CCXVII.—*The Photochemical Oxidation of Ethyl Alcohol by Potassium Dichromate. Part II.*

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BOWEN and BUNN (J., 1927, 2353) have shown that the quantum efficiency of the reaction between aliphatic alcohols and potassium dichromate to give aldehydes is independent of light intensity, of wave-length between 5000 and 3666 Å., of temperature, and, within limits, of the hydrogen-ion and the potassium dichromate concentration. It was shown also that the quantum efficiency rose with the alcohol concentration to a maximum, and that the chromate ion was photochemically insensitive.

The present work was undertaken to investigate more fully (1) the effect of neutral salts on the photochemical reaction; (2) the order of the reaction with respect to alcohol present in low concentrations; (3) the cause of the falling off of the rate at high alcohol concentrations; (4) the dependence of the rate on the hydrogen-ion and potassium dichromate concentrations.

EXPERIMENTAL.

The light source was an air-cooled, quartz, mercury-vapour lamp running at a controlled voltage, and enclosed in a " uralite " box. The reaction vessels were placed in a glass-walled thermostat, which in addition to its heating regulation was cooled by the passage of cold water through a metal spiral, on account of the proximity of the lamp. The rate of reaction was followed according to the di-chromate estimation method of Vosburgh (*J. Amer. Chem. Soc.*, 1922, **44**, 2120). In experiments where the alcohol concentration was high, the liquid was diluted with distilled water before titration.

In all the experiments described, except those at high alcohol concentration (Section 3), the amount of change was closely proportional to the time of exposure, and no precipitates were formed in the early stages of the reactions. A series of measurements was made of the amount of change at different times of exposure for every reaction mixture, and from the straight-line graph the reaction rate was obtained. The thermal rate was shown to be negligible in most of the measurements; at some of the higher alcohol concentrations a correction never exceeding 5% was obtained for it by measurement.

The amount of light absorbed and the quantum efficiencies were obtained in the following way. A glass trough 3 cm. wide containing dilute copper sulphate solution was placed in front of the lamp; behind it was a screen with a suitable aperture, at which was placed a silica cell of 1 cm. internal width and about 25 c.c. capacity, with

plane transparent ends fused on. Behind the cell was fixed a Moll " large-surface " thermopile, connected to a suitable galvanometer. Measurements were made of the light transmitted (a) with the cell removed, A, (b) with the cell filled with water, B, (c) with the cell filled with a reaction mixture, C. The light absorbed was then calculated from the approximate expression $(B - C)\sqrt{A/B}$.

The amount of light absorbed was found to be 48%, and independent of the concentration of alcohol, dichromate, and hydrogen ion, in all the mixtures used. The absorption spectra of glass and potassium dichromate, and the spectrum of the quartz lamp, limit the light absorbed to the wave-lengths 4360, 4060, and 3666 Å. From the fact that the absorption is independent of dichromate-ion concentration, it seems that these lines are completely absorbed.

The thermopile was then placed at the aperture in place of the cell, and the intensity of the light determined there. This quantity, multiplied by the absorption, the factor $\sqrt{A/B}$ to correct for cell losses, and the ratio of areas of the aperture and thermopile, gave the intensity of the light absorbed in the cell. The thermopile readings were converted to cals. per sec. by calibration against a Hefner lamp (Gerlach, *Physikal. Z.*, 1913, **14**, 577), and the number of gram-molecular quanta was calculated by dividing by 70,900 cals., taking the mean wave-length to be 4000 Å. The quantum efficiency is then the number of g.-ions of dichromate reduced, as directly measured, divided by the number of gram-molecular quanta absorbed. As the absorption is the same for all solutions, a factor was obtained from several measurements of this type from which reaction rates measured in the thermostat could be converted to quantum efficiencies.

(1) *Effect of Addition of Neutral Salts.*—No effect on the photochemical rate was produced by addition of sodium sulphate, but the amount of salt which could be dissolved in the solutions of higher alcohol concentration was not very great. Table I gives the results for additions of calcium chloride.

TABLE I.

Dichromate concentration, $0\cdot025N$.

