6. Chain lengths agreeing with experimental values may be predicted from the values of k_2.

The Photochemical Reaction between Quinine and Dichromic Acid. II. Kinetics of the Reaction

By George S. Forbes, Lawrence J. Heidt and F. Parkhurst Brackett, Jr.

This paper suggests a kinetic picture consistent with new data and with data already published.[1] The experimental methods have been described[1] except those followed (by the last-named author) at 208, and 254 mμ.

The only primary act (except possibly at 208 mμ) contributing to reduction of dichromic acid disclosed by our results is an activation of the quinine molecule or ion, Q to form Q*. In the secondary act a part of these activated molecules reduces dichromic acid. This picture could be amplified as follows. At the instant of excitation Q may be adjacent to molecules (or ions) of the other reactants, all within possibly effective ranges of distances and of orientations. That is, $n_1[Q] + n_2[H_2Cr_2O_7] + n_3[H^+] \rightleftharpoons$ potentially effective kinetic "clusters," to borrow Weigert's general designation.[2] Such clusters are conditioned by kinetic and electrostatic effects, and are in no sense stable complexes like uranyl oxalate. Photochemical reactivity, while varying with configuration, is practically independent of all activation energies except that of Q*. In a steady state and in a thin layer,

$$K_1\phi_q = [Q^*]_{cluster}/[Q^*]_{total} = K_2[Q^*]^{n_1}[H_2Cr_2O_7]^{n_2}[H^+]^{n_3}/[Q^*]$$

or

$$\log \phi_q + \log K_1/K_2 = (n_1 - 1) \log [Q^*] + n_2 \log [H_2Cr_2O_7] + n_3 \log [H^+]$$

where ϕ_q is net quantum yield referred to light absorbed by quinine and $[Q^*] = K'[Q]$ where K' depends, among other factors, upon the reaction cell used. K_1 is itself complex, involving factors such as $K_3e^{-\theta d/\theta_0 d_0}$ where θ_0 and d_0 indicate orientation and distance optimal for the secondary act.

If $[H_2Cr_2O_7]$ and $[H^+]$ are large compared with $[Q]$, or are held constant, $\log \phi_q = (n_1 - 1) \log [Q] + $ const. For correct evaluation of n_1, deviations from the reciprocity law had to be avoided by stopping down the front lens of the monochromator in each experiment to such an extent that the quinine in the first centimeter of the reaction mixture absorbed just as many quanta per minute, E_q, as in any other experiment in the series. As a consequence, $[Q^*]_{av}$ was always the same in the layer thus

(1) Forbes, Heidt and Boissonnas, This Journal, **54**, 960 (1932).
(2) Weigert, Z. physik. Chem., **102**, 416 (1922); **106**, 426 (1923).

defined, also in other layers uniformly defined. Table I gives the data for one typical series of experiments. E_0 equals quanta per minute incident upon the cell.

TABLE I

λ, 366 mμ.   Temperature, 5°

[K₂Cr₂O₇]	[H₂SO₄]	[Q]	E_0	E_q	ϕ_q
0.00016	0.8	0.000250	6.4×10^{16}	4.9×10^{16}	0.057
.00016	.8	.000025	19.2×10^{16}	4.5×10^{16}	.059
.00016	.8	.000010	47.0×10^{16}	4.8×10^{16}	.057

Table I proves that ϕ_q when properly determined is independent of [Q]. Therefore $(n_1 - 1) = 0$ and $n_1 = 1$; that is, only one molecule of Q is involved in the secondary act. Similar data plotted at 405 and 313 mμ previously given,[1] and in Fig. 1 obtained at 366, 280, 254 and 208 mμ, lead to identical conclusions.
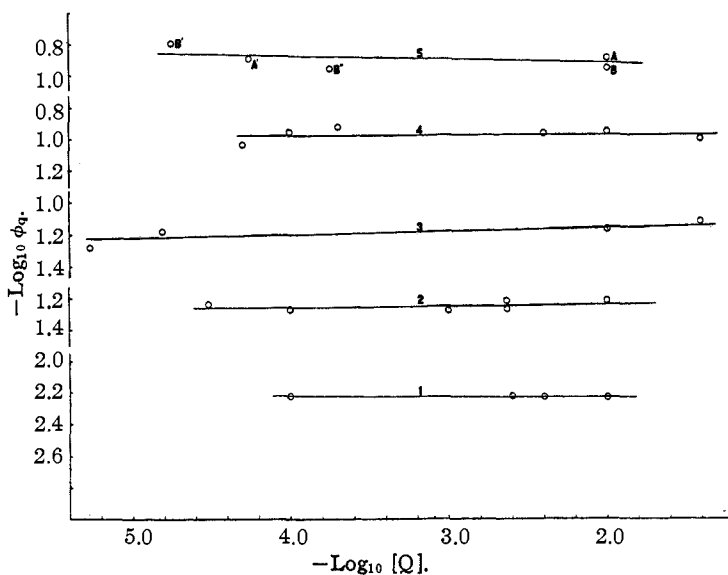

