The Photoinduced Oxidation of 2-Propanol by Acid Chromate

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The quantum yield of the photoinduced oxidation of 2-propanol by acid chromate depends on the concentration of 2-propanol, the acidity, the intensity and wave length of light and the concentration of acid chromate. At low intensity of light and high acidities the quantum yield approaches a value twice that obtained at high intensities of light and low acidities. The experimental results fit a mechanism in which chromium compounds in the oxidation states +6, +5, +4, +3 and +2 are involved. The photochemically active compound is shown to be an ester of acid chromate with 2-propanol. Furthermore the influence of the solvent on the quantum yield is discussed.

In slightly acid aqueous solutions the oxidation of aliphatic alcohols by chromic acid proceeds at negligible rate. When irradiated by ultraviolet light the oxidation takes place. Bowen *et al.*¹ have investigated these photoinduced oxidations. Their results may be summarized as follows. With the alcohols in excess the reactions are stoichiometrically pure. The quantum yields are small, not exceeding two in the pure alcohol. The oxidation therefore does not seem to be a chain process. Further Bowen and Chatwin¹ have shown, that of the two ions present in a dilute aqueous solution, HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$, only HCrO_4^- is photochemically active. Comparisons between the quantum yields obtained by oxidation of different alcohols, led to the conclusion, that only "alcoholated" forms of the acid chromate ions are photochemically active. From the relationship between quantum yield and acidity Bowen and Chatwin proposed the mechanism:

where X stands for an alcohol and Cr^{VI} , Cr^{V} , Cr^{IV} and Cr^{III} represent chromium compounds in the oxidation states +6, +5, +4 and +3, respectively. Preliminary experiments made by the present author have shown that oxygen interferes with the photoinduced oxidation of 2-propanol by acid chromate. As Bowen and Chatwin have not taken the precaution to remove oxygen a reinvestigation has been undertaken.

Westheimer *et al.*^{2,3} have investigated the kinetics of the oxidation of 2-propanol to acetone by acid chromate ions in aqueous solution, and have shown that the reaction proceeds by the way of the chromic acid ester, $(\text{CH}_3)_2\text{CHOCrO}_3\text{H}$.

The photochemical experiments reported here were made at low acidities ($< 2 \times 10^{-2} \text{ M}$), at which the dark process proceeds at negligible rate. It may therefore be concluded that at low acidities the above mentioned ester is completely ionized to $(\text{CH}_3)_2\text{CHOCrO}_3^-$, the stability constant and spectrum of which have been determined by the present author^{4,5} (in Ref.⁴ no assumption concerning the nature of the complex of 2-propanol with acid chromate has been made and the formula has been written $\text{CH}_3\text{CHOHCH}_3 \cdot \text{HCrO}_4^-$). Our experiments show that the ester $(\text{CH}_3)_2\text{CHOCrO}_3^-$ is the only photochemically active ion as suggested by Bowen and Chatwin, but it has not proved possible to verify the mechanism proposed by these authors. The experimental data agreed with the following mechanism:

- a) $\text{CH}_3\text{CHOHCH}_3 + \text{HCrO}_4^- = (\text{CH}_3)_2\text{CHOCrO}_3^- + \text{H}_2\text{O}$ equil.const.⁵ $K = 8.3$
- b) $(\text{CH}_3)_2\text{CHOCrO}_3^- + h\nu \rightarrow (\text{CH}_3)_2\text{CHOCrO}_3^{*-}$ absorption
- c) $(\text{CH}_3)_2\text{CHOCrO}_3^{*-} + \text{solvent} \rightarrow (\text{CH}_3)_2\text{CHOCrO}_3^-$ deactivation
- d) $(\text{CH}_3)_2\text{CHOCrO}_3^- \rightarrow \text{Cr}^{\text{IV}} + \text{CH}_3\text{COCH}_3$
- 1) $\text{CH}_3\text{CHOHCH}_3 + \text{Cr}^{\text{IV}} \rightarrow \text{CH}_3\text{COCH}_3 + \text{Cr}^{\text{II}}$ k_1
- 2) $\text{Cr}^{\text{II}} + \text{Cr}^{\text{IV}} \rightarrow 2\text{Cr}^{\text{III}}$ k_2
- 3) $\text{HCrO}_4^- + \text{H}^+ = \text{H}_2\text{CrO}_4$ equil.const. K_3
- 4) $\text{Cr}^{\text{II}} + \text{H}_2\text{CrO}_4 \rightarrow \text{Cr}^{\text{V}} + \text{Cr}^{\text{III}}$ k_4
- 5) $(\text{CH}_3)_2\text{CHOCrO}_3^- + \text{H}^+ = (\text{CH}_3)_2\text{CHOCrO}_3\text{H}$ equil.const. K_5
- 6) $\left\{ \begin{array}{l} \text{Cr}^{\text{II}} + (\text{CH}_3)_2\text{CHOCrO}_3\text{H} \rightarrow \text{Cr}^{\text{V}} + \text{Cr}^{\text{III}} + \text{CH}_3\text{CHOHCH}_3 \\ \text{Cr}^{\text{II}} + (\text{CH}_3)_2\text{CHOCrO}_3\text{H} \rightarrow 2\text{Cr}^{\text{III}} + \text{CH}_3\text{COCH}_3 \end{array} \right\} k_6$
- 7) $\text{Cr}^{\text{V}} + \text{CH}_3\text{CHOHCH}_3 \rightarrow \text{Cr}^{\text{III}} + \text{CH}_3\text{COCH}_3$.

