Photoinduced Oxidation of Isopropanol by Acid Chromate Studied by Flash Photolysis

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In aqueous solutions at low acidity the oxidation of isopropanol by acid chromate is a very slow process. The reaction is accelerated when the solution is irradiated with ultraviolet light¹. A kinetic study of the photochemically induced oxidation led to the conclusion that the primary process is the decomposition of monoisopropyl chromate to give Cr^{IV} and acetone^{1,2}. Further it was found that a reaction sequence which included the step

satisfactorily explained the kinetic data³. However it has now been proved that Cr^{IV} does not react directly with the alcohol^{3,4}. An alternative mechanism which fits the results so far obtained⁵ is

In search for the correct mechanism it is feasible to attempt the direct observation of the chromium intermediates by the flash photolysis technique⁶. Some preliminary experiments making use of this technique are reported here. Deaerated solutions, containing 2.5–10 M isopropanol, 5×10^{-4} – 3×10^{-3} M perchloric acid, and 5×10^{-4} – 2×10^{-3} acid chromate in a 50 ml pyrex cell, 20 cm long, were illuminated in a flash photolysis apparatus similar to those described by Porter and Windsor⁶, and Christie, Norrish and Porter⁷. Photographs of the spectrum of the reaction mixtures taken 30 μsec and 200 μsec after an 1150 Joule photolysis flash revealed a transient absorption extending from 650 $\mu\mu$ (the limit of the photographic plate) towards green and a transient decrease of the Cr^{VI} absorption band in the near ultraviolet. The change of the transient absorption in time was followed photoelectrically⁷ at 590 $\mu\mu$ after irradiation with an 810 Joule flash. Three steps in the

Fig. 1. Experimental decay curve for the third step. ($\text{CHClO}_4 = 3 \times 10^{-3}$ M, $\text{CHCrO}_4^- = 10^{-3}$ M, Calc. = 10 M).

reaction could be detected, a fast increase of the optical density completed in about 200 μsec , a fast decrease of the optical density with a halftime of about 600 μsec at $\text{CHCrO}_4^- = 10^{-3}$ M, $\text{CHClO}_4 = 10^{-3}$ M, and Calcohol = 10 M, and finally a third slow step consisting of a further decrease in optical density, the rate of which seems to be of second order independent of conditions. In the presence of 10^{-3} M manganous sulfate in the solution the third slow step disappeared and a brownish colour developed after the flash indicating a formation of MnO_2 . Figs. 1 and 2 show photographs of oscillographic recordings of the transient events. The lines A and B designate 0 % and 100 % light absorption, respectively. C is the decay curve for the intermediates and the straight line D is the absorption to infinite time giving the amount of Cr^{III} formed. In experiments as shown in Fig. 2 the sweep rate on the oscilloscope screen decreased exponentially over the sweep range with a halftime of 6.3×10^{-2} sec. The second fast step appears in these measurements as a hook on the decay curve (Fig. 2). Only two measurements were

Fig. 2. Experimental decay curve. The sweep rate decreases exponentially over the sweep range, halftime for the sweep is 6.3×10^{-2} sec. ($\text{CHClO}_4 = 3 \times 10^{-3}$ M, $\text{CHCrO}_4^- = 10^{-3}$ M, Calc. = 10 M)

Table 1. Results (Temp. 22°C ± 2°C).

$C_{\text{alc.}}$ mole/litre	C_{HClO_4} mole/litre	$C_{\text{HCrO}_4^-}$ mole/litre	D_0	D_∞	$\Delta D/D_0 - D_\infty$	$10^4 \times C_{\text{Cr}^{III}}$ mole/litre	$k/\Delta\epsilon$ sec ⁻¹
2.5	10 ⁻³	10 ⁻³	0.1	0.03	0.7	0.3	—
5	10 ⁻³	10 ⁻³	0.34	0.10	0.62	1.0	1 800
10	5 × 10 ⁻⁴	5 × 10 ⁻⁴	0.54	0.17	0.32	1.8	2 000
10	10 ⁻³	5 × 10 ⁻⁴	—	—	—	—	1 800
10	3 × 10 ⁻³	5 × 10 ⁻⁴	0.39	0.12	0.37	1.3	2 300
10	10 ⁻³	10 ⁻³	0.75	0.25	0.37	2.7	2 000
10	3 × 10 ⁻³	10 ⁻³	0.58	0.19	0.46	2.0	1 700
10	10 ⁻³	2 × 10 ⁻³	0.81	0.28	0.28	3.0	2 000
10	3 × 10 ⁻³	2 × 10 ⁻³	0.62	0.22	0.45	2.3	2 000
10*	10 ⁻³	10 ⁻³	0.74	—	—	—	—

