204. *Unstable Intermediates. Part IX.* Photolysis of Oxyanions and their Esters in Glasses.*

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Although chromate and acid chromate ions are not decomposed when rigid solutions in a variety of solvents at 77° K are exposed to light of λ 3650 or 2537 Å, solutions prepared from acid chromate and propan-2-ol, containing mainly the chromate ester, readily decompose to acetone and quadrivalent chromium. On softening, the blue Cr^{IV} compound decomposes slowly at $-120°$ to give Cr^{VI} and Cr^{III}. The visible and ultraviolet absorption spectrum of the blue compound is given. No electron-spin resonance absorption could be detected with the photolysed glasses.

Similarly, glasses containing periodate or periodic acid were unaffected, except in alcoholic solvents. Changes in the ultraviolet spectrum of periodate in anhydrous propan-2-ol are tentatively ascribed to the formation of periodate esters. After prolonged irradiation, periodate in alcoholic glasses is almost completely converted into iodide.

The efficiency and overall mechanism of photolysis may be very different in fluid and rigid media.[1] In rigid media chain processes are no longer possible, and a reaction depending on considerable movement of a reactive species is prohibited unless small particles such as hydrogen or oxygen atoms are involved. Hence, reactive entities, not detectable in fluid solutions, are often formed in relatively high concentration and retained until the glass becomes fluid.

Fig. 1.

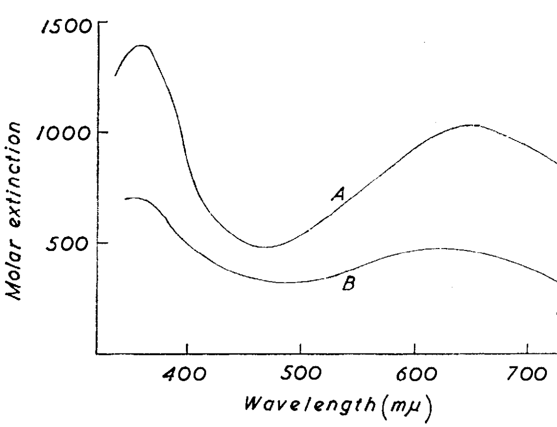

Fig. 2.

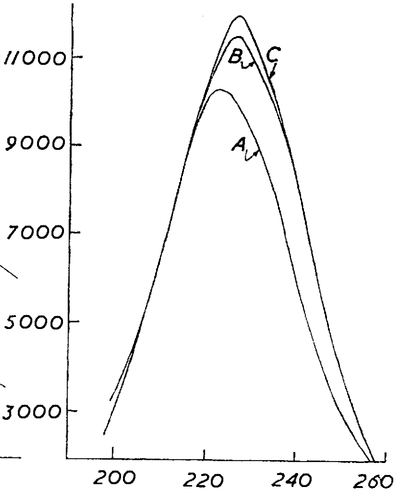

Fig. 1. *Ultraviolet and visible spectra of the blue intermediate formed by photolysis of isopropyl chromate with light of* λ 3650 Å. *A at* $-120°$, *B at* $-160°$.

Fig. 2. *Ultraviolet spectra of periodate. A in water, B in* Pr^iOH *after* 5 *min., C in* Pr^iOH *after* 30 *min.*

Such intermediates can be studied spectrophotometrically and magnetically in the glass, but later stoicheiometric analysis of the final products at room temperature may

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* Part VIII, *J.*, 1959, 2478.

[1] Symons and Townsend, *J.*, 1959, 263.

also give information about them.[2,3] Hence it has been shown that, although rigid solutions of permanganate are readily decomposed on photolysis, neither chromate nor acid chromate is decomposed by light of λ 3650 or 2537 Å in a variety of rigid glasses.[3] This contrasts with the behaviour of certain chromate esters which decompose readily[2] in rigid alcohols.

