measured optically the constant  $K = \frac{(\text{Br}_2)(\text{Cl}_2)}{(\text{BrCl})^2}$  in carbon tetrachloride solution and found a mean value of about 0.28. Both Gray and Style (loc.cit.) and Jost (loc.cit.) have measured by essentially the same method the above K (as before, in terms of molal concentrations) in the gas phase. This method involves determining the concentration of bromine in the equilibrium mixture by measuring the light absorption of the mixture at a wave length (respectively  $\lambda$  5790 and  $\lambda$  5750) such that Cl<sub>2</sub> and, probably, BrCl do not appreciably absorb. These wave lengths, however, are in a discrete region of the bromine spectrum, which requires that corrections of uncertain magnitudes be applied for the effect on the extinction coefficient of bromine of the considerable amounts of gases other than bromine itself which are present. This may lead to considerable uncertainty in K.

(See Jost, loc.cit.)



The present author became interested in bromine chloride when considering the photochemical properties of a gaseous mixture which was partially composed of bromine and chlorine. For the purposes of photochemistry it was desirable to know the equilibrium constant  $K$  for the reaction, and also the extinction coefficients of bromine chloride; for the purpose in hand it was particularly desirable to know the former at room temperature and the latter at  $\lambda$  4358. Since the published values of the former are, as was pointed out above, open to some doubt, and the latter has not been determined at all, it was undertaken to measure them by a method which differs somewhat from the previous one in being free from the necessity for applying the foreign-gas correction and in making no assumption as to the magnitude of the extinction coefficient of  $\text{BrCl}$ .

In outline, the method was as follows. The transmissions of various mixtures containing different known total amounts of bromine and chlorine were measured. Each of these transmissions gave a relationship between  $K$  and  $\mathcal{E}$ , the extinction coefficient of bromine chloride (making the well supported assumption that  $\text{BrCl}$  was the only compound present), as follows:

$$(1 - 4K)(\log \tau)^2 = (2E\frac{1}{V})[\text{Br}_{2_0} + \text{Cl}_{2_0}] \log \tau - (2E\frac{1}{V})^2 (\text{Br}_{2_0})(\text{Cl}_{2_0})$$

where  $\tau$  is the ratio of the transmission which the mixture actually has to that (calculated) which it would have if no reaction had occurred.

$$E = \frac{1}{2}(\mathcal{E}_{\text{Br}_2} + \mathcal{E}_{\text{Cl}_2}) - \mathcal{E}$$

$l$  is the length of the light path through the mixture and  $V$  the volume of the reaction vessel.  $\text{Br}_2$  and  $\text{Cl}_2$  are the known total amounts of bromine and chlorine present.

The experiments made divide themselves into two groups, those with about equivalent amounts of bromine and chlorine present, and those with large excesses of chlorine. Theoretically, any pair of runs could yield equations capable of solution for the two unknowns,  $K$  and  $\epsilon$ . Practically, however, the above equation is of such a nature that significance could be attached only to the solutions for pairs of runs of which one was from each of the groups mentioned above. There were thus obtained two sets of three solutions for  $K$  and  $\epsilon$ .

Experiments. The transmissions were measured using a mercury arc with a filter transmitting  $\lambda$  4358 only, and a photoelectric cell in series with a sensitive galvanometer. Bulbs containing known amounts of bromine and chlorine were admitted successively, by cracking with a glass-enclosed magnetic hammer, into a previously evacuated spherical liter flask of known transmission for  $\lambda$  4358. The transmission was measured after each admission, so that each run gave a value for the extinction coefficient of bromine, as well as the other data required. (In one run the chlorine was admitted first so that its extinction coefficient was measured. The value found checked that of von Halban and Siedentopf within the experimental error.) Numerous readings were taken for each transmission obtained, so as to eliminate in the average the fluctuations (which were not large) of the mercury arc.