Fig. 1.—[K₂Cr₂O₇], 0.00016; Temp., 23°; E_q, 5×10^{16}.

Curve	λ in mμ	[H₂SO₄]	Slope, n_1
1	366	0.0	0.00
2	366	.8	.00
3	254	.8	.02
4	280	.8	.00
5	208	.8	−.02
		Average	.00

At 254 and 208 mμ a zinc spark consuming 3 k. w. and automatically kept constant over long periods was used as a source of light.[3] Details of

(3) Forbes and Brackett, THIS JOURNAL, **53**, 3973 (1931).

the crystal quartz monochromator working at f2 and its operation will be somewhat amplified elsewhere. Quantum yields and absorption coefficients were measured in a rectangular quartz cell (all seams fused) 85 mm. high, 35 mm. wide and 5.7 mm. thick, placed between the exit slit and the thermopile by which the highly divergent beam was integrated. The method, precautions and corrections followed closely previous investigations in this Laboratory.[4] At these wave lengths all experimental difficulties were increased, also the radiometric corrections, made as previously described. ϕ_q is given after correction for direct photolysis of dichromic acid absorbing E_c quanta per minute. The need for such a correction appears in Table II.

TABLE II

Temperature, 25°. E_c, 5 × 10^{16}

λ	[K₂Cr₂O₇]	[H₂SO₄]	ϕ
208 mμ	0.00016	0.8	0.012
208	.00032	.8	.013
254	.00016	.8	.004
254	.00036	.8	.005
280	.003	.8	.000

In Fig. 1 at 254 mμ the curve appears nearly horizontal, as was the case at 280, 313, 366 and 405 mμ. At 208 mμ, however, the points B', A' and B'', as [Q] approaches zero, suggest that the curve may be turning upward as dichromic acid absorbs a greater share of the light. Points A and A', which average a preliminary set of experiments, should be given less weight than the others. Points B and B', on the other hand, each average three very concordant final experiments. It, therefore, appears possible that at 208 mμ we have two activated reactants, each one reacting to a measurable extent with the other in its normal state. Conclusive evidence upon this admittedly important point would require a further refinement of experimentation, hard indeed to attain. Clusters in which both reactants are simultaneously activated[5] might well be exceedingly reactive, but an event of such a type ought to be so infrequent as to contribute negligibly to the total reaction.

The data graphed in curve 1, Fig. 1, at 366 mμ were collected to test Morton's prediction[6] that the efficiency of dichromic acid as an oxidant of quinine should increase, with increase of [H₂SO₄] from zero to 0.37, to a maximum incapable of still further increase through light absorption. In the series, E_q was held constant as described above and no sulfuric acid was added, the quinine bisulfate and dichromic acid being so dilute no precipitate appeared. As in the other curves in the figure, ϕ_q is unchanged even at minimal values of [Q] where the greater part of the

(4) (a) Villars, THIS JOURNAL, **49**, 362 (1927); (b) P. A. Leighton and G. S. Forbes, *ibid.*, **51**, 3549 (1929); (c) W. G. Leighton and G. S. Forbes, *ibid.*, **52**, 3139 (1930).

(5) Compare paper of Forbes, Woodhouse and Dean, *ibid.*, **45**, 1891 (1923).

6) Morton, *J. Phys. Chem.*, **33**, 1135 (1929).

light available is absorbed by dichromic acid.   As ϕ_q does not even now increase when [Q] becomes very small, it is evident that at minimal acidity light has not measurably increased the reactivity of dichromic acid toward non-illuminated quinine.

