

acid under the various conditions tabulated (Table VI) differs from the rate<sup>11</sup> when there is no free hydrochloric acid present. In this last instance partial dissociation of the organic acid undoubtedly occurs.

### Summary

The reaction rates of potassium iodide with ethylene bromide and propylene bromide in methanol have been measured at 30, 60 and 75° and found to be of the second order. From the influence of iodine upon the rate it has been shown that in alcoholic solutions one mole of dibromide reacts with three moles of potassium iodide.

Previously reported second order constants for the reaction of the butylene bromides have been recalculated on this basis. From these rate constants, the heats of activation and temperature coefficients for ethylene bromide, propylene bromide and the three normal butylene bromides have been calculated.

Recalculation of van Duin's results show that the reactions of probably all dibromides with potassium iodide are second order and not third order as he claimed.

An increase in the ionic strength of the reaction medium by the addition of neutral salts slightly decreases the reaction rate of the non-ionic dibromides with iodide ion. On the other hand, under these conditions the reaction rate is appreciably increased in the case of ionized dibromides as the Brönsted theory demands.

<sup>11</sup> Ref. 2, p. 351:  $k_3 = 0.123 \times 10^{-3}$ ,  $k_2 = 0.246 \times 10^{-3}$ .

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## THE PHOTOCHEMICAL REACTION BETWEEN QUININE AND DICHROMIC ACID. I. QUANTUM YIELDS

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Earlier studies of this reaction<sup>2,3,4</sup> left unsolved a number of problems such as the relation of quantum yield to wave length, the consequences of light absorption by dichromic acid, and the details of the secondary processes. Bodenstein<sup>5</sup> and later Kistiakowsky<sup>6</sup> published critical discussions of these papers. Morton<sup>7</sup> has recently proposed a reaction mechanism in

<sup>1</sup> International Research Fellow, 1927-1928.

<sup>2</sup> Goldberg, *Z. physik. Chem.*, **41**, 1 (1902); *Z. Wiss. Phot.*, **4**, 56 (1906).

<sup>3</sup> Luther and Forbes, *THIS JOURNAL*, **31**, 770 (1909).

<sup>4</sup> Forbes, Woodhouse and Dean, *ibid.*, **45**, 1891 (1923).

<sup>5</sup> Bodenstein, *Z. physik. Chem.*, **85**, 329 (1913).

<sup>6</sup> Kistiakowsky, "Photochemical Processes," The Chemical Catalog Co., Inc., New York, 1928, pp. 39-41.

<sup>7</sup> Morton, *J. Phys. Chem.*, **33**, 1135 (1929).

terms of his own observations upon the photochemical reaction between dichromic acid and alcohol. A reinvestigation of the subject using modern quantitative methods was begun, with Dr. Boissonas, in 1927-1928, and continued, with Dr. Heidt, in 1930-1931.

The apparatus and radiometric procedures were similar to those developed in this Laboratory by Villars,<sup>8</sup> P. A. Leighton<sup>9</sup> and W. G. Leighton.<sup>10</sup> Several variations require mention.

An improved mercury vapor lamp<sup>11</sup> was devised in which oscillations of mercury were controlled by plungers ground into arms open to the atmosphere. The monochromator had been constructed, in its original form, by Villars. A 60° glass prism, 115 × 115 × 115 × 80 mm. ( $n_d$ , 1.69), served to separate the radiations at 436, 405 and 366  $m\mu$ , while a fused quartz prism of equal size was used for the shorter wave lengths. When desired, thermopile and cell could be mounted side by side on a single carriage, propelled at right angles to the axis of the back lens. Fine adjustments were made by a screw of 0.5 mm. pitch having a reference mark on its milled head. Through the kind coöperation of Mr. F. P. Brackett, Jr., of this Laboratory a monochromator having crystal quartz optics and a zinc spark of high intensity and constancy<sup>12</sup> were available for the range 254 to 208  $m\mu$ .

A trapezoidal quartz cell (all seams fused) was thermostated on two sides at  $5 \pm 2^\circ$  by circulating water. It had a tubulure and stirrer according to a design previously described.<sup>10</sup> The stirrer was provided with a mercury seal and was surmounted by a small windmill driven by a jet of compressed air. About three-quarters of our photolyses were run under carbon dioxide, the rest under air. No difference in quantum yield was noted, in agreement with the experience of Forbes, Woodhouse and Dean<sup>4</sup> and the statement of Weigert and Savenu<sup>13</sup> that the photolytic oxidation of quinine by oxygen is strongly inhibited by acid. A jet of carbon dioxide brought to 5° prevented dew formation on the front window. All the light from the exit slit of the monochromator (20 mm. × 1 to 2 mm.) fell upon this front window. The customary corrections for reflection were made and the emerging light, when not negligible, was properly estimated and deducted.

**Materials.**—Quinine bisulfate (Mallinckrodt U. S. P.) presumably contained less cinchonidine and other impurities than a normal sulfate. It was thrice recrystallized from 5% sulfuric acid between 60 and 0°, and the crystals centrifuged in the dark after each recrystallization. The last crop was dissolved in a large volume of water and precipitated as the base by a bare excess of dilute sodium hydroxide. The base was di-

<sup>8</sup> Villars, *THIS JOURNAL*, **49**, 326 (1927).

