readily oxidized by bromine water, and by its formation of hydrogen ion retards the precipitation of manganese dioxide.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

PARTIAL AND CONSECUTIVE REACTIONS IN THE PHOTOSENSITIVE SYSTEM: QUININE SULFATE, CHROMIC AND SULFURIC ACIDS

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The general photochemical equation of Plotnikow[1] provides for reactions involving more than one photosensitive substance, and also "dark" reactants indispensable but not activated under the given conditions

$$-\mathrm{d}M/\mathrm{d}t = KA_1A_2\ldots A_n(a-x)^{n_1}(b-x)^{n_2}\ldots(p-x)^{n_n}$$

where A_1 and A_2 are the rates of light absorption by Reactants 1 and 2, to which the concentrations of their activated molecules C_1' and C_2' are approximately proportional, while $(a-x)$, $(b-x)$ .... are concentrations of "dark" reactants. The reaction between these molecular species, determined by these concentrations, has a velocity constant k_1.

The photochemical oxidation of quinine by chromic acid in the presence of sulfuric acid was investigated in 1906–7 by Luther and Forbes.[2]

The first two reactants are known to be photosensitive in various reactions; the third is undoubtedly a dark reactant. The data of this research should, therefore, serve to test Plotnikow's equation. When the test is made, however, it is found that chromic acid seems to behave only as an inert light filter, and that the reaction velocity is independent, within the limit of error, of the light absorbed by it, and not proportional to the latter, as Plotnikow's equation requires. Plotnikow[3] is of the opinion that some experimental error or inadequate analysis of the data on absorption is responsible for the discrepancy. We desire first to show deductively that in a system containing 2 photosensitive reactants capable of reacting even in the dark, there are doubtless partial reactions not provided for in Plotnikow's equation. The discrepancy may be explained in terms of these. Also, with the help of new experimental data, we shall thereafter demonstrate the limitations inherent in that factor of Plotnikow's equation which deals with the dark reactant.

Let the concentrations of unactivated molecules of 2 photosensitive reactants be C_1 and C_2. In the dark, $-\mathrm{d}M/\mathrm{d}t = k_2C_1^pC_2^q(a-x)^{n_1}$ .... and k_2 may be evaluated. During illumination, according to the usual

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[1] Plotnikow, "Allgemeine Photochemie," Vereinigung Wissenschaftlicher Verleger, **1920**, p. 185.

[2] Luther and Forbes, THIS JOURNAL, **31**, 770 (1909).

[3] Ref. 1, pp. 215, 416, 583.

assumptions, C_1 and C_2 are still large compared with C_1' and C_2', and k_2 still applies to these unactivated portions. Then the contribution to the total reaction velocity in the illuminated system made by C_1 and C_2 is calculated from k_2 and the *total* concentrations of the reactants. This contribution is usually subtracted from the total reaction velocity in light to find $-\mathrm{d}M/\mathrm{d}t$, the photochemical reaction velocity proper,[4] due to C_1' and C_2'. Obviously, the general equation anticipates these two and only these two reaction types.

But two other partial reactions, not provided for by previous investigators, now appear inevitable. For if the unactivated C_2 reacts with unactivated C_1 and $(a - x)$, it can scarcely escape reaction with the activated C_1' and $(a - x)$, introducing the velocity constant k_3, where $k_1 > k_3 > k_2$. Likewise C_1 will react with C_2' and $(a - x)$, introducing a fourth constant k_4, where $k_1 > k_4 > k_2$. The greatest divergences from Plotnikow's equation should now occur if C_1' and C_2' are both relatively small, and k_3, for instance, is almost as great as k_1 while k_4 is but little greater than k_2. The experimenter would then conclude that $-\mathrm{d}M/\mathrm{d}t$ was closely proportional to A_1, and practically independent of A_2. If now we write quinine as Reactant 1 and chromic acid as Reactant 2 in the above picture, we have at once a rational explanation of the anomaly which led Plotnikow to object to the conclusions of Luther and Forbes.

Such a mechanism virtually assigns to chromic acid the role of a dark reactant, to whose concentration or some power of the same the reaction velocity should perhaps be proportional. But Luther and Forbes found no such relation, except when C_2 was small compared with C_1, and A_1 was relatively large. They explained this in terms of two consecutive reactions, the first involving activation of quinine, the second actual oxidation by chromic acid. When C_2 fell below 0.0005, C_1' was not, by oxidation, diminished much below the constant stationary value C_1'' which it could have attained under conditions the same except for complete absence of chromic acid. Then $-\mathrm{d}M/\mathrm{d}t$ should be closely proportional to C_2, as Luther and Forbes observed. But when C_2 was large, and especially when $a - x$ was large also, C_1' was at all times much less than C_1''. One would now expect that changes in C_2 would be relatively unimportant, but that C_1 and A_1 would practically determine reaction velocity, as was also proved.