Table III presents typical data for evaluation of n_2.

TABLE III

λ, 280 mμ.   Temperature, 25°

[Q]	[H₂SO₄]	[K₂Cr₂O₇]	E_0	E_q	ϕ_q
0.001	0.8	0.00016	2.17×10^{16}	1.26×10^{16}	0.094
.001	.8	.00008	1.71×10^{16}	1.30×10^{16}	.069
.001	.8	.00004	1.50×10^{16}	1.30×10^{16}	.048

Similar series completed at 405, 366 and 280 mμ are shown in Fig. 2, where log ϕ_q is plotted against log [K₂Cr₂O₇] at various wave lengths and temperatures.   The black dots are based upon Table VIII of Luther and
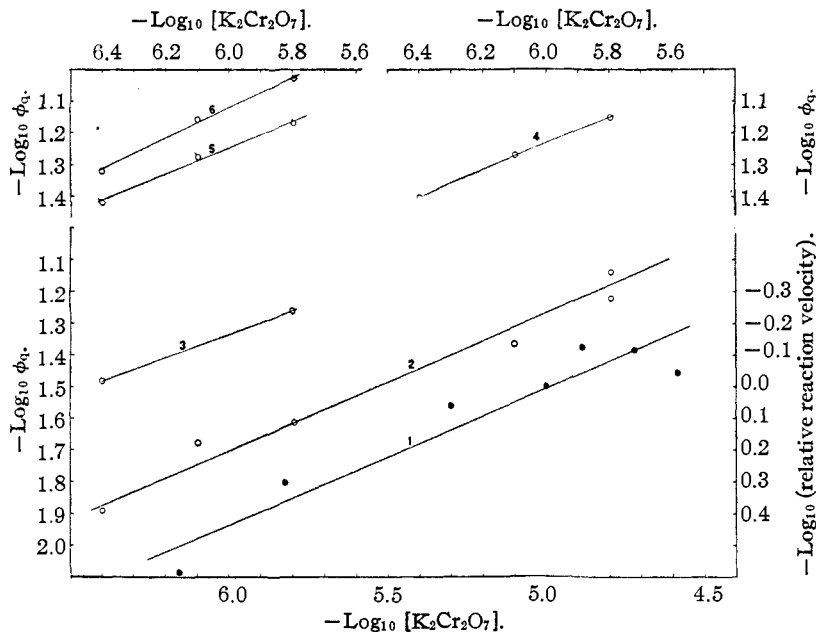

Fig. 2.—⊙, Temp. 23°; –◯, Temp. 5°; ●, Data of L. & F., Ref. 7; [H₂SO₄], 0.8; E_q, 5×10^{16}.

Curve	λ in mμ	[Q]	Slope, n_2
1	405	0.01	0.43
2	405	.004	.43
3	313	.00025	.38
4	366	.00025	.40
5	280	.001	.41
6	280	.001	.48
		Average	.42