In all experiments the total concentration of chromic acid was kept small enough to permit the neglect of the concentration of dichromate, and so small that stirring secured a uniform concentration of intermediates throughout the irradiated solutions. Denoting the quantum yield for formation of Cr^{IV} by Φ° we may therefore derive the following expression for the total quantum yield Φ , assuming a steady state concentration of the intermediates:

$$\Phi = \frac{1}{I_0} \left(-\frac{dc_1}{dt} \right) = \Phi^\circ - \left(\frac{1}{2}\Phi^\circ + c_a \cdot c_1 \cdot c_{H^+} \cdot \frac{1}{I_0} \cdot \frac{k_1 k^*}{2k_2} \right) \quad (8)$$

$$+ \left(\frac{1}{2}\Phi^\circ + c_a \cdot c_1 \cdot c_{H^+} \cdot \frac{1}{I_0} \cdot \frac{k_1 k^*}{2k_2} \right) \left[1 + \frac{c_a \cdot \Phi^\circ \cdot c_1 \cdot c_{H^+} \cdot \frac{1}{I_0} \cdot \frac{k_1 k^*}{k_2}}{\left(\frac{1}{2}\Phi^\circ + \frac{k_1 k^*}{2k_2} \cdot c_a \cdot c_1 \cdot c_{H^+} \cdot \frac{1}{I_0} \right)^2} \right]^{\frac{1}{2}}$$

where c_a and c_1 are the alcohol concentration and the total concentration of acid chromate. I_0 is the intensity of the absorbed light. k^* is given by

$$k^* = K_3 k_4 + \frac{(K_5 k_6 - K_3 k_4) K \cdot c_a}{c_w + K \cdot c_a} \quad (9)$$

where c_w is the concentration of water.

The equation (8) gives that $\Phi^\circ < \Phi < 2\Phi^\circ$, and we note that Φ approaches $2\Phi^\circ$ at high values of $c_{H^+} \cdot c_a \cdot c_1 / I_0$.

At 25°C Φ was measured at 366 m μ and at various light intensities, acidities, and alcohol concentrations. From (8), written in the form

$$\frac{k_1 k^*}{k_2} = \frac{\Phi^2 - \Phi \cdot \Phi^\circ}{(2\Phi^\circ - \Phi) \cdot c_1 \cdot c_{H^+} \cdot c_a \cdot \frac{1}{I_0}} \quad (10)$$

$k_1 k^* / k_2$ and Φ° were found by trial and error at each alcohol concentration. Tables 1, 2, and 3 show the measurements at $c_a = 1$ M, 2 M, and 3 M. The accuracy of the determination of $k_1 k^* / k_2$ is low as a change of 25 % in $c_{H^+} \cdot c_a \cdot c_1 / I_0$ give a change of not more than 4–5 % in Φ , which is the experimental error in determining Φ . The reaction, therefore, was followed to a degree of advancement of 0.3, and the values of I_0 , c_{H^+} , c_1 , and c_a used in formula (10) to calculate Φ° and $k_1 k^* / k_2$ are the values at a degree of advancement of 0.15. From the three values of $k_1 k^* / k_2$ found at $c_a = 1$ M, 2 M, and 3 M $K_3 k_4 k_1 / k_2$ and $K_5 k_6 k_1 / k_2$ were found to be 13 litre²/mole² · min and 55 litre²/mole² · min, respectively (Fig. 1).

Fig. 1. $k_1 k^* / k_2 = K_3 k_4 k_1 / k_2 + (K_5 k_6 k_1 / k_2 - K_3 k_4 k_1 / k_2) K \cdot c_a / c_w + K \cdot c_a$ (eqn. 9) plotted against the relative concentration of the complex: $c_K / c_1 = K \cdot c_a / c_w + K \cdot c_a$.