Alcohol (% by vol.).	Relative rates. Conc. of CaCl₂ in solution,			Alcohol (% by vol.).	Relative rates. Conc. of CaCl₂ in solution,		
	0.	0·255M.	0·51M.		0.	0·255M.	0·51M.
50	4·1	—	5·1	80	5·5	5·95	—
60	4·8	4·85	5·9	81	—	—	6·25
70	4·95	5·4	6·1	83	—	6·2	—
75	—	—	6·15	85	6·0	5·45	—
78	—	—	6·40	90	5·25	—	—

The effect of large quantities of salt on the rate is small, showing that extensive secondary thermal reactions do not occur—a conclusion which agrees with the temperature coefficient of unity and the measurements of the quantum efficiency. The concentration of alcohol giving the maximum rate (the nature of which is shown in Section 3) is shifted by the presence of calcium chloride, and an approximate calculation shows that this shift is reasonably accounted for by the removal of some of the solvent water by the salt. In absence of calcium chloride the maximum occurs at 85% of alcohol by volume, and with $0.51M$-calcium chloride it is at 80%. From this we find that roughly 3 g.-mols. of water are removed by 0.51 g.-mol. of salt, or each calcium chloride molecule removes 6 mols. of water. These considerations go to show that the changes of photochemical rate with alcohol concentration up to the position of the maximum is due to the variation in the proportion of hydrated to alcoholated dichromate ions, only the latter being photoactive.

(2) *Experiments at Low Alcohol Concentrations.*—In this region the gas laws may be applied to equilibria involving alcohol molecules, and information obtained as to the nature of the photoactive ions present in the solution. The results obtained are given in Table II, the % of alcohol by vol. being given under a, the quantum efficiency being γ, and the formula upon which the calculated value of γ is based being shown for each set of results.

TABLE II.

$Cr_2O_7'' = 0.025N$; $H_2SO_4 = 0.1N$.			$Cr_2O_7'' = 0.025N$; $CH_3 \cdot CO_2H = 0.1N$.			$Cr_2O_7'' = 0.0125N$; $CH_3 \cdot CO_2H = 0.1N$.		
a.	γ, obs.	γ, calc.	a.	γ, obs.	γ, calc.	a.	γ, obs.	γ, calc.
2.5	0.03	0.03	2	0.013	0.012	2	0.010	0.0105
5	0.07	0.07	4	0.027	0.027	4	0.023	0.023
8	0.12	0.13	6	0.044	0.044	8	0.049	0.053
10	0.175	0.174	8	0.066	0.064	12	0.083	0.089
12	0.225	0.225	10	0.087	0.087	16	0.133	0.133
15	0.29	0.31	12	0.116	0.112	20	0.190	0.183
			14	0.122	0.14	25	0.250	0.255

$$\gamma = 1.04 \times 10^{-2}a + 7.04 \times 10^{-4}a^2. \qquad \gamma = 5.31 \times 10^{-3}a + 3.28 \times 10^{-4}a^2. \qquad \gamma = 4.95 \times 10^{-3}a + 2.11 \times 10^{-4}a^2.$$

In each case the observed quantum efficiencies can be closely represented by an equation of the type $\gamma = k_1a + k_2a^2$. A collisional interpretation of this result is extremely unlikely because of the relative magnitudes of k_1 and k_2 compared with the probabilities of binary and ternary collisions, and also because with glycerol no k_2 term is necessary (Section 5).

These results at low alcohol concentrations are taken to show that two photoactive ions are present in the solution, *viz.*, a dichromate ion with one molecule of alcohol attached, and one with two molecules

attached. In such solutions the concentrations of these two ions will be proportional to the alcohol concentration and to its square, respectively. At high alcohol concentrations possibly ions having more co-ordinated alcohol molecules are formed, but the simple mass law cannot be applied to the equilibria in this region.