Forbes,[7] log of the relative reaction rates in polychromatic light, 405 and 366 mμ, being plotted as ordinates in place of log ϕ_q. It is noteworthy that straight lines result in all cases, log $\phi_q = n_2 \log[H_2Cr_2O_7] +$ const.; n_2 is uniformly 0.43 $\doteq$ 0.05 irrespective of wave length or temperature, which assigns only half the molecule $H_2Cr_2O_7$ to an effective cluster. Possibly chromic acid reacts more readily with Q* than dichromic acid. Since $[H_2CrO_4] = k[H_2Cr_2O_7]^{1/2}$, a plot of log ϕ_q against log $[H_2Cr_2O_7]^{1/2}$ would have a slope equal to unity within the experimental error and would represent the behavior of clusters containing one molecule of chromic acid. The residue of the chromate molecule, bereft of one oxygen atom, is unstable and would be expected to react again, doubling the immediate quantum yield.
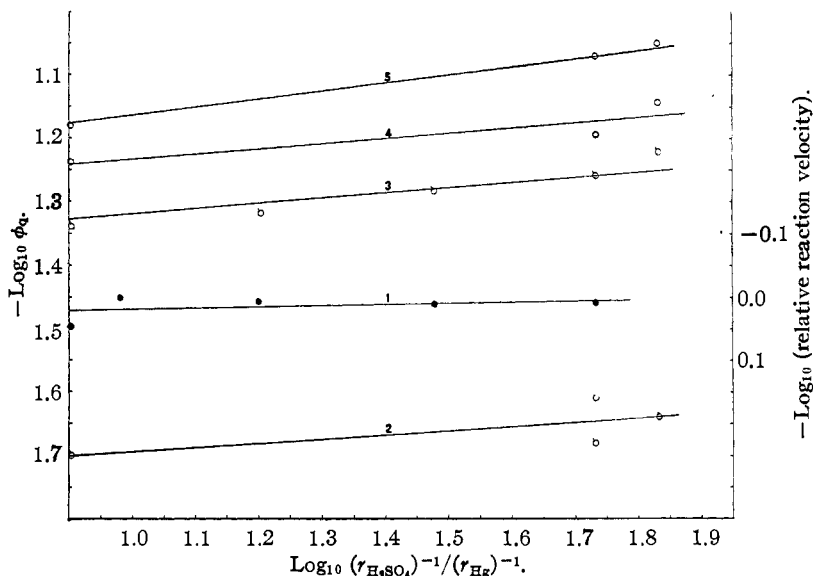

Fig. 3.—○, Temp. 23°; –○, Temp. 5°; ●, Data of F. W. & D., Ref. 5; [K₂Cr₂O₇], 0.00016; E_q, 5 × 10¹⁶.

Curve	λ in mμ	[Q]	Slope, n_3
1	405	0.006	0.02
2	405	.008	.06
3	366	.00025	.08
4	313	.00025	.08
5	280	.001	.13
		Average	.07

The evaluation of n_3, for hydrogen ion, was hampered by lack of data on activity coefficients in rather concentrated sulfuric acid. Specific conductivity, r^{-1}, is perhaps the next best measure of the activity of hydrogen ion in clusters. In Fig. 3 log ϕ_q is plotted against $\log[(r_{H_2SO_4})^{-1}/$

(7) Luther and Forbes, THIS JOURNAL, 31, 770 (1909).

$(r_{Hg})^{-1}$], taken from Kohlrausch's tables.[8] The data of Forbes, Wood-house and Dean[5] appear as black dots, log of the relative reaction rates in polychromatic light being plotted as ordinates in place of ϕ_q. Straight lines again result, but the average slopes assign to n_3 the value 0.07 and to sulfuric acid a subordinate role in the reaction. Possibly the hydrogen ion already present in $H_2Cr_2O_7$ or H_2CrO_4 usually suffices for the secondary act involving Q*, the additional hydrogen ion in the cluster increasing only slightly the probability of the same.

The data on the reciprocity law, before plotting,[9] were subjected to a correction not discussed at that time, the need for which appears in Table IV.

TABLE IV

λ, 366 mμ.   Temperature, 22°

	[Q]	[K₂Cr₂O₇]	[H₂SO₄]	$E_q \times 10^{-16}$	Minutes irradiated	Total min. before titration	ϕ_q, un-corrected
1	0.00025	0.00016	0.8	8	60	75	0.062
2	.00025	.00016	.8	8	60	1260	.077
3	.00025	.00016	.8	8	120	135	.065

As solution (2) was exposed for the same time as (1), the difference in ϕ_q is attributable to a *dark* reaction between the photochemical oxidation products and dichromic acid during twenty-one hours as the values of ϕ_q in Table IV were corrected for the dark reaction not involving photochemical oxidation products of quinine. Experiments involving exposure to weak light over long periods are misleading until corrected for this dark reaction. Solution (3) was exposed twice as long as (1) and then titrated promptly. It is clear that the oxidation products formed during the first hour contributed little if anything to the photolysis during the second hour; that is, their quantum yield cannot greatly exceed ϕ_q. A fourth solution was photolyzed (λ, 366 mμ) until about half the quinine was oxidized. Absorption of 3×10^{20} quanta (λ, 436 mμ) by the dichromic acid in the solution followed without any effect, proving that the photochemical oxidation products, like quinine, are not photochemically oxidized in blue light.