TABLE I

Run	Mols Br <sub>2</sub>	Mols Cl <sub>2</sub>	Light path Vol. of system in cm./liter	Observed		Transmissions		Calculated for Br <sub>2</sub> + Cl <sub>2</sub> , for		
				Br <sub>2</sub> alone	Cl <sub>2</sub> alone	Br <sub>2</sub> +Cl <sub>2</sub>	Cl <sub>2</sub> +Br <sub>2</sub>	K=0.12 ε = 36	K=0.135 ε = 36	K=0.05 ε = 36
1	2.85x10 <sup>-4</sup>	2.5x10 <sup>-4</sup>	10.60	0.346	—	0.469	0.468	0.464	0.494	0.485
2	2.97x10 <sup>-4</sup>	2.77x10 <sup>-4</sup>	10.20	0.339	—	0.469	0.471	0.466	0.498	0.491
3	4.79x10 <sup>-4</sup>	6.05x10 <sup>-4</sup>	10.57	0.168	—	0.317	0.308	0.302	0.342	0.332
4	3.11 x 10 <sup>-4</sup>	4.42x10 <sup>-3</sup>	10.67	0.308	—	0.477	0.479	0.475	0.487	0.515
5	4.88x10 <sup>-4</sup>	1.63x10 <sup>-2</sup>	10.65	—	0.512	0.219	0.220	0.218	0.221	0.248

The "observed" transmissions have been corrected for the transmission of the empty cell.

Results. The weighted mean of six determinations of  $\epsilon_{\text{Br}_2}$  at  $\lambda$  4358 was 154. Gray and Style found 160, Ribaud<sup>3</sup> found 149.5.

The results of five experiments give  $K = \frac{(\text{Br}_2)(\text{Cl}_2)}{(\text{BrCl})^2} = 0.115$ ,  
 $\epsilon_{\text{BrCl}} = \frac{\epsilon_{\text{Br}_2} + \epsilon_{\text{Cl}_2}}{2} - 41.9 = 35.9$  at 20° to 23°C. The data for K and  $\epsilon_{\text{BrCl}}$  are shown in the Table, from which it can be seen that although the concentrations of bromine vary only by a factor of about 1.7, the ratios of chlorine to bromine vary from 0.9 to 33.4. The Table includes values of the transmissions calculated from the mean values of K and  $\epsilon_{\text{BrCl}}$ , given above, and also, for comparison, from values differing somewhat from the means.

Discussion. It thus appears that the measured transmissions can be accounted for within the limits of experimental error by assuming first that bromine and chlorine combine to form the single compound BrCl, second that the BrCl exists in equilibrium proportions, and third that Br<sub>2</sub>, Cl<sub>2</sub>, and BrCl respectively obey Lambert's and Beer's laws in the gaseous mixtures, at the temperatures and pressures used.

The second assumption is well justified since measurements on the rate of BrCl formation<sup>4</sup> indicate that it takes place within a few minutes. Ample time for reaction and diffusion was allowed in the experiments. (Runs sometimes lasted over a week.)

The third assumption has been justified insofar as gaseous Cl<sub>2</sub> and Br<sub>2</sub> alone are concerned by various experimenters.<sup>5</sup> There seems to be no reason for expecting appreciable deviations in mixtures of the two, for a wave length ( $\lambda$  4358) which is in the region of con-

tinuous spectrum for each of the three components. (For justification of this as regards BrCl see Jost, reference 2, above.)

Granting the second and third, the first assumption is then justified a posteriori by the experimental results.

Gray and Style (loc.cit.) and Jost (ref.2 above) found K to be about 0.13. The present result is essentially in agreement, the difference being within the experimental error.

## SUMMARY

The dissociation constant  $K = \frac{(\text{Br}_2)(\text{Cl}_2)}{(\text{BrCl})^2}$  of bromine chloride at room temperature was measured and found to be 0.12 (molal concentrations used). Under like conditions the extinction coefficient of BrCl for  $\lambda 4358$  was found to be 36.7.

$(I = I_0 10^{-\epsilon (\text{BrCl})l})$ .