Table 1. Measured and calculated values of Φ_{366} .

$$\left(\frac{k^*k_1}{k_2}\right)_{\text{mean}} = 18.8 \frac{(\text{litre})^2}{(\text{mole})^2 \text{ min.}}, c_a = 1.00 \text{ M}, c_1 = 4.25 \times 10^{-5} \text{ M}, I_0 = 1.23 \times 10^{-5} \frac{\text{mole}}{\text{litre. min.}}, \Phi^\circ = 0.0385 \frac{\text{Einstein}}{\text{mole}}$$

c_{H^+} mole litre	$\frac{k^*k_1}{k_2}$ (litre) ² (mole) ² min.	Φ found mole Einstein.	Φ calc. mole Einstein
3.15×10^{-4}	16.6	0.0480	0.0497
6.6×10^{-4}	22.0	0.0567	0.0553
1.35×10^{-3}	16.3	0.0600	0.0612
3.42×10^{-3}	21.9	0.0689	0.0679
6.9×10^{-3}	17.6	0.0714	0.0715
1.38×10^{-2}	—	0.0751	0.0741

Tables 1, 2, and 3 show that k_1k^*/k_2 at constant concentration of alcohol does not vary systematically with acidity and with light intensity, thus indicating the correctness of the proposed mechanism. The variation of k_1k^*/k_2 with the alcohol concentration is interpreted as being due to the reactions 5) and 6). Introduction of 5) and 6) in the reaction scheme is very natural, remembering that the concentration of the ester is rather high (at $c_a = 3 \text{ M}$ equal to 36 % of total concentration of acid chromate). The two equilibria 3) and 5) have been introduced as the oxidation agent in acid solution in the dark process seems to be the undissociated chromic acid ⁶. The rates of 4) and 6) are proportional to c_{H^+} as both the acid chromate ion and the ester are very weak bases ^{4, 7}.

Table 2. Measured and calculated values of Φ_{366} .

$$\left(\frac{k^*k_1}{k_2}\right)_{\text{mean}} = 23.5 \frac{(\text{litre})^2}{(\text{mole})^2 \text{ min.}}, c_a = 2.00 \text{ M}, c_1 = 4.25 \times 10^{-5} \text{ M}, \Phi^\circ = 0.106 \frac{\text{Einstein}}{\text{mole}}, I_0 = 1.25 \times 10^{-5} \frac{\text{Einstein}}{\text{litre. min.}}$$

c_{H^+} mole litre	$\frac{k^*k_1}{k_2}$ (litre) ² (mole) ² min.	Φ found mole Einstein	Φ calc. mole Einstein
3.15×10^{-4}	23.7	0.135	0.134
6.6×10^{-4}	21.7	0.148	0.149
1.35×10^{-3}	24.2	0.166	0.165
3.42×10^{-3}	23.8	0.185	0.185
6.9×10^{-3}	24.0	0.196	0.195
1.38×10^{-2}	—	0.206	0.203

Table 3. Measured and calculated values of Φ_{366} .

$$\left(\frac{k_1 k^*}{k_2}\right) \text{ mean} = 28.5 \frac{(\text{litre})^2}{(\text{mole})^2 \text{ min.}}, \quad c_a = 3.00 \text{ M}, \quad c_1 = 4.25 \times 10^{-5} \text{ M}, \quad \Phi^\circ = 0.207$$

mole
Einstein

I_0 Einstein litre min.	c_{H^+} mole litre	$\frac{k^* k_1}{k_2}$ (litre) ² (mole) ² min.	Φ found mole Einstein	Φ calc. mole Einstein
1.29×10^{-5}	1.08×10^{-4}	29.2	0.232	0.231
1.29×10^{-5}	6.6×10^{-4}	26.5	0.285	0.288
1.29×10^{-5}	2.04×10^{-3}	28.3	0.337	0.337
1.29×10^{-5}	3.42×10^{-3}	27.1	0.356	0.358
1.29×10^{-5}	6.9×10^{-3}	30.6	0.382	0.380
1.29×10^{-5}	1.38×10^{-2}	—	0.388	0.394
4.38×10^{-6}	1.08×10^{-4}	22.7	0.253	0.260
2.37×10^{-6}	1.08×10^{-4}	33.9	0.290	0.284
5.25×10^{-7}	1.08×10^{-4}	27.0	0.346	0.349
* 1.96×10^{-7}	1.26×10^{-4}	31.2	0.389	0.388

* $c_1 = 4.70 \times 10^{-5} \text{ M}$.

The fraction of the absorbed light I_0 , which is absorbed by the ester is

$$\varphi = \frac{\varepsilon_k \cdot c_a \cdot K}{\varepsilon_k \cdot c_a \cdot K + \varepsilon_1 \cdot c_w} \quad (11)$$

where ε_k and ε_1 are the extinction coefficients of the ester and of the acid chromate ion, respectively. If the ester is the only photochemically active component we may expect that the following relation for the ratio between $\Phi^\circ(\lambda_1)$ and $\Phi^\circ(\lambda_2)$ at the two wave lengths λ_1 and λ_2 will be valid at constant alcohol concentration:

Table 4. Values of $\Phi^\circ(\lambda)$ and $\varphi(\lambda)$ at the wave lengths 313 m μ , 334 m μ , and 366 m μ .