The corrected decrease in ϕ_q with increase in light intensity,[9] as well as the small size of ϕ_q itself, suggests the hypothesis that photochemically efficient clusters are formed at a relatively slow rate. An increased light intensity might be expected to eliminate such clusters more rapidly, and cut down their concentration which existed in the previous steady state. Thereafter, a smaller fraction of the total quanta absorbed would activate quinine already present in efficient clusters, causing ϕ_q to decrease. This effect was found most striking in solutions most concentrated in dichromic acid, as shown in Table V.

(8) Kohlrausch, "Physical Measurements," D. Appleton and Co., New York, 1874, p. 236

(9) Ref. 1, Figs. 4, 5.

Table V

λ, 366 mμ.   Temperature, 22°

[Q]	[K₂Cr₂O₇]	[H₂SO₄]	$E_q \times 10^{-16}$	ϕ_q
0.00025	0.00016	0.8	18.0	0.058
			1.8	.070
.00025	.00008	.8	18.0	.048
			1.8	.052
.00025	.00004	.8	18.0	.039
			1.8	.040

In a previous paper[1] the relation between wave length and quantum yield was discussed. To make the data there more complete, we have since determined ϕ_q, 0.070 at 334 mμ, compared with a value of 0.060 at 366 and at 313 mμ, under conditions otherwise identical.

Using a Judd-Lewis sector spectrophotometer in a more detailed study of the variation of the extinction coefficient of quinine, K_q, with variation of [H₂SO₄] and wave length we found that from 405 to 208 mμ, log K_q is a linear function of either the log [H₂SO₄] or the log [Q], the other being held constant. A shift of 200 cm.⁻¹ of the absorption curve of [Q], 0.0001 mole per liter, toward smaller wave numbers was observed in passing from 0.004 to 4.0 m H₂SO₄. In the steeper parts of the absorption curve, accurate data regarding [H₂SO₄] are therefore indispensable.

Ten-degree temperature coefficients, $\delta_{10°}\phi_q = (\phi_q)_{t + 10}/(\phi_q)_t$, between 5 and 24° (one determination only at 29°) at various wave lengths appear in Table VI. Each entry gives the average of two or more complete experiments. Increments of [K₂Cr₂O₇] seem to lower $\delta_{10°}\phi_q$ slightly, but doubling [H₂SO₄] does not seem to affect it measurably. The increase in $\delta_{10°}\phi_q$ at shorter wave lengths is too small to warrant theoretical argument. Further, the average of $\delta_{10°}\phi_q$, 1.12, approximately equals $(273 + 20)^3/(273 + 10)^3$ which suggests an interesting possibility.

Table VI

λ in mμ	[K₂Cr₂O₇]	[Q]	[H₂SO₄]	ϕ_q at 5 ± 1°	ϕ_q	Ten-degree temperature coefficient
366	0.00004	0.00025	0.8	0.029	0.039 at 22°	1.17
	.00004	.00025	.8	.044	.055 at 29°	1.10
	.00008	.00025	.8	.052	.054 at 23°	1.02
	.00016	.00025	.8	.062	.070 at 24°	1.07
	.00016	.00025	1.7	.060	.070 at 25°	1.08
313	.00016	.00025	0.8	.056	.064 at 24°	1.14
	.00016	.0010	.8	.052	.064 at 23°	1.16
	.00004	.00025	.8	.028	.033 at 24°	1.17
280	.00004	.001	.8	.038	.050 at 22°	1.17
	.00008	.001	.8	.054	.069 at 22°	1.16
	.00016	.001	.8	.070	.083 at 21°	1.12
404	.00016	.02	.8	.022	.028 at 22°	1.15
					Average	1.12

In a gaseous system the number of bimolecular collisions, Z, experienced by a particle having a mean free path l for a mean linear displacement $\overline{X}$ is

$$Z = 3\pi\overline{X}^2/4l^2 \tag{1}$$

For a particle in a liquid system Einstein[10] and von Smoluchowski[11] showed that in one second

$$\overline{X}^2 = \frac{kT}{3\pi\eta r} \tag{2}$$

where k is the gas constant per molecule, η the viscosity of the solvent, r the radius of the particle and T the absolute temperature. Granting that (1) can be made applicable to collision numbers involving ions in a liquid system by multiplying Z by a constant factor, we can substitute (2) in (1) and note that η for water between 0 and 30° is proportional to $1/T^2$, whereupon $Z = f(T^3)$. Over the temperature range 5 to 24°, $[(297)^3/(278)^3] \times 10/19 = 1.115$.