## REFERENCES

1. See Gillam and Morton, Proc.Roy.Soc., 124, 604 (1929) for a bibliography on this subject.
2. H.Lux, Ber., 63, 1156 (1930).  
Forbes and Fuoss, J.Am.Chem.Soc., 49, 142 (1927).  
Butler and MacIntosh, Trans.Roy.Soc.Canada (3) 21, sect. 3, 19 (1927)  
Barrat and Stein, Proc.Roy.Soc., 122, 582 (1929).  
Gillam and Morton, loc.cit.  
Gray and Style, Proc.Roy.Soc., 126, 603 (1930).  
Jost, Z.phys.Chem., (A) 153, 143 (1931).  
Yost and Brass, unpublished data from This Laboratory.
3. Ribaud, Ann.de Phys., 12, 107 (1919).
4. Jost, Z.phys.Chem., (B) 14, 413 (1931).
5. von Halbran and Siedentopf, Z.phys.Chem., 103, 71 (1922).  
Ribaud, loc.cit.

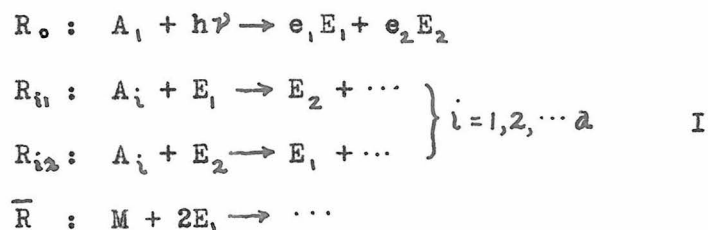
A METHOD FOR DERIVING PHOTOCHEMICAL REACTION MECHANISMS  
OF CERTAIN TYPES FROM OBSERVED REACTION RATES

The rates of photochemical reactions can be accounted for by postulating that in addition to such reaction as is caused directly by light absorption, the products of the latter initiate one<sup>or</sup> more purely thermal reactions. All of these reactions constitute the mechanism of the overall chemical change. In order to see clearly the implications of any empirical rate investigation as regards the mechanism, it is desirable to express the observed rate as some function of the absorbed light energy and of the concentrations of the reactants. The finding of the most suitable function is often difficult, however, and one of the aims of this paper is to exhibit certain type forms of this function which may be of use for this purpose.

Suppose that the observed rate is expressed as a function of the absorbed light energy and the reactant concentrations. The problem is now to find those mechanisms for the reaction for which the calculated rate is of the same functional form as that actually found. In the past this problem has nearly always been solved by a process of trial and error, the observed rate having been compared with that calculated from different assumed mechanisms until a mechanism had been found which gave the observed rate and also satisfied any other conditions imposed upon it by the experimental results, such as might relate to temperature coefficient, etc.



Since this procedure is tedious and uncertain, it was thought desirable to <sup>attempt to</sup> improve it. Such an attempt was made previously by Schwab,<sup>1</sup> who was able to derive uniquely the mechanism corresponding to a given photochemical rate, provided that reactions of the following type were responsible: Each reaction of the series must involve one intermediate present at small concentration, and one reactant present at large concentration, only. Schwab applied his method to the case of the chlorination of chloroform. Such mechanisms are very scarce, however, so that a means of treating a wider variety of reactions becomes necessary. It would of course be desirable to obtain a method of general applicability, but unfortunately the result would be prohibitively complicated; hence the results we can obtain cannot be completely general. The easiest way in which to effect the necessary limitation is to select the types of mechanisms with which to deal, picking if possible those not only of simple form but of frequent occurrence. This criterion may be satisfied, since, of the photochemical mechanisms which are now regarded as being the best known, a considerable number are of types which can be included in the following scheme:



Here  $E_1$  and  $E_2$  are the intermediate substances which are present during the course of the reaction only at very small concentrations, and  $A_1, \dots, A_a$  are the reactants the concentrations of which are not

subject to this limitation. The A's may thus include products of the reactions. The R's, as used above, are simply symbols for the reactions.  $e_1$  and  $e_2$  are defined by  $R_0$ .  $R_0$  may involve any one of the A's without affecting the following formulas at all.  $A_1$  is taken simply for definiteness. **Indeed**,  $R_0$  may include other A's or products, and even other intermediates than  $E_1$  and  $E_2$ , provided the added intermediates do not form or use up product. If, however, these intermediates can subsequently react in only one way, i.e., to form a product, the expression for the overall rate derived below is unchanged except for an additive term  $NI_{abs}$ , where  $N$  is an integer.

In the scheme above,  $E_1$  and  $E_2$  occur only where shown.  $E_1$  and  $E_2$  must reach steady state concentrations, so that when the overall rate is measured,  $\frac{d(E_1)}{dt} = 0$  and  $\frac{d(E_2)}{dt} = 0$ . (2)

We have, then

$$\frac{d(E_1)}{dt} = 0 = e_1 I_{abs} - (E_1)S_1 + (E_2)S_2 - 2\bar{k}(M)(E_1)^2 \quad (1)$$

$$\frac{d(E_2)}{dt} = 0 = e_2 I_{abs} + (E_1)S_1 - (E_2)S_2 \quad (2)$$

Where  $I_{abs}$  is the number of quanta of radiation, which is of such wave length that it produces the reaction  $R_0$ , absorbed per unit time per unit volume; the  $k$ 's are the respective reaction rate constants.

$$S_1 = \sum_{i=1}^a k_{i1}(A_i), \quad S_2 = \sum_{i=1}^a k_{i2}(A_i).$$

But, the observed rate is given by

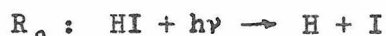
$$R = p_0 I_{abs} + (E_1)S_1^p + (E_2)S_2^p + \bar{p} \bar{k}(M)(E_1)^2 \quad (3)$$

where  $S_1^p = \sum_{i=1}^a p_{i1} k_{i1} (A_i)$ ,  $S_2^p = \sum_{i=1}^a p_{i2} k_{i2} (A_i)$ .  $p_o$ ,  $p_{ij}$ , and  $\bar{p}$  are the net numbers of mols of product appearing in the reactions  $R_o$ ,  $R_{ij}$ , and  $\bar{R}$ , respectively. (The "product" is the substance the rate of the appearance of which we are measuring. Since this as noted above may be one of the A's it would not always be correct to write in additional terms on the right-hand side of I of the form  $p_{ij} P$ .)

We can solve (1) and (2) for  $(E_1)$  and  $(E_2)$ ; substituting the values, so obtained, in (3) and then collecting terms we obtain as the final expression for the overall rate,

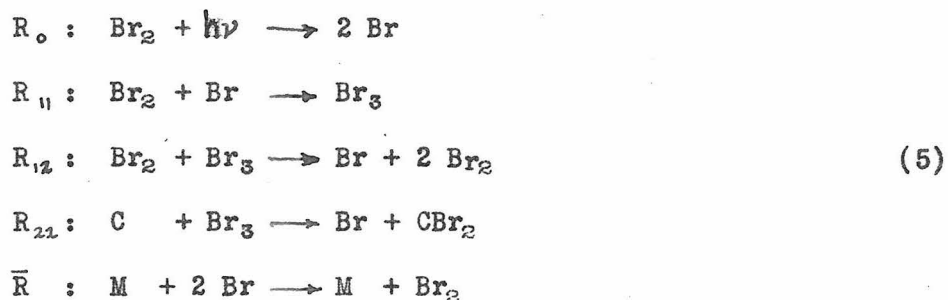
$$R = \left[ p_o + \bar{p} \frac{e_1 + e_2}{2} + \frac{e_2 S_2^p}{S_2} \right] I_{abs} + \frac{\sqrt{I_{abs}}}{S_2} \sqrt{\frac{e_1 + e_2}{2 K(M)}} \left\{ \sum_{i=1}^a k_{i1} k_{i2} (p_{i1} + p_{i2}) (A_i)^2 + \sum_{\substack{i,j=1 \\ i \neq j}}^a [k_{i1} k_{j2} (p_{i1} + p_{j2}) + k_{j1} k_{i2} (p_{j1} + p_{i2})] (A_i)(A_j) \right\} \quad (4)$$

