664. *Structure and Reactivity of the Oxyanions of Transition Metals. Part VI.* Photolysis of Chromate, Permanganate, and Related Compounds in Rigid Media at Low Temperatures.*

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Rigid solutions of permanganate in a variety of solvents at 77° K are readily photolysed by 3650 or 2537 Å light to give tervalent manganese and oxygen. Alcoholic solvents are not attacked to any extent and it is concluded, by comparison with the behaviour of chlorine dioxide, that free oxygen atoms are not involved in the photolysis.

Other tetrahedral oxyanions, including manganate, hypomanganate, chromate, and vanadate do not decompose under similar conditions.

When studying photolysis it may be informative to use a medium whose rigidity is sufficient to prevent migration of some, or all, of the molecular or ionic fragments resulting from

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* Part V, *J.*, 1959, 829.

bond fission.[1,2,3,4] Under such conditions chain decompositions cannot occur and chemically unstable intermediates may become permanently trapped and react further only when the glass softens. These intermediates can be studied spectrophotometrically or magnetically in the glass, and the course of reaction can often be deduced by analysis of the products formed on warming to room temperature.

Spectrophotometric and magnetic studies of several oxyanions of the transition metals have given a fairly detailed picture of the ground and first excited states of these ions.[5] Studies of reactivity, which have been confined to simple electron- and proton-transfer reactions, are now extended to photolyses, and the results are considered in the light of the structural studies.

An extensive study of the photolysis of permanganate was made by Zimmerman [6] who measured quantum yields between 2537 and 5780 Å for aqueous permanganate in the pH range 6·8 to 13. The quantum yield of oxygen formation, ϕ, was independent of pH and light intensity, but strongly dependent upon wavelength and, in the visible region, slightly upon temperature. At all wavelengths ϕ was small compared with unity.

Zimmerman [6] also studied the isotopic content of oxygen evolved from solutions in water enriched with $H_2{}^{18}O$ and found that all the oxygen was derived from permanganate. From these results, and a consideration of the energetics of various mechanisms, he concluded that by far the most probable route for oxygen formation was

$$MnO_4^- + h\nu \longrightarrow MnO_2^- + O_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

The small quantum yields were explained by the postulate that rapid internal conversion of excited permanganate ions gave ions in the ground state which possessed excess of vibrational energy. These could then dissociate thermally or lose energy to the solvent.

Bowen and his co-workers [7] found no photodecomposition for chromate or acid chromate ions exposed to light of wavelength greater than 3000 Å. Alkyl chromates, however, are rapidly photolysed with 3650 Å light.[8]

EXPERIMENTAL

Materials.—Water was distilled from alkaline permanganate in a nitrogen atmosphere, and other solvents and reagents were " AnalaR " or purified by standard procedures. It was established that solutions containing permanganate were quite stable during the period required for preparation. The solutions were stored, when necessary, at −70°.

Glasses.—These were prepared as described previously,[2] but phosphoric acid was not added to the alcoholic solvents. Acidic glasses were prepared by using suitable mixtures of water, syrupy phosphoric acid, and sodium hydroxide.

Electron Spin Resonance and Spectrophotometric Measurements.—These were made as described previously.[2]

Photolyses and Analytical Procedures.—Glasses in quartz test tubes were irradiated with a B.T.H. 250 w mercury arc, type ME/D, held externally to a Pyrex Dewar flask containing liquid oxygen or nitrogen and the sample tubes, or with a low-pressure 110 w mercury arc similar to that already described [2] which was immersed directly in the coolant and surrounded by sample tubes.