<sup>9</sup> P. A. Leighton, *ibid.*, **51**, 3549 (1929).

<sup>10</sup> W. G. Leighton, *ibid.*, **52**, 3139 (1930).

<sup>11</sup> Forbes and Heidt, *ibid.*, **53**, 4349 (1931).

<sup>12</sup> Forbes and Brackett, *ibid.*, **53**, 3973 (1931).

<sup>13</sup> Weigert and Savenu, *Nernst-Festschrift*, 464 (1912).

gested with several portions of boiling water, all lumps being carefully powdered. The final product was heated at 125° and kept in a vacuum desiccator over concentrated sulfuric acid. The melting point, 175°, agreed with that given in "International Critical Tables."<sup>14</sup> It left no residue on ignition, and the escaping gases gave no odor of sulfuric acid or reaction with blue litmus paper. A few photolyses run with U. S. P. quinine at 405 m $\mu$  gave quantum yields 20% higher than the material just described. Potassium dichromate (Baker's analyzed) was thrice recrystallized, with centrifuging in each case, and thoroughly dried. The other chemicals were of reagent quality. Conductivity water, for our stock solutions, was kindly furnished by Professor Grinnell Jones.

**Absorption Measurements.**—Villars<sup>15</sup> in this Laboratory proved that extinction coefficients can be accurately determined by integration of diverging light beams. For present purposes a simpler method based upon direct comparisons sufficed. Three cells were made of parallel fused quartz plates and divided into two compartments with carefully ground partitions of Pyrex glass. Their thicknesses, as measured with inside vernier calipers, averaged 3.02, 9.00 and 38.0 mm. The liquids came in contact with the de Khotinsky cement only in capillary spaces and only for short periods. One compartment contained the solution to be studied, the other water containing enough sulfuric acid to equalize the refractive indices. With the thermopile set behind the cell at the position of maximum deflection, the cell was slid back and forth perpendicular to the axis of the back lens of the monochromator, and readings taken behind the two compartments in alternation. The back focus of the lens being 410 mm., the divergence of the rays was small. After averaging the two sets of readings, the cell was well rinsed, dried and further readings taken with the solutions exchanged, so as to eliminate differences in the two compartments. Lambert's law was found to hold within 5% in all cases. The work was carried out at room temperature, after proof that  $K_{0^\circ} = K_{20^\circ} = K_{30^\circ}$ . In all cases  $K = -(\log_{10} L/L_0)/cd$ , where  $c$  is expressed in moles per liter and  $d$  in cm. In general we restricted measurements to concentrations prevailing in actual photolyses.

Quinine bisulfate,  $C_{20}H_{24}N_2O_2 \cdot H_2SO_4 = Q$ , does not follow Beer's law and  $K_q$  varies with acidity as well. Figure 1 shows  $\log K_q$ , in 1.7 molar sulfuric acid, from 405 to 208 m $\mu$ . Data graphed as solid circles were determined as described above. Mr. Brackett kindly made the measurements at 208 m $\mu$ . Open circles were located by a null photographic method, using a comparison quartz spectrograph after Judd Lewis,<sup>16</sup> kindly put at our disposal by Dr. F. L. Gates.<sup>17</sup> Squares represent data from the "International Critical Tables,"<sup>18</sup> corrected for a difference in  $[H_2SO_4]$ . The close agreement of data obtained by several methods is reassuring. Figure 2 shows how  $K_q$  varies at 405 m $\mu$  and at 366 m $\mu$  with changing acidity. The striking differences in the shapes of the curves suggest that more than one absorption mechanism is involved. This possibility is further considered below.

The solution termed dichromic acid contains various ions and molecules,

<sup>14</sup> "International Critical Tables," Vol. I, p. 266.

<sup>15</sup> Villars, *J. Opt. Soc. Am.*, **14**, 29 (1927).

<sup>16</sup> Judd Lewis, *J. Chem. Soc.*, **115**, 312 (1919).

<sup>17</sup> Gates, *J. Gen. Physiol.*, **14**, 37 (1930).

<sup>18</sup> "International Critical Tables," Vol. V, p. 371.

the concentrations of which vary with acidity as well as with total concentration. Unit concentration assumes 104 g. of chromium per liter. The extinction coefficient,  $K_c$ , at fixed wave length, is depicted by a set of plane curves. Figure 3 shows the effect of changing the acidity at each of four wave lengths,  $[H_2Cr_2O_7]$  being fixed at 0.00042. Circles give our data by thermopile. Crosses in circles are after Viterbi and Krausz,<sup>19</sup> and crosses are after Hantzsch and Clark,<sup>20</sup> for solutions not acidified. In Fig. 10,  $K_c$  is given for a solution in which  $[H_2Cr_2O_7] = 0.00016$  in 0.8  $M$   $H_2SO_4$ . The measurements at 208  $m\mu$  were made by