This equation can be used in two ways: Starting with an empirical rate expression, the conditions which the K's and p's of the mechanism in any particular case must satisfy can be deduced from it, and consequently such mechanisms of type I as are suitable (if any) can be selected; or on the other hand (4) can be used to write down immediately the rate corresponding to any assumed mechanism of type I. The former of these ways has the disadvantage <sup>of being somewhat complicated, but the advantage</sup> that it may point out more mechanisms from which to choose than are directly obvious for use with the latter. Thus in the case of the photochemical decomposition of HI, for which the rate is  $R_{HI} = -2 I_{abs}$ , the deductive method indicates the following possibilities:

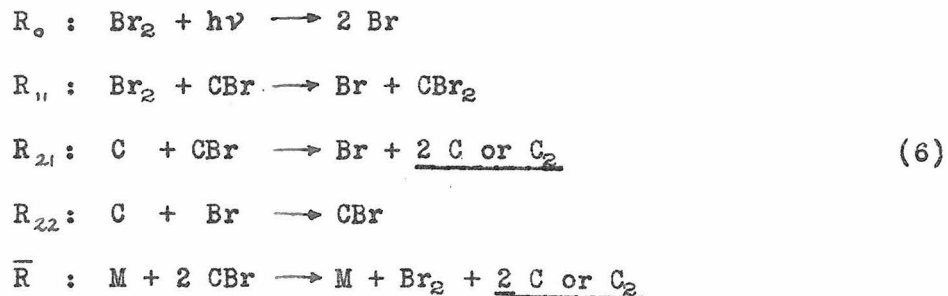


and also a mechanism with the third reaction eliminated, as well as similar mechanisms with H interchanged with I, and  $H_2$  with  $I_2$ . From quite separate information as regards the energetics of the reactions involved, the second of the mechanisms mentioned is chosen as that actually occurring.

Likewise in the case of the photochemical bromination of cinnamic acid (or of stilbene), for which the rate is  $R_{Br_2} = -K \sqrt{I_{abs}}(Br_2)$ , the deductive method indicates that the mechanism responsible for this reaction may be either of the following (in which C represents cinnamic acid):



or,



Since, from the chemical nature of the substances, it may be supposed that CBr is more likely to exist than is Br<sub>3</sub>, (6) is perhaps preferable. In (6), the derivation does not limit  $k_{21}$ , so that it may be taken as zero if desired. The mechanism is then identical with that proposed by Berthoud;<sup>3</sup> there is not, however, any obvious reason for completely excluding R<sub>21</sub>.

The procedure used in deriving the above mechanisms is, in outline, the following: The R of equation (4) must be equal identically to the empirical rate expression, so that the coefficients of the various I<sub>abs</sub> terms and also those of the various individual terms in powers of the reactant concentrations may be equated term by term. This procedure constitutes the introduction of the empirical observations into the calculation; the result is a set of equations among the as yet undetermined constants of the type scheme, which serves partially or completely to determine them. A single example is presented in some detail, as illustration, taking the somewhat complicated case of the photochemical formation of HBr, for which the rate is

$$R_{\text{HBr}} = \frac{K_1(\text{H}_2)(\text{Br}_2) \sqrt{\frac{I_{\text{abs}}}{(M)}}}{(\text{Br}_2) + K_2(\text{HBr})} \quad (7)$$

Before proceeding further with this example it is advisable to develop a general method for dealing with problems of this kind. Consider the second term of (4). Suppose that the rate is found empirically to be

$$R = \frac{\sum L_{ij}(A_i)(A_j)}{\sum Y_i(A_i)} \sqrt{\frac{I_{\text{abs}}}{(M)}} \quad (8)$$