(3) *Experiments at High Alcohol Concentrations.*—Bowen and Bunn (*loc. cit.*) found that at very high alcohol concentrations the quantum efficiency passed through a maximum and appeared to fall off beyond concentrations of about 85% by volume. This has now been traced to the formation of a pale purplish-green amorphous precipitate which reduces the efficiency by scattering the light. The formation of this precipitate is not prevented by the added acid, in contrast to the brown precipitate of chromium chromate always obtained from non-acidified dichromate–alcohol mixtures. Measurements of the light absorbed during the photochemical reactions of mixtures of different alcohol concentrations (enough acid being always present to prevent the brown precipitate forming) showed that up to 85% of alcohol the light absorption remained constant during the reaction ; beyond this concentration it increased rapidly with time, owing to the formation of the pale precipitate.

The ratio of chromium to sulphate radical in the precipitate was obtained by precipitating the chromium as hydroxide and weighing as oxide, and precipitating the sulphate as the barium salt. The ratio $Cr^{\cdots}/SO_4''$ was found to be 0·59, while that calculated from the formula $CrSO_4 \cdot X$ is 0·54. The amorphous basic sulphates of chromium of the type $CrSO_4(OH),2H_2O$ are soluble in water and insoluble in alcohol (see Abegg, " Anorganische Chemie," Vol. 4, p. 151). The formation of the precipitate does not therefore indicate a change in the nature of the reaction, but is due to the insolubility of basic chromium sulphates in strong alcohol.

(4) *The Variation of the Quantum Efficiency with Hydrogen-ion and Dichromate-ion Concentration.*—It has already been shown (Bowen and Bunn, *loc. cit.*) that in alkaline solution no oxidation takes place, proving that the chromate ion is photochemically ineffective, and that in neutral or very faintly acid solutions brown precipitates are deposited which cloud the solution. When the acidity reaches a certain value, no precipitates are formed, except in solutions above 85% of alcohol (see Section 3), and the photochemical rate does not vary with time. Further additions of acid beyond this point increase the quantum efficiency up to a limiting value, as shown in Table III.

The quantum efficiency, calculated from the rate after allowing for the different light absorptions, also varies with the dichromate concentration, as shown in Table IV.

TABLE III.

Dichromate concentration, $0.025N$.

$a=10\%$ (by vol.).			$a=30\%$ (by vol.).			$a=60\%$ (by vol.).		
H_2SO_4 added (N).	γ.	$K\times 10^3$, calc.	H_2SO_4 added (N).	γ.	$K\times 10^3$, calc.	H_2SO_4 added (N).	γ.	$K\times 10^3$, calc.
0	0·0316	8·6	0	0·082	3·9	0	0·172	3·7
0·005	0·109	2·53	0·001	0·175	2·60	0·001	0·361	2·05
0·01	0·123	3·29	0·002	0·234	3·10	0·002	0·526	1·8
0·02	0·132	3·66	0·005	0·310	4·20	0·005	0·655	2·4
0·05	0·160	3·0	0·01	0·413	4·10	0·01	0·725	3·0
			0·02	0·480	2·69	0·02	0·830	2·8
			0·05	0·579	3·10			

TABLE IV.

a.	Cr_2O_7'' (N).	H_2SO_4 (N).	γ.	$K\times 10^3$, calc.	a.	Cr_2O_7'' (N).	H_2SO_4 (N).	γ.	$K\times 10^3$, calc.
10	0·0125	0·005	0·117	2·2	30	0·0125	0·05	0·579	3·5
10	0·03	0·005	0·129	2·1	30	0·03	0·05	0·59	2·2
10	0·1	0·005	0·14	1·88	30	0·05	0·05	0·602	1·5
10	0·0125	0·02	0·117	4·0	60	0·0125	0·001	0·374	2·4
10	0·025	0·02	0·129	4·3	60	0·025	0·001	0·432	2·45
10	0·03	0·02	0·135	4·0	60	0·1	0·001	0·48	2·8
10	0·1	0·02	0·146	2·1	60	0·0125	0·01	0·627	2·77
					60	0·025	0·01	0·725	3·0
					60	0·05	0·01	0·772	2·55