λ m μ	c_a mole litre	I_0 Einstein litre.min	c_{H^+} mole litre	Φ mole Einstein	Φ° mole Einstein	φ
313	2.00	2.06×10^{-6}	3.42×10^{-3}	0.175	0.080	0.323
	3.00	2.06×10^{-6}	3.42×10^{-3}	0.337	0.175	0.438
334	2.00	2.19×10^{-6}	1.42×10^{-3}	0.145	0.076	0.249
	3.00	2.19×10^{-6}	1.35×10^{-3}	0.276	0.145	0.352
366	2.00	1.27×10^{-5}	6.9×10^{-3}	0.195	0.106	0.368
	3.00	1.29×10^{-5}	6.9×10^{-3}	0.380	0.207	0.490

Table 5. φ_{366} and Φ°_{366} at varying concentration c_a of 2-propanol, $c_1 = 4.25 \times 10^{-5}$ M, $c_{H^+} = 6.9 \times 10^{-3}$ M.

$\frac{c_a}{\text{mole}} \frac{\text{litre}}{\text{litre}}$	$\frac{I_0}{\text{Einstein}} \frac{\text{litre}}{\text{litre} \cdot \text{min}}$	φ_{366}	$\frac{\Phi_{366}}{\text{mole}} \frac{\text{Einstein}}{\text{Einstein}}$	$\frac{\Phi^{\circ}_{366}}{\text{mole}} \frac{\text{Einstein}}{\text{Einstein}}$
0.25	1.19×10^{-5}	0.060	0.0123	0.0065
0.50	1.20×10^{-5}	0.116	0.0311	0.0167
1.00	1.22×10^{-5}	0.214	0.0715	0.0385
1.50	1.245×10^{-5}	0.298	0.135	0.073
2.00	1.27×10^{-5}	0.368	0.195	0.106
2.50	1.285×10^{-5}	0.434	0.282	0.153
3.00	1.29×10^{-5}	0.490	0.380	0.207

$$\frac{\Phi^{\circ}(\lambda_1)}{\Phi^{\circ}(\lambda_2)} = \frac{\varphi(\lambda_1)}{\varphi(\lambda_2)} \quad (12)$$

$\varphi(\lambda)$ may be calculated as K and the absorption spectra of the ester and of the acid chromate ion are known⁵. Table 4 shows φ_{313} , φ_{334} , φ_{366} , Φ°_{313} , Φ°_{334} , and Φ°_{366} at the alcohol concentrations 2 M and 3 M. It may be noted that the agreement between $\frac{\varphi(\lambda_1)}{\varphi(\lambda_2)}$ and $\frac{\Phi^{\circ}(\lambda_1)}{\Phi^{\circ}(\lambda_2)}$ is rather good, proving that the ester is the only photochemically active ion in the solutions.

Table 5 shows Φ°_{366} at various concentrations. It may be noted that Φ°_{366} is not directly proportional to φ_{366} , but $\Phi^{\circ}_{366}/\varphi_{366}$ increases linear with the alcohol concentration indicating that the probability for the excited ester to decompose to Cr^{IV} and acetone increases if one of the nearest neighbours to the excited ester is an alcohol molecule (Fig. 2). To get a complete picture

Fig. 2. $\Phi^{\circ}_{366}/\varphi_{366}$ plotted against c_a .

of the mechanism of deactivation the photoinduced oxidation of several alcohols would have to be investigated in a larger concentration interval.

EXPERIMENTAL

The light source was a mercury lamp (Osram HQA 1000, the outer bulb removed, operated on d-c with an adjustable ballast resistance). The light was made parallel with quartz lenses. The optical path of the quartz cell was 10 cm. The cell was furnished with a magnetic stirrer and was immersed in a 25°C thermostated water bath provided with windows of Uviol glass. The solutions to be irradiated were freed from oxygen by the bubbling through of nitrogen, deoxygenated over copper wire at 500°C. The light intensity was determined by means of the uranyl oxalate actinometer⁸. The actinometer solution was irradiated in the same cell as used in all experiments. The mercury lines 365–366 m μ , 334 m μ , and 312.6–313 m μ were isolated by means of filters described by Kasha⁹. The reaction was followed by measuring the change in optical density by means of a Baldwin Photometer M.N.D. The water was redistilled in Pyrex from alkaline permanganate, 2-propanol (Shell chemically pure) was distilled in a Glinzky still (b.p. 780 mm Hg 81.5–81.7°C (uncorr)) and controlled for acetone content by measuring the optical density at 280 m μ . Perchloric acid and potassium dichromate were Mercks pro analysi.

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