

CCL.—*The Photochemical Oxidation of Alcohols by Potassium Dichromate. Part III.*

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IN earlier papers of this series (Bowen and Bunn, J., 1927, 2353; Bowen and Yarnold, J., 1929, 1648) it has been shown that the quantum efficiency of the photochemical oxidation of alcohols to aldehydes or ketones by solutions of potassium dichromate is independent of the light intensity, temperature, and wave-length between 5000 and 3660 Å. at high hydrogen-ion concentrations, and that it varies with the alcohol, hydrogen-ion, and dichromate concentrations.

This paper describes further work on the effect of hydrogen-ion and dichromate concentration on the photochemical rate. Bowen and Yarnold's measurements were made only at high hydrogen-ion concentrations, obtained by adding sulphuric acid, and their accuracy was affected over part of the range by the precipitation of chromium chromate during the reaction. Their conclusion that no ion other than  $\text{HCr}_2\text{O}_7'$  was photoactive depended also on the use of a constant obtained by Sherrill (*J. Amer. Chem. Soc.*, 1907, **29**, 1641) which now appears to be incorrect. In this work measurements have been made at lower hydrogen-ion concentrations, kept constant by means of buffer solutions, and even down to  $[\text{H}^+] = 10^{-7}$  no difficulties due to precipitate formation occurred in the early stages of the reaction.

## EXPERIMENTAL.

The experimental arrangements were similar to those used by Bowen and Yarnold. A quartz mercury lamp running off the mains, the voltage being kept constant by hand control, served as the light source. Monochromatic light was obtained by using the special glass filters made for isolating the mercury lines by the Corning Glass Company, U.S.A. The photochemical cells were of quartz with plane parallel sides 1 cm. apart, and held about 20 c.c.

The hydrogen-ion concentrations were fixed by means of the standard sodium acetate-acetic acid mixtures of Walpole (J., 1914, 2501) and the potassium dihydrogen phosphate-sodium hydroxide mixtures of Clark and Lubs (*J. Bact.*, 1917, 2, 1, 109, 191). Experiments were made with methyl, ethyl, and *isopropyl* alcohols at different dichromate and alcohol concentrations, in two wave-lengths from the mercury lamp, and between hydrogen-ion concentrations of  $10^{-4}$  to  $10^{-7}$ . The solutions were exposed for a series of different times, the amount of change measured, and the initial rate obtained from the almost linear change-time curves. The thermal reaction between the dichromate and alcohol was in all cases found to be negligible.

Two distinct methods of estimating the amounts of change were employed. Method I, which was applicable to all the alcohols, consisted in measuring the amount of dichromate left by adding the solution to potassium iodide solution and titrating the iodine liberated with sodium thiosulphate. This method was not capable of great accuracy, as the results show. The results depended on the small difference, less than 10%, between the initial and final dichromate concentrations. To effect a rapid reaction between the potassium iodide and the dichromate, acid must be added to produce a high hydrogen-ion concentration, and errors are introduced by the action of air on acid iodide solutions. These difficulties were minimised by careful choice of acidity and time of the iodide dichromate reaction, depending on the alcohol used. The solutions were then diluted to reduce the acidity for the thiosulphate titration.

Method II was a micro-colorimetric method of estimating acetone, based on the formation of a straw-yellow colour with vanillin (Alyea and Bäckström, *J. Amer. Chem. Soc.*, 1929, 51, 90), and was therefore applicable only to experiments with *isopropyl* alcohol. The acetone content of the *isopropyl* alcohol used was first reduced to a very low value by refluxing it with *p*-nitrophenylhydrazine in an atmosphere of nitrogen for six hours, followed by distillation in a current of nitrogen, the treatment being repeated. Measurements

were then carried out as follows. Two reaction mixtures of potassium dichromate and buffer solutions and *isopropyl* alcohol after exposure to the light were treated with barium acetate solution to precipitate the dichromate. Two standard solutions of different acetone concentrations of the same order as the amount of change expected (between 0.0005 and 0.002*M*-acetone) were prepared. 2 C.c. of potassium hydroxide solution (100 g. in 60 c.c. of water) were added to each of the four mixtures, followed, after shaking, by 1 c.c. of vanillin solution (10% in methyl alcohol, freed from acetone as above). The mixtures, contained in test-tubes, were then placed immediately in a thermostat at 65° for exactly 20 mins.; they were then withdrawn, cooled with ice, the precipitates of barium chromate filtered off, sodium carbonate added to precipitate the excess barium ion, and the solutions again filtered. The solutions were then each diluted to 50 c.c. and the colours of the unknowns and standards compared immediately in a Duboscq colorimeter. The results could be duplicated to within 3—5%.