These results, which are relevant to an understanding of the mechanism of light-induced decomposition in fluid solutions,[4] are now reported in detail; the visible and ultraviolet spectrum of a blue chromium species, thought to be Cr^{IV}, is recorded in Fig. 1.

Solutions of periodate at room temperature readily give iodate and oxygen on irradiation with ultraviolet light.[5] It has been suggested that a free-radical chain mechanism may be important,[6] but quantitative studies of aqueous solutions showed that the quantum yield is somewhat less than unity, being a maximum in the pH range 3—6.[7] This result neither proves nor disproves the original postulate,[6] but the fact that, when alcohols are added, induced photo-oxidation is much faster[5] means that a chain mechanism is predominant, at least under these conditions.

We have therefore studied the influence of ultraviolet light on rigid solutions of periodates and periodic acid at 77° K. It is concluded, by analogy with chromate, that the only photochemically active compound under these conditions is an alkyl periodate. Possible spectrophotometric evidence for ester formation in solutions of periodate in isopropyl alcohol at room temperature is presented (Fig. 2) and the spectra of aqueous solutions of periodates are discussed.

EXPERIMENTAL AND RESULTS

General experimental procedures were as described earlier.[1]

Polymerisation.—Experiments on the light-induced polymerisation of aqueous acrylonitrile by periodate have already been described.[6] Similar experiments have been carried out for chromate–alcohol systems. 0·5M-Solutions of acrylonitrile containing isopropyl alcohol and acid chromate were irradiated with light from a 250 w high-pressure mercury lamp filtered through soda glass. The results of these and of other experiments at higher acid strengths in the dark are given in Table 1. In contrast with the periodate system,[6] here polymerisation was not extensive, the highest yields occurring when the light intensity was low. The results do not prove that free-radical reactions are involved: indeed all other evidence for both thermal and light-induced reactions is to the contrary. It is possible that, fortuitously, there are unimportant side reactions involving free radicals, but it seems probable that Cr^{IV} or Cr^{V}

TABLE 1. *Polymerisation of acrylonitrile induced by acid chromate–isopropyl alcohol solutions (acrylonitrile = 0·5M).*

Pr^iOH (mole/l.)	Relative light intensity	$HCrO_4^-$ (10^{-4} mole/l.)	$HClO_4$ (mole/l.)	Yield of polymer	Hr.	Cr^{VI} consumed (%)
0	0	2·5	0·5	0	6	0
0	1	0	10^{-3}	0	2	—
0	1	2·5	10^{-3}	0	2	0
3	0	2·5	0·5	0	0·1	100
0·6	0	2·5	0·5	Turb.	0·3	100
0·3	0	2·5	0·5	Pr.	12	100
0·6	0	200	0·5	Pr.	24	100
3	1	2·5	10^{-3}	0	0·1	100
3	10^{-2}	2·5	10^{-3}	10%	1	10

Turb. = turbidity. Pr. = precipitate.

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[2] Kläning and Symons, *Proc. Chem. Soc.*, 1959, 95.
[3] *Idem, J.*, 1959, 3269.
[4] Kläning, *Acta Chem. Scand.*, 1958, **12**, 576.
[5] Head and Hughes, *J.*, 1952, 2046.
[6] Symons, *J.*, 1955, 2794.
[7] Smith, Ph.D. Thesis, Southampton, 1957.

intermediates can initiate polymerisation. If this is so, then we conclude that this test for free radicals is of limited utility in the presence of transition-metal ions.

Chromate Photolysis.—Solutions were prepared and stored at −80° in order to reduce the thermal oxidation. During photolysis at 77° or 90° K with light from a 250 w high-pressure mercury lamp, a blue colour developed which was intensified as the solution softened at −120°. Photolysis of the fluid solution at this temperature also gave a blue product, but at −110° this intermediate was decomposed too rapidly for it to accumulate in the solution. In the absence of added phosphoric or perchloric acid, solutions were violet rather then blue. After irradiation, on warming gradually the solution lost its blue colour, becoming green and giving the spectrum expected from a mixture of Cr^{III} and Cr^{VI}. At high temperatures this colour changed again, to orange, and at room temperature a precipitate of basic Cr^{III} salts was obtained. The orange colour is thought to be due to a chromic–chromate complex.

