Photoanation Reactions of Hexa(dimethyl sulphoxide)chromium(III) Ion by Azide and Thioycanate: Evidence for Associative Reaction

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Summary Quantum yields for the anation of $[Cr(dmso)_6]^{3+}$ (dmso = dimethyl sulphoxide) by N_3^- are distinctly larger than those for anation by SCN^- at all concentrations, including those where limits imposed by ion association are approached; in conjunction with a measurement on the solvent exchange process, these results are taken to support an associative mechanism.

ALTHOUGH many quantum yields have been measured for photosubstitution reactions of Cr^{III}, some in conjunction with sophisticated luminescence studies, there is as yet little information on the dependence of these reactions on the entering ligand. Dependence on the entering ligand has been a crucial factor in deciding the mechanism of thermal substitution reactions as it is central to the distinction between dissociative and associative pathways. This study is concerned with photoanation at Cr^{III}. The use of a solvent of moderate polarity follows the examples of Tobe and Hughes[1] and Langford and Johnson[2] who used such solvents for thermal anation studies to encourage the approach to ion pair limiting rates. It is easier to interpret relative reactivity at the ion pair limit.

Associative photosolvolysis in mixed ligand amine complexes of Cr^{III} has been proposed. Evidence summarized recently by Wong and Kirk[3] indicates that the great propensity for these compounds to undergo isomerization in conjunction with photosolvolysis is most simply and directly explained by an associative mechanism.

Our experiments were carried out in dimethyl sulphoxide (dmso) solution at 25 °C. Chromium complex concentrations were between 10^{-2} and 10^{-3} mol dm^{-3} and sodium azide and potassium thiocyanate were in large excess. The chromium complex $[\mathrm{Cr(dmso)_6}](\mathrm{ClO_4})_3$ (possibly hazardous with respect to detonation) was prepared as previously described.[4] The light source was a Spectra Physics 1 W krypton ion laser at 647 nm or an Oriel Optics 1000 W Hg/Xe lamp used in conjunction with a Jarrell-Ash ¼ meter grating monochromator at 576 nm. Irradiation at these wavelengths corresponds to excitation of the longer-wavelength spin-allowed (quartet) band of the complex in a region where the absorption spectrum is unaffected by the added salts. The quantum yields obtained in these experiments as a function of salt concentration are summarized in the Figure. The light intensities were estimated using reineckate actinometry[5] with absorbance-matched samples. No reactions were carried beyond 5% conversion in order to minimize contributions of product absorption. Analyses were carried out spectrophotometrically using the new stronger absorption bands of the products which appear at shorter wavelength.

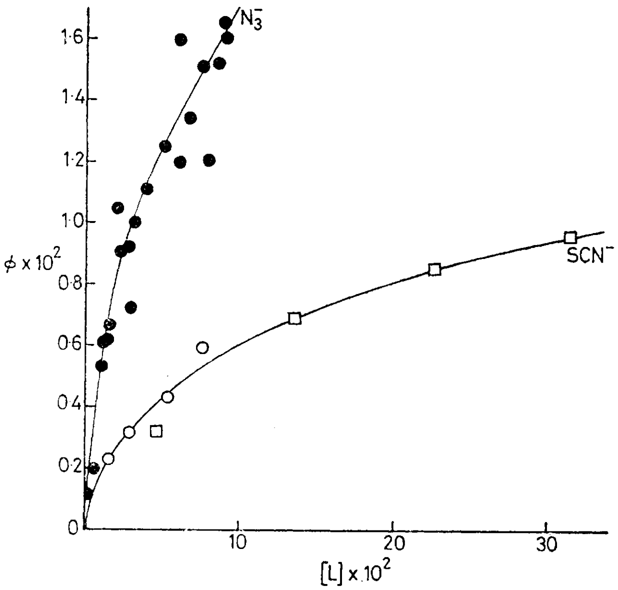

Figure. Quantum yield, ϕ, for anation of $[\mathrm{Cr(dmso)_6}]^{3+}$ in dmso as a function of anion concentration[L]. Points relate to several $\mathrm{Cr^{III}}$ concentrations ranging from 1·19 to 6·35 × 10^{-3} mol dm^{-3}. Results are presented for irradiation at both 576 and 647 nm and no wavelength dependence can be identified.

An additional experiment involved an attempt to estimate the quantum yield for solvent exchange of the complex with $\mathrm{C_2D_6SO}$ using the n.m.r. monitoring procedure of Langford, Scharfe, and Jackson[4] under the same conditions as above for photoreaction. Irradiation for 5 h led to zero exchange within the error of measurement. This allows us to set a generously estimated upper limit on the quantum yield for solvent exchange of 0·007.

It is clear from the figure that yields for $\mathrm{N_3^-}$ are at least twice as great as yields for $\mathrm{SCN^-}$ at all concentrations studied. This immediately suggests *associative* reactions with the substitution being assisted by azide more than thiocyanate. Although the azide curve is cut off prematurely by solubility limits, it seems very unlikely that the limiting thiocyanate values could approach those values for azide. It would be necessary for the limiting yields to coincide for the present results to be consistent with a dissociative pathway; this would be very unlikely.

In such a case, the argument for a dissociative pathway would parallel precisely arguments concerning the thermal anation of Co-haematoporphyrin IX with a limiting rate equal to the rate of solvent exchange.[6] Since the solvent exchange yield seems to be too small we conclude that the reaction is associative.

The present results are not inconsistent with one other report on photoanation at $\mathrm{Cr^{III}}$.[7] Reactions of $[\mathrm{Cr(OH_2)_6}]^{3+}$ with $\mathrm{SCN^-}$ and $\mathrm{Cl^-}$ show somewhat different yields in water but since the yields at moderate ligand concentration are linear functions of anion concentration it is difficult to attempt a separation of reactivity effects and ion association effects. It is interesting that the ion $[\mathrm{Cr(OH_2)_6}]^{3+}$ seems to be a bit more reactive than $[\mathrm{Cr(dmso)_6}]^{3+}$. This could be due to a steric inhibition by dmso consistent with an associative process. Reaction of $\mathrm{SCN^-}$ with $[\mathrm{Cr(NH_3)_5OH_2}]^{3+}$ [7] was also described. Assumption of a normal ion pair equilibrium constant (*ca.* 0·3) leads to an estimated limiting yield of 0·25 which is larger than the aquation yield for $[\mathrm{Cr(NH_3)_5OH_2}]^{3+}$ [8] and is probably greater than the solvent exchange yield in agreement with predictions based on an associative pathway.

Finally, as the term associative enters discussion of photosubstitution, we advance a cautionary note. The role of an entering ligand will be different in a photoreaction. In a thermal reaction, a system must await a thermal fluctuation to achieve the energy to react. When the entering ligand can stabilize the transition state, it makes that thermal fluctuation much more probable. The corresponding photoreaction begins from an excited state which has energy in excess of the transition state for the thermal reaction. The role of a good attacking group is to favour a relaxation pathway that ends up on a product potential surface in preference to a reactant potential surface. This may turn out to be a more subtle role than experience with thermal reactions has revealed to us. Note that the differentiation between $\mathrm{N_3^-}$ and $\mathrm{SCN^-}$ found here is smaller than that reported by Watts and his collaborators for the corresponding thermal reactions.[9]

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