Equating coefficients

$$\begin{aligned}
 (a) \quad C Y_i &= k_{i2} \\
 (b) \quad L_{ii} &= \sqrt{\frac{e_1 + e_2}{2K}} Y_i k_{i1} (p_{i1} + p_{i2}) \\
 (c) \quad L_{ij} &= \sqrt{\frac{e_1 + e_2}{2K}} \left[ Y_j k_{ji} (p_{i1} + p_{i2}) + Y_i k_{ij} (p_{j2} + p_{j1}) \right]
 \end{aligned} \tag{9}$$

where C is an undetermined constant.

Return now to the formation of HBr. Here, as in many other cases, the nature of the products of light absorption may be regarded as known from independent spectroscopic data. It is not necessary to make use of this information in order to derive results of interest from the formula, but its use simplifies the treatment and makes the results more specific. In the present case  $R_0$  is  $\text{Br}_2 + h\nu \rightarrow 2 \text{Br}$ . We follow a precedent found usually to be valid in neglecting the effect of the excitation energy of one of the Br atoms on the reaction rate.

Hence  $E_S = \text{Br}$ ,  $S = 1$  or  $2$ .  $e_S = 2$ ,  $e_t = 0$ .  $t = 2$  or  $1$ .

Let  $A_1 = \text{Br}_2$ ,  $A_2 = \text{H}_2$ ,  $A_3 = \text{HBr}$ .

Then, from (7) and (8),

$$L_{12} = K_1, \text{ the other } L\text{'s} = 0. \quad Y_1 = 1, \quad Y_2 = 0, \quad Y_3 = K_2.$$

Let us apply (9):

$$\begin{aligned}
 (a) \quad C &= k_{12} ; \quad 0 = k_{22} ; \quad CK_2 = k_{32} \\
 (b) \quad 0 &= \sqrt{\frac{1}{K}} k_{11} (p_{11} + p_{12}) ; \quad 0 = 0 ; \quad 0 = \sqrt{\frac{1}{K}} K_2 k_{31} (p_{31} + p_{32}) \\
 (c)_{12} \quad K_1 &= \sqrt{\frac{1}{K}} k_{21} (p_{12} + p_{21}) \\
 (c)_{13} \quad 0 &= \sqrt{\frac{1}{K}} \left[ K_2 k_{11} (p_{11} + p_{32}) + k_{31} (p_{12} + p_{31}) \right] \\
 (c)_{23} \quad 0 &= \sqrt{\frac{1}{K}} K_2 k_{21} (p_{21} + p_{32})
 \end{aligned}$$

Consequently, from  $(c)_{12}$ ,  $k_{21} \neq 0$ , and hence, from  $(c)_{23}$ ,  $p_{21} = -p_{32}$ . Likewise, from  $(c)_{12}$ ,  $p_{12} + p_{21} > 0$ . Therefore, combining equations,

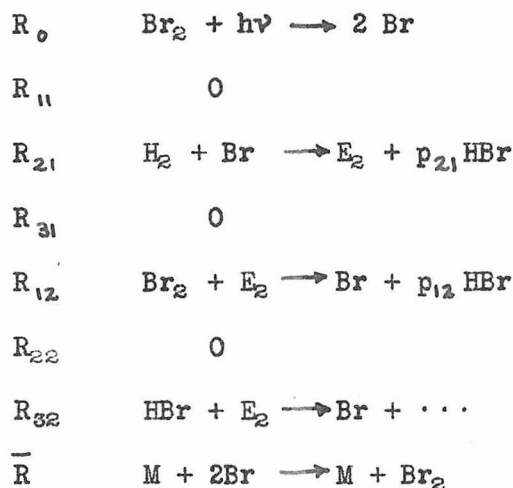
$$0 = (K_2 k_{11} - k_{31})(-p_{12} + p_{32}) \quad \text{from (b) and (c)}_{13}$$

$$K_1 = \sqrt{\frac{1}{K}} k_{21}(p_{12} - p_{32}) \quad \text{from (c)}_{12} \text{ and (c)}_{23}$$

Hence  $K_2 k_{11} - k_{31} = 0$ . But also, from (9)(a),  $K_2 = \frac{k_{32}}{k_{12}} \neq \frac{0}{0} \neq 0$ .