After irradiation, solutions to be analysed were softened and mixed with 1 ml. of aqueous 1M-sodium hydroxide, which converted all Cr^{VI} species, formed by disproportionation of the products of irradiation, into chromate. After warming to room temperature the solution was diluted with alkali and filtered. The overall loss of Cr^{VI} on irradiation was found by comparing optical densities at 373 mμ with those of unphotolysed solutions made alkaline in the same way. Solutions de-aerated before photolysis gave identical results. Results are in Table 2.

Periodate Photolysis.—Details are given in Table 3. Solutions containing phosphoric acid and sodium dihydrogen phosphate had ultraviolet spectra identical with that expected for H_5IO_6. These solutions gave good glasses which were unchanged after prolonged irradiation with light of λ 2537 Å from a 125 w low-pressure mercury arc immersed directly in the coolant.[1]

Neutral solutions composed of appropriate mixtures of water, sodium borate, and sodium phosphates had spectra which resembled that of periodate at pH ~1·9, under which conditions small quantities of H_5IO_6 are present. Dilution with water shifted the broad peak in the 220 mμ region back to 222·5 mμ, and at the same time narrowed and intensified the band. Whilst we do not know the reason why the normal spectrum of neutral periodate is not obtained under these conditions, we conclude that a considerable proportion of the periodate is nevertheless present as the species responsible for the band at 222·5 mμ in neutral solution.[8] These solutions also froze to clear glasses at 77° K, and again, there was no change in spectrum after prolonged exposure to light of λ 2537 Å.

TABLE 2. *Photolysis of* Cr^{VI} *with light of* λ 3650 Å *at* 77° *or* 90° K.

Ion	Concn. (10^{-2} mole/l.)	Glass	Time (hr.)	Conversion into Cr^{IV} (%)
CrO_4^{2-}	0·1	NaOH	12	0
$HCrO_4^-$	0·1	Phosphate	12	0
$Bu^t_2CrO_4 + Bu^tCrO_4^-$	2	Bu^tOH, 0·1M-H_3PO_4	5	22
$Bu^t_2CrO_4 + Bu^tCrO_4^-$	2	Bu^tOH, 0·1M-$HClO_4$	11	48
[a] $Pr^iCrO_4^-$	2	98% Pr^iOH, 0·1M-H_3PO_4	2	90
[a] $Pr^iCrO_4^-$	2	98% Pr^iOH, 0·1M-H_3PO_4	6	94
[a] $Pr^iCrO_4^-$	2	98% Pr^iOH, 0·1M-H_3PO_4	12	101
[a] $Pr^iCrO_4^-$	2	98% Pr^iOH, 0·04M-H_3PO_4	8	102
[a, b] $Pr^iCrO_4^-$	2	98% Pr^iOH, 0·07M-H_3PO_4	12	94
[a, b] $Pr^iCrO_4^-$	0·5	98% Pr^iOH, 0·07M-H_3PO_4	3	98

[a] Some $Pr^i_2CrO_4$ also present. [b] Deærated.

TABLE 3. *Photolysis of* I^{VII} *with light of* λ 2537 Å *at* 77° K.

Compound	Concn. (10^{-3} mole/l.)	Glass	Time (hr.)	Conversion into I^- (%)
$NaIO_4$	10	Borate + phosphate	4	0
H_5IO_6	10	Phosphate	8	0
H_5IO_6 [a]	0·5	Pr^iOH	11	91
$NaIO_4$	0·05	Pr^iOH	7	97
H_5IO_6 [a]	0·05	Pr^iOH	7	95

[a] The spectrum of H_5IO_6 in Pr^iOH is identical with that of $NaIO_4$.