After warming to room temperature, irradiated permanganate solutions were analysed spectrophotometrically or titrimetrically with ferrous ammonium sulphate. When phosphate glasses were used, the irradiated solutions did not change in appearance on warming, and the

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[1] Norman and Porter, *Proc. Roy. Soc.*, 1955, *A*, **230**, 399.
[2] Symons and Townsend, *J.*, 1959, 263.
[3] Gibson, Symons, and Townsend, *J.*, 1959, 269.
[4] Kläning and Symons, *Proc. Chem. Soc.*, 1959, 95.
[5] Cf. *J.*, 1956, 3373, 4710; 1957, 659, and Carrington, Thesis, Southampton, 1959.
[6] Zimmerman, *J. Chem. Phys.*, 1955, **23**, 825.
[7] Bowen and Chatwin, *J.*, 1932, 2081; Bowen and Bunn, *J.*, 1927, 2353.
[8] Kläning, *Acta Chem. Scand.*, 1958, **12**, 807.

resultant spectrum was that expected for manganese(III) in this solvent. A marked evolution of gas was observed on warming. In alcohol, disproportionation of the manganese(III) present in the glass gave manganese(II) and precipitated manganese dioxide. The total oxidizing power was estimated titrimetrically and the results of these experiments are given in Table 1.

For all other oxyions studied, it was established that, after irradiation and warming to room temperature, the visible and ultraviolet spectra had not changed. The results are summarised in Table 1.

TABLE 1. *Details of the photolyses of various oxyanions.*

Ion	$10^3 \times$ Concn. (M)	Medium	Temp. (°K)	Wavelength [a] (Å)	Time (hr.)	Decomposition [b] (%)
MnO_4^-	0·1	Phosphate	90	3650	12	85
,,	3	,,	,,	,,	25	98
,,	2	,,	,,	,,	12	82
,,	,,	,,	,,	,,	18	95
,,	,,	,,	77	2537	36	98
,,	,,	$Me_2CH{\cdot}OH$	90	,,	40	99
MnO_4^{2-}	1	Hydroxide	90	3650	27	0
,,	,,	,,	77	2537	10	0
,,	2	,,	293	3650	6	0
MnO_4^{3-}	1	,,	77	2537	15	0
CrO_4^{2-}	1	Phosphate	,,	,,	12	0
$HCrO_4^-$ [c]	1	,,	,,	,,	12	0

[a] See text for the types of lamp used. [b] Based on conversion into manganese(III) for MnO_4^-.
[c] Some $Cr_2O_7^{2-}$ was also present.

No electron spin resonance absorption was detected after prolonged irradiation of permanganate glasses, and a test for acetone after irradiation of a rigid solution of permanganate in isopropyl alcohol showed that very much less than 1 equiv. had been formed. The small quantity detected was probably produced by thermal reactions before and after irradiation.

Photolysis of Chlorine Dioxide.—Some details have already been given.[2] Norman and Porter have shown [1] that in a mixed hydrocarbon glass photolysis is rapid and chlorine monoxide is formed. (They considered the possibility that chlorine dioxide dimerised at 77° K, but our results show conclusively that the monomer is still present as a major component in the unirradiated glass.)

Our results show that in methylcyclohexane the electron spin resonance spectrum due to chlorine dioxide is rapidly lost and a new spectrum consisting of a broad single peak at $g = 2{\cdot}003$ and a shoulder at $g = 2{\cdot}028$ appears. However, in alcoholic solvents the latter spectrum, which is attributed to chlorine monoxide, is superimposed upon a second spectrum with hyperfine lines characteristic of the alcohol radicals.[3] At the same time a violet colour appears, which may also be characteristic of alcohol radicals.[2]

DISCUSSION

Photolysis of Permanganate.—The relevant results are (i) that photolysis proceeds readily to manganese(III) but no further, (ii) that no alcohol radicals are trapped in the glass, and (iii) that photolysis proceeds readily even in inert glasses. These results should be compared with those for chlorine dioxide. On photolysis chlorine monoxide was formed but in solvent alcohol, an equivalent number of alcohol radicals were formed concurrently.