The above calculation would be also in accord with our tentative view that activated quinine reacts with dichromic (or chromic) acid in a bimolecular process requiring no additional energy of activation. It should be noted that this is not in harmony with the views held by Moelwyn-Hughes[12] and others, namely, that Z is directly proportional to the viscosity and hence has a negative temperature coefficient. If Moelwyn-Hughes' contentions are correct, a positive heat of activation, smaller than that of the average thermal reaction, would be indicated for the secondary act, and no obvious evidence of a bimolecular reaction would appear.

The investigation of quinine derivatives is being continued.

Summary

The photochemical reaction between quinine and dichromic acid apparently occurs in photochemically efficient clusters (not complexes) containing the above. Individual concentrations were varied; other variables, including concentration of activated quinine, were fixed. Seven wave lengths over the range 405 to 208 mμ were used. By graphical methods, reaction order was found to be zero for quinine and 0.43 for $H_2Cr_2O_7$ or 0.86 for H_2CrO_4. These values correspond to 0.50 and 1.00, respectively, within experimental error. A reaction order of 0.07 for H_2SO_4 assigns a subordinate role to this reactant. It is barely possible that at 208 mμ only, both the quinine and the dichromic acid are photosensitive.

It is shown that when the total absorbed light is divided between two (or more) constituents of the solution, the total intensity must be regulated so as to maintain the same concentration of the effectively activated constituent in all the experiments used to establish the effect of changing the concentration of some other reactant.

(10) Einstein, *Ann. Physik*, [4] **17**, 549 (1905); **19**, 371 (1906).
(11) Von Smoluchowski, *ibid.*, **21**, 756 (1906).
(12) Moelwyn-Hughes, *J. Chem. Soc.*, 95 (1932).

Quinine concentration being held constant, an increase in sulfuric acid concentration from 0.004 to 4 moles per liter shifts the whole absorption curve 200 cm. $^{-1}$ toward the red.

The ten-degree temperature coefficient, 1.12, agrees with one mode of calculating the temperature coefficient of the collision number in solution of a bimolecular reaction between activated quinine and H_2CrO_4 without additional energy of activation.   Another calculation predicts a small energy of activation.

Ammines of the Lower Chlorides of Titanium

BY WALTER C. SCHUMB AND RICHARD F. SUNDSTRÖM

Although anhydrous titanium dichloride and trichloride have been the subject of numerous investigations, conflicting statements relative to some of their properties, and the absence of data concerning others, make the further study of these compounds desirable.   In particular, the recorded observations which concern the preparation of the two chlorides appear in some respects to be in need of revision, and comparatively little is known concerning the reactions of these two substances with ammonia.   The aim of the present paper is to contribute further information on each of these subjects.

Ruff and Neumann[1] prepared the anhydrous trichloride by reducing the tetrachloride with various metals.   They obtained it as violet crystals, which when heated in a vacuum slowly began to sublime at 425°, and to decompose at 450° into the di- and tetrachlorides.   At 475° this decomposition proceeded rapidly, and the dichloride thus obtained was very stable to heat and not volatile in a vacuum even at 600°.   It is interesting to note that they were unable to obtain samples of high purity; they accounted for their high titanium content and low chlorine content by assuming that their samples had become oxidized during the course of the preparation.   Earlier investigators similarly had failed to obtain pure specimens.

Meyer and co-workers[2] prepared the trichloride by the reduction of the tetrachloride with hydrogen at high temperatures, employing the hot-cold tube previously used by Georges and Stähler.[3]   At 800–1000° they obtained a mixture of the di- and trichlorides, which was converted completely into the trichloride by heating to 300° in a stream of hydrogen and

(1) Ruff and Neumann, *Z. anorg. allgem. Chem.*, **128**, 81 (1923).
(2) Meyer, Bauer and Schmidt, *Ber.*, **56**, 1908 (1923).
(3) Georges and Stähler, *ibid.*, **42**, 3200 (1909).