Solutions in propan-2-ol, which developed, on storage, the spectrum shown in Fig. 2, froze to clear glasses which did not alter in appearance on photolysis until the glass was allowed to

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[8] Crouthamel, Hayes, and Martin, *J. Amer. Chem. Soc.*, 1951, **73**, 82.

soften. Then, however, a yellow or brown colour appeared, and iodine was sometimes precipitated, showing that extensive decomposition had occurred.

After warming to room temperature solutions were analysed either by acidification, addition of excess of potassium iodide, and titration with thiosulphate, or by dilution with water and measurement of the ultraviolet spectrum. After extensive photolysis, bands were found at 292 and 365 (I_3^-) and 226 mμ (aqueous iodide). By interpolation the relative amounts of iodine and iodide were determined. Results obtained by these alternative methods agreed.

Iodate Photolysis.—It seemed possible that the first step in the photolysis of periodate in an alcoholic glass would give ketone and iodate. Accordingly the behaviour of iodate has been studied, but solutions in alcohols were too cloudy and unstable to warrant study. In concentrated alkaline glasses there was very little change after prolonged irradiation. In acid phosphate glasses, after irradiation for 9 hr. with light of λ 2537 Å a faint pink colour appeared, possibly due to iodine. However, analysis after warming showed that only about 10% of the iodate had decomposed. Since these glasses were always slightly cloudy, we incline to the view that the photosensitive species was not simple iodate, but rather a polynuclear compound which gave some iodine in the glass.

Spectrophotometric Measurements.—These were made by using a Unicam SP.500 spectrophotometer fitted with an R.S.V. photomultiplier detector. Spectra at low temperatures were measured with the attachment described elsewhere.[9] Since readings below about 250 mμ were unreliable with this apparatus only the spectra of chromium intermediates could be studied at low temperature. The temperature in the cell housing was read by means of an Alumel–chromel thermocouple, calibrated in liquid nitrogen, oxygen, and a bath of melting diethyl ether. For measurement of the spectra of glasses, the temperature was adjusted to about −160° by means of a potentiometer connected to a heating-coil immersed in the liquid-nitrogen coolant. In experiments with the softened glass the temperature was about −120°.

The cell correction due to cracks in the glass was about 0·6 and varied somewhat with wavelength. The correction for the softened glass was far smaller (about 0·06), so these readings are more reliable. At −120° the spectrum of the blue intermediate decayed slowly, and the spectrum given in Fig. 1 was obtained by extrapolation to zero time. The time at which the glass softened was taken as the time when a sudden fall in optical density occurred. Separate measurements were made to determine the contraction of the solutions from room temperature to −120°.

The slow colour change at −120° was followed spectrophotometrically. The rates of decrease in optical densities at 360 and 650 mμ were comparable, and the spectrum of the resulting green solution was close to that expected for the disproportionation $3Cr^{IV} \longrightarrow Cr^{VI} + 2Cr^{III}$. A subsequent general increase in optical density may have been due to the formation of a precipitate or to slight frosting on the cell windows.

Electron-spin Resonance Measurements.—These were made at 77° K as previously described.[10] Irradiated glasses were checked whenever decomposition was detected after softening (see Tables 2 and 3). In no instance was resonance detected which could be attributed to alcohol radicals. With periodate in isopropyl alcohol there was no detectable resonance under any conditions. With chromate in isopropyl alcohol a very weak, broad band was observed with a *g*-value slightly greater than the free-spin value. The intensity of this signal corresponded to a "radical" yield of about 0·2% based on the amount of chromate photolysed and was probably due to chromic ion formed in traces before irradiation. Marked increase in absorption in this region after warming is in accord with this postulate. Although any Cr^{IV} present should be paramagnetic, the degeneracy of the levels containing the two electrons would almost certainly be lifted by zero-field forces and this effect, together with spin–orbit coupling effects, would smear the resonance beyond the limit of detection in a glass.