* $C_{\text{MnSO}_4} = 10^{-3}$ M.

made with a halftime of 5×10^{-4} sec for the sweep, revealing the two first fast steps. The findings are compiled in Table 1. D_0 is the maximum transient optical density taken from the experiments where the sweep rate decreased exponentially. D_∞ is the optical density after infinite time. In the expression for the relative extent of step two $\Delta D/D_0 - D_\infty$, ΔD is somewhat arbitrarily taken as the change of the optical density in 2×10^{-3} sec (Fig. 2). The concentration of Cr^{III} formed on photolysis was calculated using 47 litre/mole cm for the molar extinction coefficient of Cr^{III}, a value found by reducing thermally 5×10^{-4} M acid chromate in an aqueous solution, 10 M in isopropanol and 3×10^{-3} M in

perchloric acid. The last column shows second order rate constants k for the third step divided by the difference in the extinction coefficients $\Delta\epsilon$ between the intermediate in question and Cr^{III}; $k/\Delta\epsilon$ is calculated from experiments with constant sweep rates (Fig. 1). Fig. 3 shows a second order plot for the third slow process. From Table 1 one may note that D_0/D_∞ does not vary appreciably with conditions, whereas $\Delta D/D_0 - D_\infty$ varies somewhat with conditions. This indicates that reactions by which chromium intermediates disappear by disproportionation are faster than is the oxidation of the alcohol by the intermediates. Further it seems that the relative extent of the second step $\Delta D/D_0 - D_\infty$ increases with increasing acidity.

Although the data are not sufficient to establish the mechanism we may tentatively ascribe the first step to be the breakdown of excited Cr^{VI} esters to give Cr^{IV} and acetone. In presence of Mn^{II} the next step is probably*

The variation of the extent of the second fast step with conditions suggests reactions like

the third slow step could then be the reverse reaction of 7)

The experimental work was made at the Department of Physical Chemistry, University

Fig. 3. The experimental decay curve in Fig. 1 as a second order decay.

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Note on the Infrared Spectra of Pro- γ -carotene and Neo- γ -carotene P

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These two *cis* isomers of γ -carotene are natural products and can be isolated easily from ripe berries of *Pyraeantha angustifolia*^{1,2}. In the visible spectral region, hexane solutions of pro- γ -carotene show two almost equal maxima (434, 457 m μ) while the neo- γ -carotene curve contains only a single main maximum (459 m μ)^{3,4}. In spite of this difference a comparison of the infrared spectra showed near-identity⁴.

Although, as was pointed out⁴, several pairs of *cis* forms are possible in this sterically unsymmetrical set whose IR spectra are expected to be (almost) identical, an experimental error such as mislabeling of samples could not be excluded considering the great number of stereoisomeric carotenoids studied.

At the recommendation of Prof. L. Zechmeister, the author has now reinvesti-

Fig. 1. Infrared spectra of: —, neo- γ -carotene P and - - -, pro- γ -carotene (1 % solutions in carbon disulfide, 1.0 mm cells).

gated the IR spectra using solutions of authentic samples of pro- γ -carotene (m. p. 133–134°) and neo- γ -carotene P (m. p. 89–90°). The identity of the two curves was confirmed in the 2–12 μ region; an important difference was observed, however, in the 12–14 μ region. As Fig. 1 shows, only the neo P curve possesses a band at 13.02–13.19 μ (doublet). This band lies in the region that has been assigned to unmethylated *cis* double bonds⁴. Consequently, our earlier interpretations must be revised. It is proposed that the neo- γ -carotene P molecule contains both methylated and unmethylated *cis* double bond(s) while the latter type is absent from pro- γ -carotene. This difference has a profound influence on the spectra observed in the visible region.

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