It is very unlikely that the ratio of two velocity constants should have exactly the same value as the ratio of two others. The equation above can be satisfied, however, if  $k_{11}$  and  $k_{31}$  are vanishingly small.

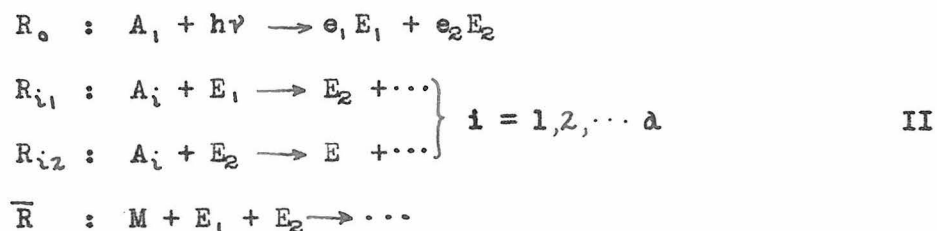
Hence,  $k_{31} = 0$ ,  $k_{11} = 0$ . Now, our reaction scheme does not include such a reaction as  $\text{Br}_2 + \text{Br} \rightarrow \text{E}_t + \dots$  unless  $\text{E}_t$  is  $\text{Br}_3$ . If we wish from chemical considerations to try to exclude this case we must set  $k_{15} = 0$ . But,  $k_{12} = C \neq 0$ , so that  $S$  must be 1. Hence  $e_2 = 0$ , and we see immediately that the requirement of our mechanism that  $\bar{p}$  be zero satisfies also the condition that the first term of (4) be zero. The mechanism is now



It appears immediately from an inspection of these equations that they can satisfy the conditions derived above on the  $p$ 's if  $E_2$  is H and  $p_{21} = 1$ ,  $p_{12} = 1$ ,  $p_{32} = -1$ , or if  $E_2$  is  $H_2Br$  and  $p_{21} = 0$ ,  $p_{12} = 2$ ,  $p_{32} = 0$ . If on the other hand, the reaction  $Br + Br_2 \rightarrow Br_3$  is allowed, the above scheme cannot be satisfied. The customary mechanism is that with  $E_2 = H$ .

Examples of the second method mentioned above for the use of (4) are hardly necessary since the procedure is one of simple substitution in the formula directly.

Since mechanisms of type I are known, it might be supposed that mechanisms of the following type would occur:



Following the same procedure as for type I, the overall rate is found to be

$$\begin{aligned}
 R = & \left[ p_0 + \frac{e_1 + e_2}{2} \bar{p} + \frac{S_1^p \cdot S_2 - S_2^p \cdot S_1}{4 S_1 \cdot S_2} (e_1 - e_2) \right] I_{abs} \\
 & + \frac{S_1^p \cdot S_2 - S_2^p \cdot S_1}{4 S_1 \cdot S_2} \sqrt{I_{abs}} \sqrt{(e_1 - e_2)^2 I_{abs} + \frac{8(e_1 + e_2)}{K(M)} S_1 \cdot S_2}
 \end{aligned} \quad (10)$$

where the symbols have the same meaning as before. (See under equations (2) and (3))



Equation (10) is too complicated for convenient direct use, but is considerably simplified in two special cases.