DISCUSSION

Chromate Photolysis.—The stoicheiometric results alone strongly support the postulate that monochromate esters are photolysed to give ketone and Cr^{IV} in one step.[2,4] The alternative, that Cr^{III} is formed directly in the glass, would require the coincidence that a limit to photolysis was reached after two-thirds of the original chromate had been lost.

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[9] Symons and Townsend, *Spectrovision*, 1957, **4**, 5.

[10] Gibson, Ingram, Symons, and Townsend, *Trans. Faraday Soc.*, 1957, **53**, 914.

Photolysis to Cr^{V} and alcohol radicals, followed by further decomposition on warming, would require loss of Cr^{V} at least in part by attack on the solvent. Reasonable steps, giving the correct stoicheiometry, are not readily formulated, and the mechanism seems improbable because no alcohol radicals could be detected by electron-spin resonance.

By elimination, the blue intermediate must be a Cr^{IV} species. There is a considerable increase in optical density at the band maxima when the glass softens, but no shift (Fig. 1). Since, in the rigid glass, Cr^{IV} will not be at equilibrium with its ligands, this very rapid change is attributed to a change in the ligand field around Cr^{IV}.* The fact that, in the absence of acid, a violet colour appears on softening is in accord with this postulate since phosphate is expected to co-ordinate strongly to Cr^{IV}, and hence there should be different ligands in the two cases.

The spectral changes followed at −120° suggest that the main route for loss of Cr^{IV} is:

$$2Cr^{IV} \longrightarrow Cr^{V} + Cr^{III}$$
$$Cr^{IV} + Cr^{V} \longrightarrow Cr^{VI} + Cr^{III} \text{ (Fast)}$$

There is no sign of a new band during the decomposition at −120°, other than those attributable to Cr^{VI} and Cr^{III}. Since hypochromate (CrO_4^{3-}) absorbs quite strongly in the visible and near-ultraviolet region[11] we should expect detectable absorption from Cr^{V} under the present conditions if this species were formed in appreciable quantity. Rapid interaction between Cr^{IV} and Cr^{V} was a necessary stage in the mechanism proposed for photolysis at room temperature,[2] and it is significant that Cr^{IV} does not react with alcohol at −120°.[4]

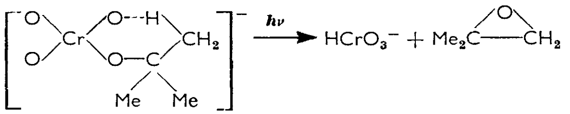
If our assignment is correct, the extinction coefficient at 650 mμ is unusually large for a 3*d*–3*d* transition, and the band may instead involve transfer of ligand electrons towards chromium.

The simplest detailed picture of the breakdown of isopropyl hydrogen chromate is by way of the cyclic transition state (see 1).

. . . . . . (1)

Light absorption in the first two bands of the ester, whose spectrum closely resembles that of acid chromate,[12] involves transfer of oxygen *p*-π-electrons from oxygen to chromium.[13] Since the photolysis requires transfer of two electrons into the chromium 3*d*-level this transfer facilitates the breakdown shown (1). A similar transition state can be written for the thermal breakdown which occurs on protonation. There has long been controversy regarding the mechanism of the thermal reaction, one reason being that α-hydrogen can be lost as either a proton or a hydride ion. These differences merge if a cyclic transition state is involved, since one can arbitrarily symbolise the electron flow in any of three possible ways.[14] That addition of a proton facilitates breakdown of the ester arises because chromium thereby becomes more electrophilic.

That the t-butyl ester is photolysed far less readily is in accord with formulation (1). We have not undertaken an analysis of organic products, but tentatively suggest formulation (2) for the transition state.



