291. *The Photochemical Oxidation of Alcohols by Potassium Dichromate. Part IV.*

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In this paper is described an extension of the work (J., 1927, 2353; 1929, 1648; 1931, 1866) on the photochemical oxidation of alcohols by potassium dichromate in aqueous solution. The lower aliphatic alcohols up to butyl, and some other oxidisable substances, have been used, at molar fractions of 0·005—0·5. The hydrogen-ion concentrations of the solutions have been varied from 10^{-5} to 10^{-1}, and the dichromate-ion concentration from *N*/25 to *N*/100.

EXPERIMENTAL.

The photochemical technique and methods of analysis have already been described. The accurate determination of the amount of change after exposure presents great difficulties. The solutions contain relatively a large amount of alcohol, while the dichromate is very dilute in order that measurable fractional changes may be produced by reasonable exposures to light. Measurements must be confined to the early stages of the oxidation to minimise errors due to the inner-filter action of the chromium ion formed. For the same reason the solutions must be kept well stirred. The suitability of colorimetric methods has been investigated. A method involving the colorimetric estimation of acetone for the particular case of the oxidation of *iso*propyl alcohol (J., 1931, 1866) cannot be extended to other alcohols. The colorimetric estimation of the residual dichromate using filtered light of any position in the spectrum is not very accurate owing to the absorption by the chromium ion, while the inverse process of colorimetric estimation of the chromium ion in presence of the dichromate in yellow light, not absorbed by the latter, is complicated by the variable colour of the chromium ion, which first appears in the green form and changes into the violet. Volumetric estimation of the $K_2Cr_2O_7$ in presence of the excess of alcohol leads to "induced oxidation" errors which are very large for ferrous or titanous sulphate titrations. The most satisfactory method of following the change was found to be that used in the earlier work, *viz.*, the estimation of the residual $K_2Cr_2O_7$ by titration of the I liberated by it from KI aq.

Results.—The effect of two variables, the Cr_2O_7'' ion, and the $H^\cdot$ concns. between 10^{-4} and 10^{-1}, had not been satisfactorily examined in the earlier work. In Table I are typical results, obtained by the KI method of estimation, showing the effect of these variables. At concns. below $10^{-3\cdot2}$ the $H^\cdot$ ion was controlled by AcOH–AcONa buffers, and above $10^{-1\cdot5}$ by additions of H_2SO_4. For the intermediate region phthalate buffers were tried : although they were attacked photochemically by the dichromate, they could be used at the higher end of their range ($[H^\cdot] = 10^{-2\cdot5}$) in presence of high alcohol concns. No other sufficiently stable buffer has been found, and until a suitable one is discovered the complete range of $[H^\cdot]$ cannot be covered by measurement. The results of Table I, when plotted, give an **S**-shaped curve, showing that the efficiency at high $[H^\cdot]$ tends to a limit about twice that at $[H^\cdot] = 10^{-4}$.

TABLE I.

$\lambda = 3665$ Å.

(*a*) *Mixtures containing* 50% (*by vol.*) *of methyl alcohol.*

Relative quantum efficiencies.

p_H of mixture	4·05	3·5	2·5	1·5	1·2
γ, obs. at $K_2Cr_2O_7 = N/100$	1·01	1·03	1·27	1·75	1·82
γ, obs. at $K_2Cr_2O_7 = N/50$	0·97	1·03	1·24	1·65	1·77
γ, obs. at $K_2Cr_2O_7 = N/25$	0·96	1·03	1·23	1·72	1·82
γ, calc.	1·01	1·03	1·24	1·75	1·85

(*b*) *Mixtures containing* 15% (*by vol.*) *of ethyl alcohol.*

Dichromate concentration = *N*/25.

Relative quantum efficiencies.

p_H of mixture	4·05	3·2	1·5	1·2
γ, obs.	1·02	1·10	1·64	1·72
γ, calc.	1·01	1·05	1·75	1·85

The results for ethyl and higher alcohols are less accurate than those for MeOH because of the larger corrections necessary for thermal reactions.