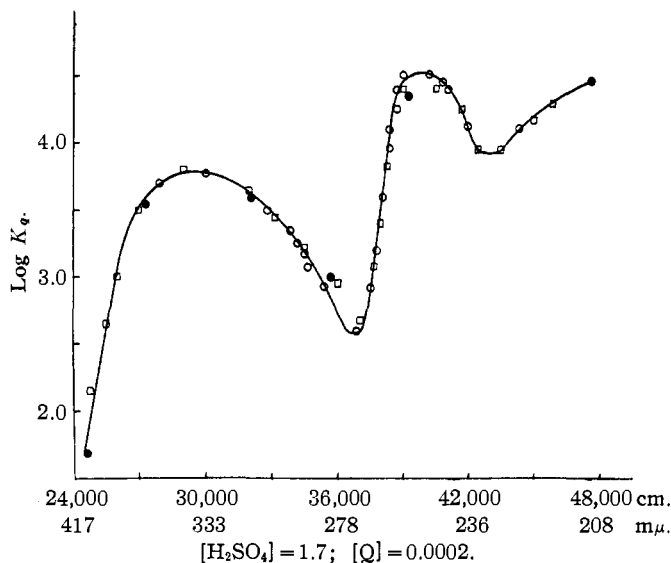


Fig. 1.—□, Values from "I. C. Tables," Vol. V; ○, values by null photographic method; ●, values by spectroradiometer with thermopile.

Mr. Brackett. We refrain from presenting all our data. It was found that  $K_c$  increases 15% at 405  $m\mu$ , and 20% at 366  $m\mu$ , in passing from 0.0001 to 0.001  $M$ , the sulfuric acid being 0.125  $M$  in all cases. The rate of increase in  $K_c$  falls off slowly as  $[H_2Cr_2O_7]$  increases. Measurements on samples of dichromic acid reduced by sulfite showed that  $K_{Cr^{+++}}$  was negligible in comparison with  $K_c$  at 405, 366, 313 and 280  $m\mu$ , so no correction for inner filter effect of chromic ion formed by reduction was made.

Radiometric procedures described in other papers<sup>8,9,10</sup> from this Laboratory were simplified after proof, by Mr. Brackett,<sup>12</sup> that  $E$ , the total energy flux of the beam diverging from the exit slit of the monochromator, as determined by integration over the entire width of the beam, was closely

<sup>19</sup> Viterbi and Krausz, *Gazz. chim. ital.*, **57**, 690 (1927).

<sup>20</sup> Hantzsch and Clark, *Z. physik. Chem.*, **63**, 367 (1908).

proportional to  $D$ , the maximum galvanometer deflection obtainable during the excursion, provided that no part of the optical train was displaced. Before every other run,  $E/D$  was redetermined as above. During runs the maximum deflection  $D_n$  was frequently redetermined, whereupon  $E_n = D_n \times E/D$ . Fluctuations in  $E_n$  were thus taken into account. From the various values of  $D_n$  and the time, the total quanta incident upon the front window of the cell was built up by summation or by graphical integration. Suitable corrections were always made for reflection and

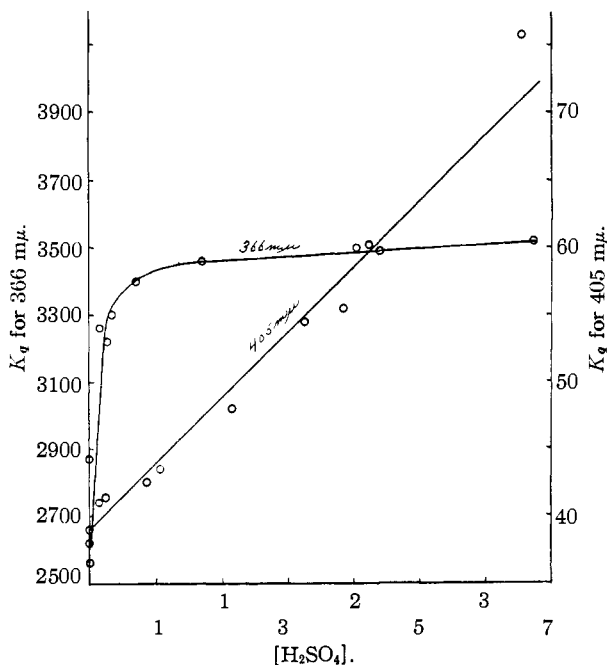


Fig. 2.—Upper scale for 366 mμ; lower scale for 405 mμ;  
 $\lambda$  405 mμ,  $[Q]$ , 0.0080;  $\lambda$  366 mμ,  $[Q]$ , 0.0004.

absorption at the front window, and whenever absorption was incomplete, reflection and transmission at the rear window were estimated as well. The absence of infra-red light was demonstrated, at each wave length, by the use of electric smoke glass. The sensitivity of the thermopile-galvanometer system was rechecked daily to eliminate a number of influences not easily definable. About once in six weeks, absolute calibrations were made against radiation standard C 69 of the Bureau of Standards according to accompanying directions.