These variations can all be explained on one assumption, *viz.*, that the ion HCr_2O_7' is photochemically effective. A potassium dichromate solution contains the ions HCr_2O_7', Cr_2O_7'', and $HCrO_4'$. The equilibrium constant $K = [H^{\cdot}][Cr_2O_7'']/[HCr_2O_7']$ does not seem to be recorded in the literature. The constant of the equilibrium $[HCrO_4']^2/[Cr_2O_7'']$ has been found by Sherrill (*J. Amer. Chem. Soc.*, 1907, **29**, 1841) to be 0.016 approximately. Viterbi and Krausz (*Gazzetta*, 1927, **57**, 690) have shown that in the visible region the ions HCr_2O_7' and Cr_2O_7'' have the same absorption, and that the ion $HCrO_4'$ absorbs to a much smaller extent. We make the assumption then that the ion HCr_2O_7' only is effective, and that the Cr_2O_7'' ion acts as an " inner filter." In the equilibria

$$HCr_2O_7' \rightleftarrows H^{\cdot} + Cr_2O_7''(+ H_2O) \rightleftarrows 2HCrO_4'$$
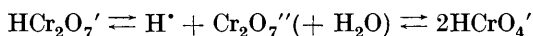
if x/v, $(1 - x - b)/v$, and $2b/v$ are the concentrations of the HCr_2O_7', Cr_2O_7'', and $HCrO_4'$ ions, respectively, then on the above assumption we have $\gamma \propto x/(1 - b)$. Also, applying the mass law, $[H^{\cdot}](1 - x - b)/x = K$ and $4b^2/(1 - x - b)v = 0.016$ (Sherrill, *loc. cit.*). From these relations, if γ is the quantum efficiency at a given acid con-

centration S, and γ_0 is the limiting efficiency at high acid concentrations, then

$$\left(S + \frac{b^2}{0 \cdot 004v^2}\right)\left(\frac{b^2}{0 \cdot 004v - 0 \cdot 004vb - b^2}\right) = K$$

and
$$b = \frac{\gamma - \gamma_0 + [(\gamma - \gamma_0)^2 - 4(\gamma - \gamma_0)\gamma_0/0 \cdot 004v]^{\frac{1}{2}}}{\gamma_0/0 \cdot 002v}$$

Eliminating b, K can be calculated from values of γ, S, and v. The values of K are given in Tables III and IV as " K calc." It will be seen that, considering the large change in K produced by slight errors in measurement, especially in Table IV, and the fact that the value of the constant $[\mathrm{HCrO_4}']^2/[\mathrm{Cr_2O_7}'']$ is not known with accuracy, and has been assumed not to vary in the different alcohol–water mixtures, the values of K obtained are sufficiently constant to justify the original assumption. Incidentally the magnitudes of the hitherto unknown constant K are obtained in the different alcohol–water mixtures.

(5) *Experiments with Glycerol.*—The assumption that the $\mathrm{HCr_2O_7}'$ ion only is photoactive is quantitatively supported by experiments on the oxidation of glycerol by potassium dichromate. Table V shows that the variation of the quantum efficiency of the reaction at various glycerol concentrations with the hydrogen-ion concentration gives a value of K in agreement with that deduced from the experiments with ethyl alcohol. The thermal reaction under the conditions chosen was negligible.

TABLE V.

Dichromate concentration, $0 \cdot 025N$.

$C_3H_8O_3$, % by vol.	H_2SO_4 (N).	γ.	$K \times 10^3$, calc.	$C_3H_8O_3$, % by vol.	H_2SO_4 (N).	γ.	$K \times 10^3$, calc.
10	0	0·029	1·02	40	0·002	0·148	1·44
10	0·01	0·043	5·3	40	0·01	0·204	1·40
10	0·02	0·120	5·0	70	0	0·189	2·25
10	0·04	0·144	2·24	70	0·0004	0·263	1·30
40	0	0·07	2·25	70	0·002	0·320	1·94
40	0·0004	0·126	0·94	70	0·008	0·366	4·00

In these measurements, again, it must be remembered that small changes in the measured quantum efficiencies produce large changes in the value of K.