The available primary steps are (1) together with

$$MnO_4^- + h\nu \longrightarrow MnO_3 + O^{\cdot -} \tag{2}$$

$$MnO_4^- + h\nu \longrightarrow MnO_3^- + O \tag{3}$$

$$MnO_4^- + h\nu \longrightarrow MnO_2 + O_2^{\cdot -} \tag{4}$$

Of these, (2) represents the usual mode of bond fission, after excitation, namely, homolysis. Whilst it is conceivable that MnO_3 would undergo further photolysis, there can be little doubt that $O^{\cdot -}$, which is the conjugate acid of $\cdot OH$, would readily attack isopropyl alcohol, the resulting radicals ($Me_2\dot{C}OH$) becoming trapped.[3] Similar arguments apply to step (3). The results obtained with chlorine dioxide show that oxygen atoms can extract hydrogen from alcohols under these conditions. It is conceivable, but unlikely, that the primary dark back-reaction

$$O + MnO_3^- \longrightarrow MnO_2^- + O_2 \quad . . . . (5)$$

can compete so efficiently that reaction with solvent is eliminated. Step (4) has nothing to commend it. Although MnO_2 is stable when polymeric, the monomer is unknown, and would certainly be extremely reactive.[9] Also, the electron resonance spectrum of the superoxide ion is quite characteristic.[10]

We conclude that reaction (1) is correct. Such a reaction, involving heterolysis of two bonds, is not often met in the field of photochemistry.

Other Oxyanions.—The stability of chromate under these conditions is not surprising since it is far less chemically reactive than permanganate. However, our failure to photolyse either manganate or hypomanganate is remarkable. Hypomanganate, in particular, is generally considered to be extremely unstable and both ions readily disproportionate. However, this instability is thought to be a function of the protonated ions [5] and is not observed in strongly alkaline media.[11] Some relevant thermodynamic constants are in Table 2.

TABLE 2. *Some thermodynamic data for oxyanions (kcal./mole).*

	MnO_4^- [a]	MnO_4^{2-} [a]	MnO_4^{3-} [a]	CrO_4^{2-} [b]	$HCrO_4^-$
ΔF°	$-107{\cdot}4$	$-120{\cdot}3$	$-127{\cdot}0$	$-176{\cdot}1$	$-184{\cdot}9$
ΔH°	$-129{\cdot}7$	$-160{\cdot}5$	$-185{\cdot}8$ [c]	$-213{\cdot}8$	$-220{\cdot}2$

[a] Taken from ref. 11. [b] Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, 1952. [c] This value refers to MnO_4^{3-} in concentrated aqueous potassium hydroxide.

A consideration of the structure of the ions MnO_4^-, MnO_4^{2-}, and MnO_4^{3-} might shed light on the problem. Manganate and hypomanganate are thought to have one and two unpaired electrons, respectively, in a doubly degenerate antibonding π-orbital of symmetry e. This orbital, which may be pictured as being constructed from filled p–π oxygen orbitals and the d_{z^2} and $d_{x^2-y^2}$ orbitals of manganese is the antibonding analogue of an e bonding orbital. In particular, such overlap may tend to link adjacent oxygen atoms weakly, so that the extrusion of an oxygen molecule from a vibrationally excited permanganate ion need not involve free oxygen atoms at any stage. However, in manganate and hypomanganate the presence of electrons in the antibonding e level must reduce the effective overall bonding so that the structure will tend towards an extreme in which π-bonding is insignificant. The extrusion of molecular oxygen might then require greater activation energy, as is found experimentally.

Alternatively, if Zimmerman is correct in suggesting that vibrationally excited permanganate ions in the ground state decompose rather than electronically excited ions, then the differences noted may simply be linked to the relative shapes of the configurational co-ordinate curves for the ground and excited states. Other factors which may be important are the greater organisation of solvent molecules by the highly charged ions, and the relative stabilities of the labile ions MnO_2^-, MnO_2^{2-}, and MnO_2^{3-} which must be formed if oxygen molecules are lost by the corresponding tetrahedral ions.

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[9] Lott and Symons, *J.*, 1959, 829.

[10] Bennett, Ingram, Symons, George, and Griffith, *Phil. Mag.*, 1955, **46**, 443.

[11] Carrington and Symons, *J.*, 1956, 3373.