**Analyses** were carried out electrometrically, using weight burets. A weighed sample of solution after photolysis was in each case compared with a sample of the original solution preserved meanwhile at the same tem-

perature in the dark. In the earlier work, following a suggestion by Dr. J. G. Aston, the reducing agent was potassium ferrocyanide, 0.0007 *M*. The e. m. f. against a calomel electrode was directly measured, and plots for the two samples were made side by side. The end-point of the photolyzed sample was recognized by a sharp divergence of its plot from the other. In the later work the method of Forbes and Bartlett<sup>21</sup> was followed, using, however, a half-cell of mercury, mercurous sulfate and sulfuric acid. Mohr's salt (0.0005 to 0.01 *N*) made up from clear green crystals was added

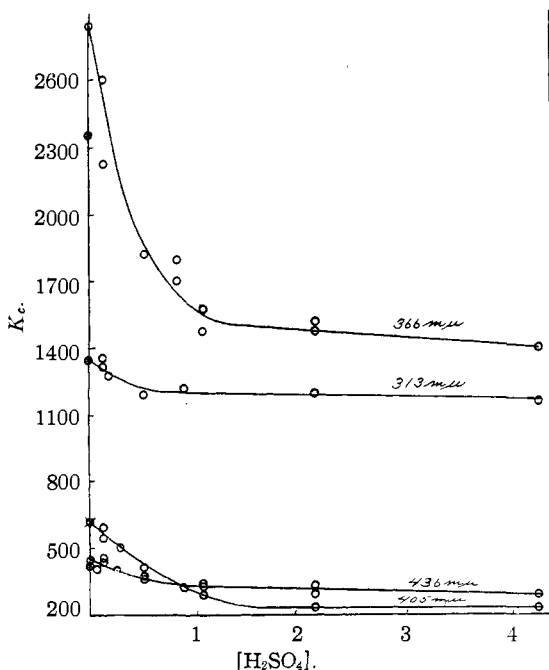


Fig. 3.— $[K_2Cr_2O_7]$ , 0.00042;  $\times$ , Hantzsch and Clark;  
 $\circ$ , Viterbi and Krausz.

until the anomalous rise in oxidizing potential gave way to a precipitous decline at the end-point. The reducing solution, in each method, was frequently compared with standard dichromate, and the true factors at other times interpolated. Changes in titer during photolysis were calculated to oxygen atoms lost by dichromic acid. Reduction of dichromic acid varied between  $10^{-7}$  and  $10^{-5}$  mole, usually about 5% of the initial amount but as much as 30% in a few cases. As the end-point in many cases could be fixed only within 10% of the dichromic acid photolyzed, the analysis was distinctly less accurate than the radiometric work, and much attention was given to small improvements in the former.

<sup>21</sup> Forbes and Bartlett, *THIS JOURNAL*, **35**, 1527 (1913).

The dark reaction at  $5 \pm 2^\circ$  was proved to be less than the analytical errors unless  $[Q][H_2Cr_2O_7][H_2SO_4] > 2.5 \times 10^{-6}$  and  $[H_2SO_4] > 1$ . The correction, which never exceeded two-tenths of the light reaction, was made wherever desirable. It was proved, in separate experiments, that the oxidation products of quinine absorb light to about the same extent as the original quinine. Special experiments on solutions previously exposed to light indicated that the quantum yield,  $\phi$ , increases slowly as the reaction continues, which suggests that the oxidation products of quinine are more reactive than quinine itself. We are now photolyzing various quinine derivatives in the hope of correlating  $\phi$  with structural peculiarities.

Gross quantum yields,  $\phi$ , signify total oxygen atoms transferred from dichromic acid to quinine divided by total quanta absorbed within the solution. The quanta absorbed by water could always be neglected. The net quantum yield,  $\phi_q$ , is referred to quanta absorbed by quinine alone. These were calculated by the use of formulas of Luther and Weigert,<sup>22</sup> introducing the values of  $K_q$  and  $K_c$  measured separately at the same concentration and acidity. The additivity of absorptions presupposed by these formulas was proved by special experiments at widely varied concentrations and wave lengths. Thus it appears that the present system is not analogous to uranyl oxalate, where the photolysis occurs within a stable complex having an absorption very different from that calculated by simple addition.

To conserve space we present most of our bulky data on two hundred photolyses by graphs embodying the end results. Each point on a graph represents the average of at least two, usually three and sometimes four, photolyses. Single values of  $\phi$  at the worst are subject to an error of about twenty per cent., usually not more than ten per cent.

Experiments carried out at different light intensities are comparable only after correction for deviation from the reciprocity law. Figure 4, at 366, 313 and 280  $m\mu$ , shows that  $\phi$  and  $\phi_q$  decrease as  $E$  increases. In a later paper the complicated kinetic phenomena underlying this effect will be analyzed. Unfortunately, still higher light intensities were not available, and the photolytic rate at still lower light intensities would have been too small to measure accurately. The values of  $\phi_q$  as given correspond to the actual  $\phi_q$  in a thin layer about one-third of the distance between the front window and a point where some 99% of the light has been absorbed. Rigorous mathematical treatment would require an integration over the entire absorbing layer<sup>23,24</sup> in which the energy flux  $E_d$  varies with  $d$ , the depth of solution already traversed, and  $\phi_q$  in turn varies with  $E_d$ .

**Activation.**—Three apparently perfect experiments in blue light,

<sup>22</sup> Luther and Weigert, *Z. physik. Chem.*, **53**, 408 (1905).

<sup>23</sup> Forbes, *J. Phys. Chem.*, **32**, 488 (1928).