The variation of the quantum efficiency with glycerol concentration follows quite a different curve from that for ethyl alcohol, as shown :

$C_3H_8O_3$ (% by vol.)	15	30	40	50	60	70	80	90
γ_0		0·21	0·41	0·48	0·52	0·53	0·51	0·53 0·52

At low glycerol concentrations, the quantum efficiency is proportional to the concentration, indicating that only one glycerol molecule co-ordinates with a $\mathrm{HCr_2O_7}'$ ion. At higher concentrations

the quantum efficiency quickly reaches a limiting value of about 0·52, while that for ethyl alcohol approximates to unity. The probable meaning of this is discussed later.

In these preliminary measurements on glycerol it was not possible to determine the exact nature of the oxidation product. Table VI gives the results of measurements on solutions containing an excess of potassium dichromate. The reactions were very slow on account of the low glycerol concentration.

TABLE VI.

Volumes of	$C_3H_8O_3$ (0·25M-sol.).			$K_2Cr_2O_7$ (0·5N).			H_2SO_4 (N).	
Solution A	15 c.c.			25 c.c.			10 c.c.	
Solution B	30 c.c.			50 c.c.			10 c.c.	

Period of exposure (hrs.)	0	15	25	33	55	75	92	100
Relative amounts { Sol. A	0	1·15	3·5	4·8	9·2	10·7	12·0	12·9
of reaction in { Sol. B	0	5·6	9·3	11·25	15·8	16·6	18·3	19·2

An amount of reaction of 7·75 for Solution A and 15·5 for Solution B would correspond to oxidation to the monoaldehyde stage. The curves show that the oxidation approaches the dialdehyde stage. These measurements will be continued.

Summary.

As the result of these measurements on the change of quantum efficiency of this reaction with the variables alcohol, hydrogen-ion, and potassium dichromate concentrations, presence of neutral salts, and temperature, it is possible to arrive at the following conclusions. Of the ions HCr_2O_7', Cr_2O_7'', and $HCrO_4'$ in the solution only the first is photoactive, and then only when it has one or more alcohol molecules attached to it. In strong alcohol solutions the quantum efficiency is approximately unity; in weaker solutions it is diminished owing to the presence of non-alcoholated HCr_2O_7' ions and of Cr_2O_7'' ions, which by absorbing light act as "inner filters." The variation of the quantum efficiency with low alcohol concentration shows that HCr_2O_7' ions combined with one or two alcohol molecules are photoactive; at higher alcohol concentrations presumably photoactive co-ordinated compounds of greater complexity are formed.

The fact that these compounds are photoactive and that stoicheiometrically three alcohol molecules are oxidised for each dichromate ion reduced, necessitates the assumption that intermediate chromium compounds are formed, which react thermally with alcohol molecules to complete the reduction. It is not, of course, possible to do more than to guess at their nature, but the following equation illustrates one possibility :

$$(HCr_2O_7,C_2H_5OH)' + h\nu \longrightarrow CH_3 \cdot CHO + Cr(OH)_3 + \tfrac{1}{2}Cr_2O_8'',$$

followed by the interaction of the chromium hydroxide with hydrogen ions and the non-photochemical oxidation of further alcohol molecules by the perchromate ion.

An approximate value for the second dissociation constant of dichromic acid has been obtained in solutions containing varying amounts of alcohol.

The reaction between glycerol and potassium dichromate has been investigated in a preliminary way, and the results show that the HCr_2O_7' ion with one combined glycerol molecule forms the photo-active substance. The values of the second dissociation constant of dichromic acid deduced from these measurements agree with that found from those with ethyl alcohol.

The fact that the limiting quantum efficiency for ethyl alcohol is about unity while that for glycerol is about 0·5 may throw some light on the mechanism of the reaction discussed above for alcohol. In the possibility suggested, it is only necessary to assume that the Cr_2O_8'' ion is reduced thermally by ethyl alcohol to the chromic stage, while with glycerol it is thermally only reduced to the dichromate stage, to explain quantitatively the difference in the limiting quantum efficiencies. This point can only be elucidated by further work on these lines, which is already in progress.

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