In previous work it had been found that the quantum efficiency varied a little with the $K_2Cr_2O_7$ concn. The above and other measurements show that no variation of this kind exists, and the effect has now been traced to inadequate stirring during exposure in the earlier work.

Discussion.

The results of this and of preceding work may now be summarised. The photoactive substance is the $HCrO_4'$ ion, the ionic form of " dichromate " in solution. The quantum efficiency of the oxidation of an acceptor (lower aliphatic alcohol) by this ion is: (1) practically independent of temperature between 0° and 60°; (2) independent of wave-length between $\lambda = 4360$ and 3665 Å.; (3) independent of the dichromate-ion concentration; (4) dependent on the hydrogen-ion concentration independently of the dichromate and acceptor concentration between $[H^{\bullet}] = 10^{-4}$ and 10^{-8} because of the inner-filter action of the CrO_4'' ion on the photoactive $HCrO_4'$ ion (J., 1931, 1866): above about $[H^{\bullet}] = 10^{-4}$, the dichromate solution is practically wholly in the form of the photoactive $HCrO_4'$ ion; the quantum efficiency at higher hydrogen-ion concentrations, however, does not remain constant (Table I), but rises, at first slowly, then more rapidly, and appears to tend to a limit at high hydrogen-ion concentrations (this second effect of the hydrogen ion is discussed below); (5) varies linearly with the acceptor concentration at low values of this (see Table II); (6) at very high acceptor concentrations appears to reach a limit of about $2HCrO_4'$ ions reduced at high hydrogen-ion concentrations, and about 1 at $[H^{\bullet}] = 10^{-4}$, per $h\nu$ absorbed.

These results point to a simple reaction mechanism, the most probable being as follows:

$$HCrO_4' + h\nu \longrightarrow HCrO_4'^{*}$$

$$HCrO_4'^{*} + CH_3{\cdot}OH \longrightarrow CH_2O + OH' + H_2O + CrO_2.$$

In this first stage the sexavalent chromium is reduced to quadrivalent, and one alcohol molecule is oxidised per quantum absorbed. At low hydrogen-ion concentrations the quadrivalent chromium probably reacts with itself to give quinque- and ter-valent chromium, the former thermally oxidising another alcohol molecule and becoming tervalent. The apparent doubling of the quantum efficiency at high hydrogen-ion concentrations was earlier attributed tentatively to the appearance of the dichromate ion HCr_2O_7'; this now seems very unlikely because of the trifling change in the absorption spectrum produced by additions of small amounts of acid to solutions of dichromate (Hantzsch, *Z. physikal. Chem.*, 1910, **72**, 362). Since the limiting efficiency at very high acceptor and hydrogen-ion concentrations appears to be 2 ($HCrO_4'$ ions per $h\nu$), the following additional mechanism suggests itself for acid solutions:

$$H^{\bullet} + Cr^{IV} + Cr^{VI} \longrightarrow 2Cr^{V}$$

followed by thermal oxidation of 2 mols. of acceptor by the quinquevalent chromium. The variation of the efficiency with hydrogen-ion concentration should then be given by the equation

$$\text{efficiency} = (1 + 2k[H^{\cdot}])/(1 + k[H^{\cdot}])$$

it being assumed that the rate of the last reaction is proportional to the concentrations $[H^{\cdot}]$ and $[Cr^{IV}]$. The line "γ, calc." in Table I is obtained with a value of $k = 100$, and the results are probably in agreement with those measured within the experimental error.

Experiments at Low Acceptor Concentrations.—Since in a simple photoreaction the number of molecules activated per sec. can be found much more precisely than in a thermal reaction, it was hoped that a study of the rates of the photoreaction at low concentrations of different acceptors would throw light on the question of collisional rates in liquids (see Moelwyn Hughes, this vol., p. 95; *Chem. Rev.*, 1932, **10**, 241). Unfortunately, the results do not seem to lend themselves for this purpose: those for a number of acceptors are given in Table II, in which n represents the molar fraction of acceptor, γ the quantum efficiency ($HCrO_4'$ ions per $h\nu$), and r is explained below.

TABLE II.

$\lambda = 3665$ Å.