<sup>24</sup> Allmand, *J. Chem. Soc.*, 1557 (1929)

436  $m\mu$ , produced no detectable photolysis in a solution in which  $[H_2Cr_2O_7] = 0.02$ ,  $[H_2SO_4] = 0.8$  and  $[Q] = 0.2$ , all in spite of strong absorption by dichromic acid. The latter when activated by such quanta readily attacks alcohol<sup>7,25,26</sup> and other compounds, but it must attack non-activated quinine with negligible velocity. This conclusion is identical with that of Luther and Forbes.<sup>3</sup> As it is impracticable to work with a solution of such thickness and concentration that quinine absorbs a significant fraction of incident light at 436  $m\mu$ , it must remain an open question whether quinine can be activated by such quanta<sup>27</sup>. In Fig. 5,  $\phi$  and  $\phi_q$  are plotted against  $[Q]$  at each of six wave lengths,  $[H_2Cr_2O_7]$  and  $[H_2SO_4]$

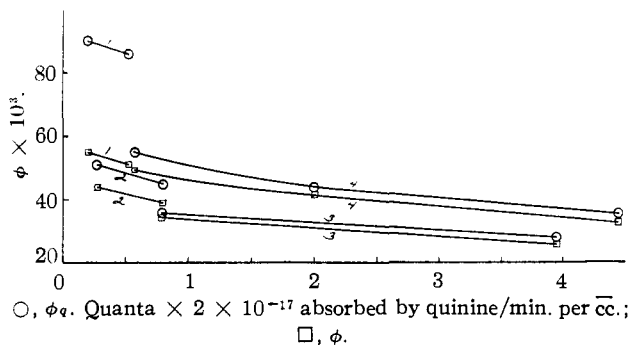


Fig. 4.—Temp., 25°.

Number	$\lambda$ in $m\mu$	$[K_2Cr_2O_7]$	$[Q]$	$[H_2SO_4]$
1	280	0.00016	0.001	0.8
2	280	0.00004	0.001	0.8
3	313	0.00004	0.00025	0.8
4	366	0.00004	0.00025	0.8

being held constant at 0.00016 and 0.8, respectively. The lines for  $\phi_q$  have a negative slope, partly because, as  $[Q]$  increases, it absorbs a greater fraction of the total energy flux, which was approximately the same in all cases. The deviations from the reciprocity law have been shown in Fig. 4, where total light intensity was varied while keeping constant the fraction absorbed by quinine. The indicated corrections when applied to the points in Fig. 5 would change somewhat the slopes of the curves. Obviously  $\phi_q$  is independent of the fraction of the total energy flux absorbed by quinine, provided only that this flux and  $[H_2Cr_2O_7]$  and  $[H_2SO_4]$  remain constant. Identical conclusions follow from other sets of experiments carried out in other (constant) concentrations of dichromic acid. On the other hand, the net quantum yield,  $\phi_c$ , referred to quanta absorbed by dichromic acid in our experi-

<sup>25</sup> Bowen and Bunn, *J. Chem. Soc.*, 2353 (1927).

<sup>26</sup> Bunn and Yarnold, *ibid.*, 1648 (1929).

<sup>27</sup> We shall show in a later paper that when quinine is replaced by cinchonine, the absorption curve of which resembles that of quinine shifted some 2000  $cm.^{-1}$  toward the ultraviolet, no photolysis occurs at 405  $m\mu$ , but at 366  $m\mu$ ,  $\phi$  for cinchonine approximates that for quinine at 450  $m\mu$  under conditions otherwise identical.



ments assumed values from 0.007 to 2000, when the fraction of the total energy flux which was absorbed by dichromic acid was widely varied. The above facts may be interpreted through the hypothesis that the reaction between activated dichromic acid and non-activated quinine is slow in comparison with that between activated quinine and dichromic acid whether activated or not. The conclusion of Luther and Forbes<sup>3</sup> that photolysis at 405 and 366  $m\mu$  depends upon activation of quinine alone when  $[H_2SO_4] > 1$ , thus receives strong support. On the other hand, it has long been known that dichromic acid, at shorter wave lengths, is directly photolyzed to

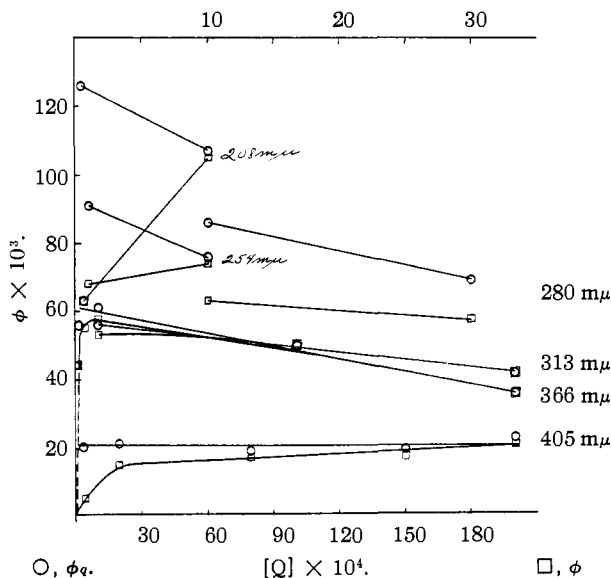


Fig. 5.—Lower scale for 405, 366 and 313  $m\mu$ ; temp., 5°; upper scale for 280, 254 and 208  $m\mu$ ; temp., 25°;  $[H_2SO_4]$ , 0.8;  $[K_2Cr_2O_7]$ , 0.00016.