In the case of the faster reactions taking place in light of wavelength 3660 Å., it was found that considerable errors were introduced if the solutions were not stirred; this effect was due to the almost complete absorption of the light in the first thin layer of solution, leading to local exhaustion of hydrogen ion uncorrected by diffusion.

#### *Discussion of Results.*

Bowen and Yarnold accepted the value 0.016 for the equilibrium constant  $[\text{HCrO}_4']^2/[\text{Cr}_2\text{O}_7'']$ , as given by Sherrill (*loc. cit.*), for the interpretation of their results. There is strong evidence, however, for rejecting this value. Sherrill's conclusions were based on calculations from measurements such as the freezing points of solutions uncorrected for the modern conceptions of activity. Viterbi and Krausz (*Gazzetta*, 1927, 57, 690) have shown that solutions of potassium dichromate between *M*/100 and *M*/1,000 approximately obey Beer's law of light absorption over a long range of wavelength. Between these dilutions, therefore, the above equilibrium must lie substantially over to one side—a condition not fulfilled by Sherrill's value of the equilibrium constant. Britton (J., 1924, 125, 1572), from a study of the electrometric titration of chromic acid by alkali, concluded that the ion  $\text{Cr}_2\text{O}_7''$  did not exist in dilute solution, and that the ion in a solution of potassium dichromate was  $\text{HCrO}_4'$ . The value of the equilibrium constant,  $[\text{HCrO}_4']^2/[\text{Cr}_2\text{O}_7''] = 2.5$ , found by Beck and Stegmüller (*Arbeiten Kaiserl. Gesundheit*, 1910, 34, 446) from solubility measurements on lead chromate, satisfies the condition that ordinary dilute solutions of potassium dichromate contain practically only the  $\text{HCrO}_4'$  ion, and

is the only experimental value which fits all the facts. We therefore assume that the values of the extinction coefficients for potassium dichromate solutions given by Viterbi and Krausz refer to the  $\text{HCrO}_4'$  ion, and that those for potassium chromate refer to the  $\text{CrO}_4''$  ion.

When solutions of potassium dichromate are buffered to low hydrogen-ion concentrations, they will contain the  $\text{CrO}_4''$  ion in equilibrium with the  $\text{HCrO}_4'$  ion according to the equation

$$[\text{H}^+][\text{CrO}_4'']/[\text{HCrO}_4'] = K \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Both ions absorb light, and if the  $\text{HCrO}_4'$  ion only is photoactive, the  $\text{CrO}_4''$  ion will act as an inner filter to an extent depending on the extinction coefficients and the concentrations. Since the reaction cells had parallel walls 1 cm. apart, the fraction of the incident light absorbed, scattering losses being neglected, is  $1 - 10^{-e_1c_1 - e_2c_2}$ , where  $e_1$ ,  $e_2$ , and  $c_1$ ,  $c_2$  are respectively the extinction coefficients and concentrations of the ions  $\text{HCrO}_4'$  and  $\text{CrO}_4''$ . The fraction of the light absorbed by the former ion is

$$(1 - 10^{-e_1c_1 - e_2c_2})[e_1c_1/(e_1c_1 + e_2c_2)] \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and this quantity should be proportional to the photochemical rate.

The following tables give the results. Column A gives the experimental photochemical rates, expressed relatively to the values in thick type, each value being the mean of at least three rate curves. Column B gives the values of the expression (2). The extinction coefficients  $e_1$  and  $e_2$  are taken from the results of Viterbi and Krausz (*loc. cit.*) as: at  $\lambda = 3660 \text{ \AA.}$ ,  $e_1 = 1137.5$ ,  $e_2 = 3990$ ; at  $\lambda = 4360 \text{ \AA.}$ ,  $e_1 = 197$ ,  $e_2 = 224$ . The corresponding concentrations  $c_1$  and  $c_2$  of the two ions are calculated from the equation (1) with  $K = 3.9 \times 10^{-7}$ , the actual values recorded for this constant being  $3.7 \times 10^{-7}$  (Beck and Stegmüller, *loc. cit.*),  $4.4 \times 10^{-7}$  (Britton, *loc. cit.*), and  $10^{-7}$  (Hughes, J., 1928, 491).