But it was the influence of the dark reactant proper (sulfuric acid in this case) that chiefly interested us. According to Plotnikow's equation the reaction velocity should be in all cases proportional to some constant power one, for instance of the concentration of such a dark reactant. The previous data bearing on this problem are scanty. Most workers on photochemistry, Luther and Forbes among them, have evaded it by keep-

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[4] Plotnikow, *Z. physik. Chem.*, **58,** 219 (1907).

ing $a - x$ both large and unvaried. Some, like Chapman,[5] in his work on the chlorine-hydrogen reaction, mentions the minimum concentration which is without influence on reaction velocity. We know of no adequate experimental study of such questions.

Materials.—U. S. P. Quinine sulfate, thrice recrystallized and dried over sulfuric acid, melted at 204.6°. The potassium dichromate was recrystallized and dried at 110° before weighing out. Standard sodium thiosulfate solutions made up from thrice recrystallized salt a month before the work began gave titers of 0.01091 and 0.02285 against dichromate.

The light source was a Cooper-Hewitt quartz mercury lamp, type designed for 110 volts and 4 amperes. Owing to the well-known inconstancy of such lamps, each new reaction mixture was exposed to light side by side with a reference solution in which the initial concentrations were invariably: $C_1 = 3$ g./liter, $C_2 = 0.010$ g. equivalent (0.0033 mole) per liter, $a = 0.977$ g. equivalent per liter.

The reaction vessel was a 95mm. crystallizing dish divided into semicircular segments by a vertical partition. We proved by special experiments that typical reaction mixtures maintained their titer unchanged for a long time in contact with considerable surfaces of the de Khotinsky cement used. The 95mm. dish was placed inside a 140mm. dish on ledges several millimeters high, and surrounded by water and ice frequently renewed. The temperature variations were unimportant. The combination was mounted on a pivoted wooden disk which, by means of a geared-down electric motor and an eccentric, was made to turn back and forth through an angle of 150° a dozen times per minute. Glass grids dragging through the solutions in the inner dish kept them well stirred. The lamp was fastened in a position always the same with respect to the reaction vessel, about 10 cm. above it. As the segments were not exactly equal in area, or in illumination received, experiments were made at intervals with identical solutions in both segments. The ratio between the quantities of chromic acid reduced was used as a factor to correct the ratios found in the regular experiments. The time of exposure to light was planned, as closely as possible, to reduce about 10% of the reference solution, and it was then assumed that the corrected ratio between the quantities of chromic acid reduced represented nearly enough the ratio between total reaction velocities at the start of the given experiment.

In each experiment a third solution, identical with the new reaction mixture, was made up simultaneously, left in the dark during the run, and then titrated under strictly parallel conditions. Less frequently the dark reaction of the reference solution was checked. Upon subtraction, $-dM/dt$ resulted with elimination of systematic titration errors.

Iodimetry was adopted in spite of well recognized uncertainties, some of which have since been cleared up.[6] The contents of reaction vessels, with rinsings, were transferred to conical flasks. Oxygen was excluded by a stream of carbon dioxide. Equal quantities of water were added, and of acid also, except when the original solutions contained a sufficient excess. The iodine set free when excess of iodide was added was at once discharged by standard thiosulfate solution, adding the starch at the end. The flasks, sealed for half an hour were again titrated, and once more after an additional 2 hours, if necessary. Thus the liberation of iodine, very

[5] Chapman and Whiston, *J. Chem. Soc.*, **115**, 1267 (1919).

[6] Vosburgh, THIS JOURNAL, **44**, 2120 (1922).

slow in presence of very dilute chromic acid, became complete without error from atmospheric oxygen.

Weigert and Saveanu[7] have investigated the photochemical oxidation of quinine by atmospheric oxygen. Fearing that this might complicate the oxidation by chromic acid, we repeated typical experiments previously made in air, surrounding the reaction vessel with a tall cylinder kept full of carbon dioxide from a tank. Actual analyses gave 70% to 90% by volume. The results were unchanged, within the limit of error.

With acid concentrations not greater than 0.02 *N* the quantities of acid consumed during illumination were estimated through preliminary experiments, and enough 0.5 *N* acid was gradually added to keep its concentration nearly constant.

Data and calculation of a typical experiment follow.