chromic ion and oxygen. We irradiated dichromic acid, without quinine, and noted no photolysis at wave lengths exceeding 280  $m\mu$ . At 254  $m\mu$ ,  $\phi = \phi_c = 0.006$ , and at 208  $m\mu$ ,  $\phi = \phi_c = 0.015$ . At 254 and at 208  $m\mu$ ,  $\phi_q$  is therefore subject to a correction in consequence of this side reaction. Of course dichromic acid activated by such large quanta may oxidize non-activated quinine directly instead of evolving oxygen. Such a situation, assuming two activated components, was outlined by Forbes, Woodhouse and Dean.<sup>4</sup> We are continuing measurements at 208  $m\mu$  to clarify this aspect of the problem.

Gross and net quantum yields alike increase with increasing acidity as shown in Figs. 6, 7, 8 and 9 and Table I. The acidity in the more acid solutions was not recalculated to hydrogen-ion activity. Separate experiments

showed that potassium and sodium ions had a negligible effect upon quantum yields. Experiments at very low acidities must be made unduly long owing to minimal quantum yields; also chromate ion is precipitated by quinine and by chromic ion formed by reduction unless all concentrations are extremely

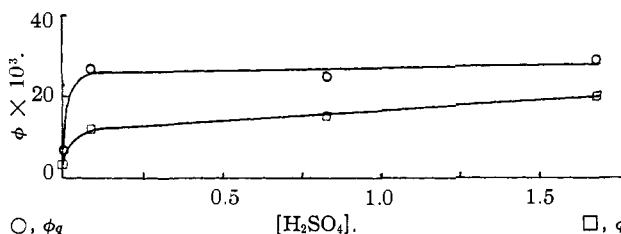


Fig. 6.— $\lambda$ , 405  $m\mu$ ;  $[K_2Cr_2O_7]$ , 0.00016;  $[Q]$ , 0.002; temp., 23°.

small. Any turbidity, of course, would bar interpretation of results. It was therefore inadvisable to follow Plotnikow's<sup>28</sup> suggestion that the reaction be followed in neutral solution. We are, however, making experiments at low acidities and varying quinine concentrations to test Morton's<sup>7</sup>

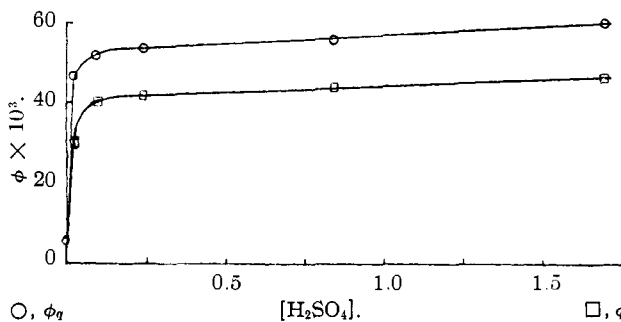


Fig. 7.— $\lambda$ , 366  $m\mu$ ;  $[K_2Cr_2O_7]$ , 0.00016;  $[Q]$ , 0.00025; temp., 5°.

Table 1. Temp., 5°.

$\lambda$ , in $m\mu$	$[K_2Cr_2O_7]$	$[Q]$	$[H_2SO_4]$	$P_H$	Buffer	$\phi$	$\phi_q$
366	0.00016	0.00025	0.0	2	NaHSO <sub>4</sub>	0.030	0.047
366	0.00016	0.00025	0.0	6	KH <sub>2</sub> PO <sub>4</sub> + Na <sub>2</sub> HPO <sub>4</sub>	0.000	0.000
366	0.00008	0.00025	0.2			0.041	0.048
366	0.00008	0.00025	0.4			0.047	0.052
366	0.00008	0.00025	0.8			0.041	0.048

hypothesis that activation of dichromic acid increases with increasing  $[H_2SO_4]$  up to 0.37 molar, where it reaches a maximum value incapable of further increase through absorption of light quanta.

<sup>28</sup> Plotnikow, "Lehrbuch der Photochemie," Walter de Gruyter and Co., Berlin and Leipzig, 1920, p. 215.

Inspection of Figs. 1, 2 and 3 and of Figs. 6, 7, 8 and 9 shows that extinction coefficients and quantum yields do not, in general, change in corresponding fashion when acidity is varied. The increase in photolytic efficiency due to increase in acidity might then better be discussed upon the basis of other considerations. These will be presented in a subsequent paper.

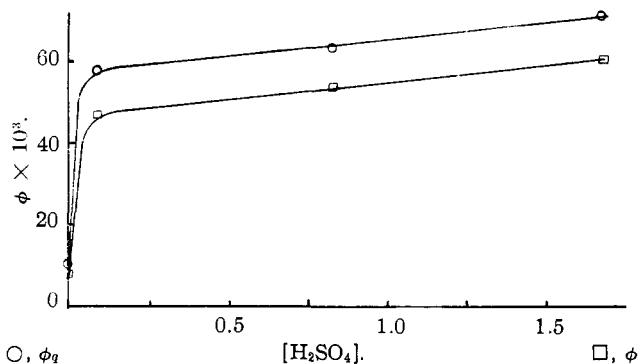


Fig. 8.— $\lambda$ , 313  $m\mu$ ;  $[K_2Cr_2O_7]$ , 0.00016;  $[Q]$ , 0.00025; temp., 23°.