Dichromate concn. $N/50$; $[H^{\cdot}]$ buffered at 10^{-4}.

Acceptor.	n.	γ.	γ/n, mean.	r.	Acceptor.	n.	γ.	γ/n, mean.	r.
MeOH	0·0136	0·0096	0·71	8·5	Pr$^{\beta}$OH	0·0073	0·018	2·6	9·1
	0·0224	0·016				0·0123	0·033		
CH_2O	0·0137	0·011	0·70	9·0	n-BuOH	0·0061	0·028	4·5	9·1
	0·0276	0·019				0·0103	0·047		
EtOH	0·0088	0·020			*iso*-BuOH	0·0060	0·025	4·2	9·2
	0·0154	0·034	2·3	9·0		0·0101	0·043		
	0·0312	0·070			$C_3H_7\cdot CHO$	0·0063	0·029	4·5	
$CH_3\cdot CHO$	0·0098	0·022	2·2	9·0	Glycol	0·0098	0·028	2·9	8·0
	0·0168	0·037				0·0168	0·048		
Pr$^{\alpha}$OH	0·0074	0·021	2·6	9·0	Glycerol	0·0076	0·036	4·9	7·9
	0·0125	0·034				0·0128	0·063		
					Glucose	0·0012	0·0146		
						0·0023	0·031	12·9	
						0·0046	0·061		

The mechanism by which the $HCrO_4'$ ion becomes reactive may be one of the following four possibilities:

$$(1)\quad HCrO_4' + h\nu \rightleftharpoons HCrO_3' + O \begin{array}{l} \nearrow + CH_3\cdot OH \longrightarrow CH_2O \\ \searrow \quad + \; ? \qquad \longrightarrow O_2 \end{array}$$

$$(2)\quad HCrO_4' + h\nu \longrightarrow HCrO_4'^{*} \begin{array}{l} \nearrow + CH_3\cdot OH \longrightarrow CH_2O \\ \searrow + H_2O \quad \longrightarrow \text{deactivation.} \end{array}$$

(*a*) every collision with an alcohol or a water molecule leading to reaction or deactivation, respectively; (*b*) certain favourable collisions only leading to reaction or deactivation :

(3) $(HCrO_4{}')(CH_3{\cdot}OH) + h\nu \longrightarrow$ reaction
$(HCrO_4{}')(H_2O) + h\nu \longrightarrow$ deactivation.

Possibility (1) was tested by focusing sunlight reflected from a 24-inch searchlight mirror on about 1 c.c. of a dilute solution of potassium dichromate in water. The solution was raised to the b. p. almost immediately by the condensed radiation, so no dissolved oxygen could remain to reverse a possible dissociation, but no change of colour or deposition of a precipitate could be observed.

The mechanism (2*a*) is the simplest, and accounts for the remarkable equality between the quantum efficiencies of the alcohols and those of the corresponding aldehydes. It is not, however, in accordance with recent work (Moelwyn Hughes, *loc. cit.*), which shows that collisional rates in liquids can be calculated with considerable accuracy from the ordinary collisional rate equation for gases. In col. 5 of Table II, r gives the relative collisional frequencies between the dichromate ion and acceptor molecules at equal molar fractions, calculated from the gas collisional equation. The figures, which would be altered only slightly by inaccuracy in the values taken for the molecular diameters, show that the collisional rates are almost equal, while the quantum efficiencies of the reactions with different acceptors at equal molar fractions vary from 0·7 to 12·9. The approximate accuracy of col. 5 being accepted, it seems necessary to assume that the photoreaction is of type (2*b*), in which specific fractions only of the collisions are effective, or of type (3), where reaction or non-reaction of an activated $HCrO_4{}'$ ion depends on whether it is " alcoholated " or " hydrated." The equality of the efficiencies of corresponding alcohols and aldehydes on either of these views must be regarded as fortuitous. At present a decision cannot be made between the possibilities discussed, but it is noteworthy that the photochemical efficiencies of the oxidation of the alcohols by dichromate lie in the same order as their thermal rates. It seems likely, then, that a complete study of the kinetics of the thermal reactions at different temperatures would throw further light on the oxidation mechanism.

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