. . . . . (2)

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* Hagihara and Yamazaki (*J. Amer. Chem. Soc.*, 1959, **81**, 3160) have prepared a deep blue compound thought to be chromium tetra-t-butoxide, $Cr(OBu^{t})_4$; this is in agreement with our assignment.

[11] Bailey and Symons, *J.*, 1957, 203.

[12] Kläning, *Acta Chem. Scand.*, 1958, **12**, 807.

[13] Bailey, Carrington, Lott, and Symons, *J.*, 1960, 290.

[14] Lewis and Symons, *Quart. Rev.*, 1958, **12**, 230.

Periodate Photolysis.—The postulate[8] that the band at 222·5 mμ characteristic of aqueous solutions of periodate at pH 3—6 is a property of the ion IO_4^- rather than of $H_4IO_6^-$ is generally accepted. However, diffuse reflectance spectra of solid KIO_4 in the ultraviolet region, although showing clearly a weak band in the 315 mμ region (detected also as a shoulder in aqueous solutions), show no sign of an intense band at 222·5 mμ.[15] The present results also appear to cast doubt upon this assignment. If the band at 222·5 mμ is due to IO_4^- and if $H_4IO_6^-$ has a negligible absorption in this region,[8] then the change on addition of isopropyl alcohol must be simply a solvent shift, coupled possibly with further dehydration of $H_4IO_6^-$. This offers no explanation for the slow build-up of the band at 226 mμ in isopropyl alcohol. We postulate instead that the new band is characteristic of a periodate ester, possibly $(Pr^iO)_4IO_2^-$, formed at a measurable rate from aqueous periodate. It is significant that Buist, Bunton, and Miles[16] observed a similar increase in optical density in this region during the initial stages of interaction between periodate and certain glycols, which they attributed to the formation of a complex, probably a cyclic diester.

If this is correct, the ion $H_4IO_6^-$ may be responsible for the band at 222·5 mμ in aqueous solution, since it has the same symmetry as the postulated ester. However, the problem is still unresolved.

The results obtained on photolysis in rigid media seem hard to understand if the above postulate is incorrect. Possible modes of breakdown of simple oxyions have been discussed,[3] and those considerations, taken in conjunction with the present results, seem to eliminate all possibilities other than that the photo-active compound is an ester, which probably breaks down in a manner analogous to that of the alkyl hydrogen chromate discussed above. The fact that prolonged photolysis converts periodate into iodide and iodine, taken in conjunction with the comparative inertness of iodate, suggests a stepwise breakdown:

$$\left.\begin{aligned} (Pr^iO)_4IO_2^- &\xrightarrow{h\nu} Me_2CO + (Pr^iO)_2IO_2^- \\ (Pr^iO)_2IO_2^- &\longrightarrow Me_2CO + IO_2^- \\ IO_2^- &\longrightarrow I^- + O_2 \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

where the first and either of the subsequent steps are photoinduced.

In light of these postulates, the mechanism for photolysis at room temperature requires reconsideration. A mechanism similar to that proposed for permanganate[3,17] seems ruled out. Breakdown to hydroxyl radicals, as originally postulated,[6] certainly does not seem to occur readily in rigid media; but, if a chain reaction is involved, it would be possible for the first stage to have a very low quantum efficiency and yet for the overall reaction to have a quantum yield close to unity.[7] Since photolysis in the presence of alcohols is very rapid, there must be a change in mechanism from a free-radical chain process to the non-radical breakdown (3) on passage from fluid to rigid media. A similar change in mechanism has been observed for the photolysis of ethyl iodide.[1,18]

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[15] Griffiths, Lott, and Symons, *Analyt. Chem.*, 1959, **31**, 1338.

[16] Buist, Bunton, and Miles, *J.*, 1957, 4575.

[17] Zimmerman, *J. Chem. Phys.*, 1955, **23**, 825.

[18] Luebbe and Willard, *J. Amer. Chem. Soc.*, 1959, **81**, 761.