Quantum yields at various wave lengths, roughly corrected to a basis of equal average light intensities expressed as quanta absorbed by quinine, appear in Fig. 10. All points at 254 and 208  $m\mu$  have been subjected also to small corrections for direct photolysis of potassium dichromate. It is

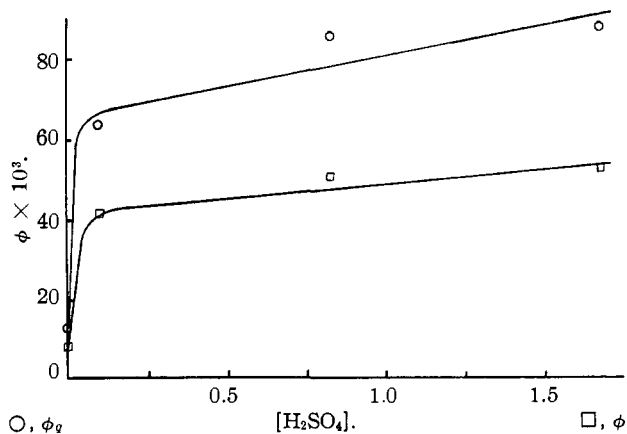


Fig. 9.— $\lambda$ , 280  $m\mu$ ;  $[K_2Cr_2O_7]$ , 0.00016;  $[Q]$ , 0.001; temp., 23°.

seen that  $\phi_q$  is smallest at 405  $m\mu$ , rises sharply to 366  $m\mu$ , is unchanged at 313  $m\mu$ , then climbs steeply to 208  $m\mu$ . The conclusion of Luther and Forbes<sup>3</sup> that photochemical efficiency at 405  $m\mu$  is nearly four times as great as at 366  $m\mu$  is in error because of their assumption, since disproved

by Winther,<sup>29</sup> that spectral energy distribution of an uviol lamp can be taken without serious error as equal to that of a quartz lamp. The absorption curves of quinine and of dichromic acid are inserted for comparison and it appears that the plot of  $K_c$  follows that of  $\phi_q$  much more closely than the plot of  $K_q$ . This coincidence, however, does not necessarily imply a causal relation. Between 405 and 366  $m\mu$  a new type of absorption mechanism for quinine seems to assert itself as suggested from a comparison of curves correlating  $K_q$  with  $[H_2SO_4]$  at 405 and 366  $m\mu$ . Beyond 313  $m\mu$  the apparent quantum yield rises with increasing frequency except for a second dip at 254  $m\mu$ .

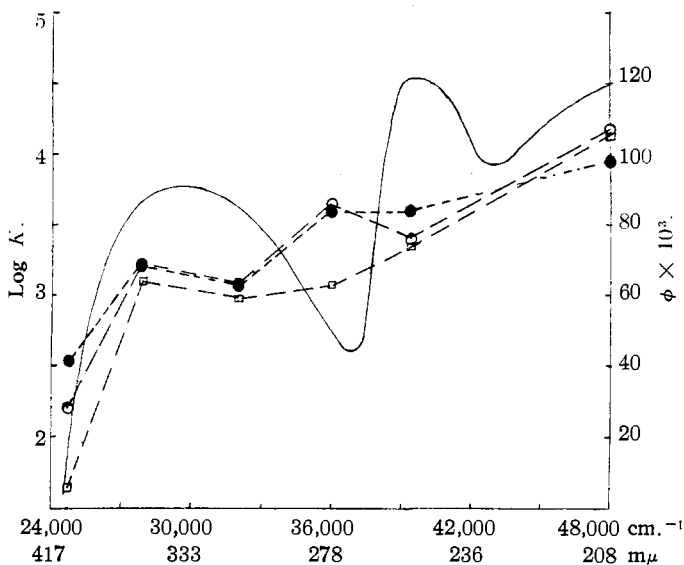


Fig. 10.—Temp., 26°;  $[K_2Cr_2O_7]$ , 0.00016;  $[Q]$ , 0.001;  $[H_2SO_4]$ , 0.8;  $\circ$ ,  $\phi_q$ ;  $\square$ ,  $\phi$ ;  $\bullet$ ,  $\log K$  for  $K_2Cr_2O_7$  in 0.8  $M$   $H_2SO_4$ ; —,  $\log K$  for quinine in 0.8  $M$   $H_2SO_4$ .

Fifty experiments, to be described in a later paper, fixed  $[\phi_q]_{T+10}/[\phi_q]_T$  between 2 and 29° at  $1.12 \pm 0.03$ . Tentative calculations (L. J. H.) show that a bimolecular collision number in aqueous solution has the same coefficient. This agreement would be expected if the secondary act involved reduction of dichromic acid, following a bimolecular collision with activated quinine, and requiring no additional activation energy.

A superficial examination of the structure of the quinine molecule shows that it consists of a quinoline group connected through a secondary hydroxyl to a saturated ring structure. The absorption curve is mainly conditioned by the former group as pointed out by Dobbie and Lauder,<sup>30</sup>

<sup>29</sup> Winther, *Z. Elektrochem.*, **19**, 389 (1913).