If  $e_1 = e_2 = e$

$$R = (p_0 + e\bar{p})I_{\text{abs}} + \sqrt{\frac{e}{k(M)}} \cdot \frac{S_1^p \cdot S_2 - S_2^p \cdot S_1}{\sqrt{S_1 \cdot S_2}} \sqrt{I_{\text{abs}}} \quad (11)$$

If on the other hand  $e_1 \neq e_2$ , while  $E_2$  reacts only by  $R_0$  and  $\bar{R}$ ,

$$R = \left[ p_0 + \frac{e_1 + e_2}{2} \bar{p} + \frac{e_1 - e_2}{2} \cdot \frac{S_1^p}{S_1} \right] I_{\text{abs}} \quad (12)$$

A similar rate expression evidently obtains if we change the condition to apply to  $E_1$  instead of  $E_2$ . Sometimes when  $R_0$  is  $A_1 + h\nu \rightarrow e_1 E_1 + e_2 E_2$ ,  $E_1$  and  $E_2$  are simple substances which can recombine in only one way, i.e., to form  $A_1$  again. Moreover, it is usually the case that if  $e_1 = e_2 = e$ , then  $e = 1$ . This gives  $p_0 = -\bar{p}$ . In this case the first term of (11) disappears, so that the rate is proportional to  $\sqrt{I_{\text{abs}}}$ .

Examples of types (11) and (12) are not given. It seems likely that they occur, particularly (11), but that this form of rate expression because of its unfamiliarity has not been used to express the empirical results in some cases where it would apply.

## SUMMARY

By postulating one of two types of mechanism (i.e. I or II) expressions for the corresponding reaction rates are derived. These may be written (giving I and the simple cases of II) as:

$$R = \left(N_1 + \frac{P_1}{P_2}\right) I_{\text{abs}} + \frac{Q_1}{P_2} \sqrt{\frac{I_{\text{abs}}}{(M)}} \quad \text{type I} \quad (4')$$

$$R = N_2 I_{\text{abs}} + \frac{Q_1}{\sqrt{Q_2}} \sqrt{\frac{I_{\text{abs}}}{(M)}} \quad \text{Type IIa} \quad (11')$$

$$R = \left(N_1 + \frac{P_3}{P_2}\right) I_{\text{abs}} \quad \text{type IIb} \quad (12')$$

The N's are integers, the P's are homogeneous linear polynomials in the concentrations of the reactants (the A's), the Q's are homogeneous quadratic polynomials in these same concentrations. The equations (4), (11), and (12), corresponding to those just given, can be used to calculate directly the rate corresponding to mechanisms of type I, type IIa or type IIb, respectively. Examples of the converse process, the derivation of mechanisms from given empirical rate expressions, are given for type I, in detail for the photochemical formation of HBr. Similar procedures could of course be used for rate expressions having the form (11') or (12'). Note, however, that if the rate expression has the form (12'), which is a special case of (4'), the mechanism may be of either type and both should be tried. Likewise if  $R = N I_{\text{abs}}$  all three should be tried.

(For the sake of completeness it may be mentioned that if we start with a scheme like I except that the reactions  $R_{i1}$  and the reactions  $R_{i2}$  may be of the respective types  $R_{i1} : A_i + E_1 \rightarrow g_{i1} E_2 + \dots$ ,

$R_{i2} : A_i + E_2 \rightarrow \xi_{i2} E_1 + \dots$ , we find that

$$R = \left( p_0 + \frac{P}{P'} \right) I_{abs} + \frac{Q}{(M)(P')^2} \left( -Q' + \sqrt{(Q')^2 + Q'' I_{abs}} \right) \quad (13)$$

The second term of (13) is proportional to  $I_{abs}$  for relatively very small  $I_{abs}$ , while it is proportional to  $\sqrt{I_{abs}}$  for relatively very large  $I_{abs}$ . Rates depending upon mechanisms of type II, however, show exactly the opposite change in form with  $I_{abs}$ , as can be seen from an inspection of the second term of (10).)

## REFERENCES

1. G. M. Schwab, *Zeit.phys.Chem.*, B 8, 147 (1930).
2. Bodenstein, *Ann. Physik*, 82, 138 (1927).
3. Berthoud, *Trans.Faraday Soc.*, 21, 560 (1926).