TABLE I (Method I).

Alcohol.	Conc., % by vol.	[H <sup>+</sup> ].	$\text{K}_2\text{Cr}_2\text{O}_7 = 0.02N.$				$\text{K}_2\text{Cr}_2\text{O}_7 = 0.01N.$				$\text{K}_2\text{Cr}_2\text{O}_7 = 0.005N.$			
			$\lambda = 3660 \text{ \AA.}$		$\lambda = 4360 \text{ \AA.}$		$\lambda = 3660 \text{ \AA.}$		$\lambda = 4360 \text{ \AA.}$		$\lambda = 3660 \text{ \AA.}$		$\lambda = 4360 \text{ \AA.}$	
			A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.
MeOH	40	$10^{-4}$	1.04	1.0	1.19	1.23	1.0	1.0	1.0	1.0	1.03	1.0	0.70	0.68
EtOH	25	$10^{-4}$	1.0	1.0	1.16	1.23	1.0	1.0	1.0	1.0	1.0	1.0	0.75	0.68
PrOH	25	$10^{-4}$	1.0	1.0	1.18	1.23	1.0	1.0	1.0	1.0	1.0	1.0	0.79	0.68
MeOH	40	$10^{-5.6}$	0.77	0.66	1.05	1.13	0.70	0.66	0.84	0.93	0.65	0.66	0.54	0.59
EtOH	25	$10^{-5.6}$	0.65	0.66	1.11	1.13	0.66	0.66	0.91	0.93	0.65	0.66	0.55	0.59
PrOH	25	$10^{-5.6}$	0.67	0.66	1.02	1.13	0.68	0.66	0.81	0.93	0.72	0.66	0.61	0.59
MeOH	40	$10^{-7}$	0.14	0.07	0.35	0.23	0.11	0.07	0.20	0.19	0.09	0.07	0.20	0.14
EtOH	25	$10^{-7}$	0.08	0.07	0.17	0.23	0.07	0.07	0.13	0.19	0.065	0.07	0.09	0.14
PrOH	25	$10^{-7}$	0.13	0.07	0.27	0.23	0.11	0.07	0.18	0.19	0.09	0.07	0.18	0.14

TABLE II (Method II).

$$K_2Cr_2O_7 = 0.02N.$$

[H'].	Pr $\beta$ OH, % by vol.			[H'].	Pr $\beta$ OH, % by vol.		
	5.	25.	B.		5.	25.	B.
$10^{-4}$	1	1	1	$10^{-5.9}$	0.47	0.50	0.495
$10^{-5}$	0.91	0.87	0.90	$10^{-6.4}$	0.20	0.28	0.24
$10^{-5.4}$	0.76	0.77	0.77	$10^{-7}$	—	0.12	0.07

Though the errors of measurement were high, for reasons already explained, the agreement between columns A and B for two wave-lengths and three alcohols is sufficient to show that the simple inner-filter theory is probably correct for hydrogen-ion concentrations between  $10^{-4}$  and  $10^{-7}$ . The further increases of reaction rate at much higher hydrogen-ion concentrations can still be explained by the formation of appreciable amounts of the ion  $HCr_2O_7'$  in that range, although a quantitative treatment cannot at present be given for lack of precise data.

#### Summary.

1. Measurements have been made of the rate of photochemical oxidation of methyl, ethyl, and *isopropyl* alcohols by solutions of potassium dichromate in light of two different wave-lengths and at hydrogen-ion concentrations between  $10^{-4}$  and  $10^{-7}$ .

2. The results in this range can be quantitatively accounted for on the assumption that the photoactive ion is  $HCrO_4'$  and that the  $CrO_4''$  ion also present acts as an inner filter.

3. Bowen and Yarnold's conclusion that the  $HCr_2O_7'$  ion is the only photoactive ion in potassium dichromate solutions is shown to be based on the acceptance of incorrect constants for the equilibria in dichromate solutions, but their results are still qualitatively to be explained by the appearance of the  $HCr_2O_7'$  ion at the higher hydrogen-ion concentrations (*ca.*  $10^{-2}$ ) used by them.

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