<sup>30</sup> Dobbie and Lauder, *J. Chem. Soc.*, **99**, 1254 (1911).

and as further demonstrated by comparing the absorption curve of quinine with those of numerous quinoline derivatives as given in "International Critical Tables."<sup>31</sup> Rabe,<sup>32</sup> however, has demonstrated that in the purely thermal reaction between quinine and dichromic acid it is the secondary hydroxyl, not the quinoline group, that is first attacked, since the initial oxidation product is the corresponding ketone. We have examined the absorption coefficients of a number of secondary alcohols, but have found them negligible in comparison with those of compounds containing the quinoline group except perhaps at 208  $m\mu$ . To explain the apparent anomaly it might be assumed that vibrational energy transmitted through the activated quinoline group to the secondary hydroxyl can activate the latter. The increase in  $\phi_q$  in passing from 313 to 208  $m\mu$  might possibly result from the increasing excess of vibrational energy set up in the quinoline group by the ever-increasing quanta. Such an hypothesis does not explain the dips of the curve near absorption maxima. We are now investigating various quinine derivatives to test these tentative suggestions.

### Summary

The photochemical reaction between quinine and dichromic acid has been reinvestigated quantitatively at each of seven wave lengths from 436 to 208  $m\mu$  with analytical and radiometric precautions sufficient to establish quantum yields within 10%.

Extinction coefficients of quinine and dichromic acid were measured at each of these wave lengths, and over a wide range of concentrations and acidities using various apparatus and methods. Quantum yields change similarly with  $[H_2SO_4]$  for 405, 366, 313 and 280  $m\mu$  and cannot be correlated with changes in  $K_q$  or  $K_c$  with  $[H_2SO_4]$ . Extinction coefficients proved to be additive within the limit of error; it is improbable, therefore, that quinine and dichromic acid form a stable complex analogous to that of uranyl oxalate.

The hypothesis that activation of quinine is the decisive factor in the photolysis is strongly supported by the outcome of about two hundred photolyses. Apparently irradiation of dichromic acid does not increase its tendency to react with non-activated quinine except perhaps at wave lengths shorter than 280  $m\mu$ . Further experiments in this spectral region are in progress.

Tentative calculations indicate that the reaction's temperature coefficient,  $1.12 \pm 0.03$ , equals that of a bimolecular collision number in aqueous solution, presumably involving dichromic acid and activated quinine, and resulting in reduction of the former without additional activation energy.

A plausible scheme of reaction mechanism begins with the capture of

<sup>31</sup> "International Critical Tables," Vol. V, pp. 363-372.

<sup>32</sup> Rabe, *Ann.*, **365**, 353 (1909).

a quantum by the quinoline group of the quinine molecule. Vibrational energy, transferred to the secondary hydroxyl group adjacent, may increase the reactivity of the latter.

Parallel experiments with quinine derivatives are being made. Temperature coefficients and the effects of variable dichromate concentrations, especially at low acidities, are being investigated.

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## ATTEMPTED PHOTOSYNTHESIS OF CARBOHYDRATES IN VITRO WITH VISIBLE LIGHT

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The appearance in 1927 of three papers<sup>1</sup> by E. C. C. Baly and others on the "Photosynthesis of Naturally Occurring Compounds" was of very great interest to those concerned with photosynthesis as it occurs in the living green plant. Particular importance was attached to the second paper of this series, in which was described a method for the photosynthesis of carbohydrates from carbonic acid by means of visible light and colored solid catalysts. Forty futile attempts were made by the writer to repeat the experiments of Baly with visible light and nickel and cobalt carbonates as catalysts, with hopes of extending these experiments. Special precautions were taken to eliminate contamination of the photosynthetic system by impurities from various sources, precautions which were more rigorous than those described by Baly in the second paper mentioned above.

In paper II, Baly describes a precipitation method for preparation of carbonates of nickel and cobalt by adding cold solutions of nickel or cobalt nitrate and of potassium carbonate together and washing the precipitate with hot water to remove all foreign ions and alkali. The precipitate is then dried at 100° and powdered. The powder requires activation before introduction into the photosynthetic chamber, this activation being accomplished either by heating at 120–140° for thirty minutes or by exposing the powder to ultraviolet light for thirty minutes. The powder is then placed in conductivity water through which a stream of carbon dioxide is bubbled, this system being illuminated by visible light from electric lamps. After two hours, the mixture is filtered and the filtrate evaporated. The final residue is extracted with methanol, which removes the photosynthesized substance. This substance is said to reduce Benedict's solution, as well as to give other tests for carbohydrates. Baly's directions are rather incomplete as to details but they were followed as closely as possible, with some refinements, in the experiments described below.

An effort was made to exclude all sources of contamination, both organic and in-

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<sup>1</sup> E. C. C. Baly, J. B. Davies, M. R. Johnson and H. Shanassy, *Proc. Roy. Soc.* (London), **A116**, 197 (1927); E. C. C. Baly, W. E. Stephen and N. R. Hood, *ibid.*, **A116**, 212 (1927); E. C. C. Baly and J. B. Davies, *ibid.*, **A116**, 219 (1927).