Solution 1: Segment I, 0.15 g. of quinine, 0.0245 g. of potassium dichromate, 0.0239 g. of sulfuric acid, volume, 50 cc. Then $C_1 = 3$ g. per liter, $C_2 = 0.01$ equivalent normal, $a = 0.977$ equivalent normal. Solution 2: volume 50 cc., Segment II, $C_1 = 3$ g. per liter; $C_2 = 0.01$, $a = 0.106$. Dark solutions 3 and 4, identical with 1 and 2.

Titers after 2 hours at 0°, nearly: (1) = 42.65 cc. of sodium thiosulfate, (3) = 46.85 cc.; $-\Delta C_2 = 4.20$. (2) = 43.20 cc., (4) = 46.48 cc.; $-\Delta C_2 = 3.28$.

Ratio corrected for inequality of segments = 3.28/4.20 × 0.971 = 0.78.

Let us first predict the effect of changing chromic acid concentration, C_1 and a being constant. In the present research A_1 was much greater than in the work of Luther and Forbes through substitution of a quartz lamp for one of uviol glass, and by eliminating 2 layers of common glass between lamp and solution. This fact, and our lower acid concentrations, should make the order of reaction with respect to chromic acid increase beyond zero before its concentration fell below 0.0005 *N*. This point is reserved for later investigation.

As the experimental conditions were not reproducible, complete data are not given. The results, where C_2 was constant, are presented simply by plotting against acid concentrations the ratios of reaction velocities in various solutions to that in 0.977 *N* acid under conditions otherwise the same. Above 0.5 *N*, velocity is nearly independent of acid concentration. No explanation for the slight but unmistakable maximum could be found. Perhaps there is an increased absorption in this region. Below 0.5 *N* the order of reaction with respect to acid rapidly increases. Between 0.02 *N* and 0.01 *N* it is 1, and at lower concentrations it presumably tends toward 2, the order in the dark which we established by special experiments over long periods. Insoluble precipitates, forming when $a < 0.01$, discouraged investigations in such solutions. It is clear, however, that photochemical reaction velocity could be proportional to the expected power of this dark reactant only at very low concentrations of the latter. Here the actual rate of oxidation of the quinine is slow in comparison with

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[7] Weigert and Saveanu, *Nernst-Festschrift*, **1912**, 464.

its speed of activation, and determines the total reaction speed. In this region, and in this region only, Plotnikow's generalization as to the dark reactant is applicable. On the other hand, it would apply over the widest ranges of concentration, in reactions where the velocity of the reaction stage involving the dark reactant was always small in comparison with the speed of activation.

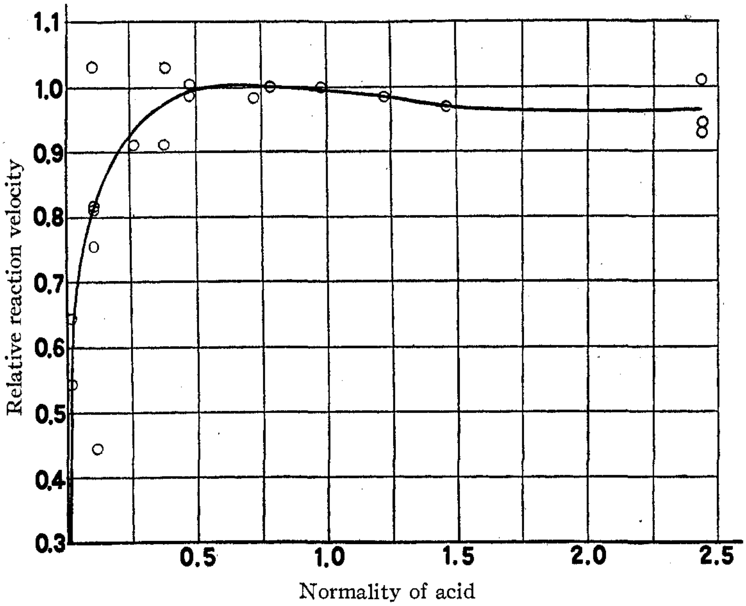

Fig. 1

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Summary

With 2 photochemically activated reactants the total reaction velocity should be the sum of 4 partial reactions with 4 different velocity constants. One involves 2 activated molecular species, another only unactivated species, and 2 others involve 1 activated and 1 unactivated species. It is shown how species known to be activated in some reactions may give no evidence of activation in others.

The concentration of a photochemically unactivated reactant is shown to be without effect upon the velocity of a photochemical reaction provided that its concentration is not so small that its reaction with activated reactants does not become the slow stage of the total process.

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