Inorganica Chimica Acta, *128* (1987) L1–L2

Photo-oxidation of Vanadium(II) in Acidic Solution

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(Received October 14, 1986)

Aquo-vanadium(II) ion is a mild reducing agent, $E° = -0.25$ [1], and while thermal redox reactions of this ion have been extensively investigated [2, 3] the photoredox reactions of the V^{II}/V^{III} couple have received little attention. Dainton and James [4] pointed out that photolysis of aqueous solutions of V(II) salts eventually leads to the production of H atoms, and Schrauzer *et al.* [5] showed the production of hydrogen gas under similar conditions. The photo reduction [6] of V(III)–chloro complexes in alcohol has provided the first example of a transition-metal complex displaying both photochemistry and luminescence from an upper-excited state in fluid solution. Careful monitoring of the V(III)–aquo complexes in our system showed no evidence of such a process occurring in the absence of alcohols.

Experimental

Vanadium(II) solutions were prepared by reducing V(III) or V(IV) solutions with zinc amalgam. Vanadium(II) concentrations were determined by the method described by Sutin [7]. Photolysis was carried out using an Oriel 500-watt light source aligned to a monochrometer fitted with 2 mm slits. The reaction was followed, under nitrogen atmosphere, by monitoring the rate of formation of hydrogen gas using a volumeter described elsewhere [8]. The quantum yields were derived from the relationship

$$\frac{dV^{3+}}{dt} = 2\frac{d(H_2)}{dt} = \phi I_0(1 - 10^{-A})(A/A_t)$$

where A is the absorbance of vanadium(II) and A_t is the total absorbance of all species present. Taking into account the relative absorbtivities of the reduced and the oxidized forms of the system and the fact that the quantum yields were determined from the initial rates of hydrogen formation (first 5% of the reaction), A/A_t is taken as unity. The intensities of the light used were determined by ferrioxalate actinometry [9]. Stoichiometric experiments indicate that the reaction under consideration is

$$2V^{2+}{}_{(aq)} + 2H^{+}{}_{(aq)} \longrightarrow 2V^{3+}{}_{(aq)} + H_{2(g)}$$

Results and Discussion

Photolysis at 313 nm of acid solutions of 0.02 M V(II) produced hydrogen gas and V(III) ions. The results of variation of the quantum yield of V^{3+}, $\phi_{V^{3+}}$, with added hydrochloric acid is linear with respect to $\sqrt{H^+}$ in the range 10^{-2} to 2 M HCl, reaching an apparent plateau value of $\phi_{V^{3+}} = 0.15$ at $[H^+] > 2$ M. The relationship ($H^+ < 1.5$ M) is

$$\phi = 0.069[H^+]^{1/2} + 0.047$$

Similar results have been reported for Fe(II) [10], Eu(II) [11] and Cu(I) [12]. A mechanistic rationale for the photolysis of low-valent metal ions based on Noyes' geminate-pair recombination model [13] as modified by Jortner *et al.* [14] yields the expression

$$\phi = \phi_0 + \alpha\Gamma[S]^{1/2}$$

where ϕ_0 is the residual yield of pairs escaping both primary and secondary recombination without competitive scavenging and Γ is the yield of primary pairs escaping primary recombination only. Associating Γ with the plateau-value of the quantum yield at high H^+ concentration allows the estimation of α which in the Noyes model [13] is

$$\alpha = 2a(\Pi k_s)^{1/2}$$

where a is a diffusion parameter estimated to be 1.6×10^{-6} $s^{1/2}$. Using the observed value of slope and plateau, k_s, the second-order rate constant for the scavenging reaction is calculated to be 6.7×10^{9} M^{-1} s^{-1} which is similar to the values of 0.8 to 1.9×10^{10} M^{-1} s^{-1} observed in the photolysis of $CuCl_3{}^{2-}$ at ionic strengths from 1 M to 5 M [12].

In addition to hydronium as a scavenger, these V(II) solutions contain about 0.01 M Zn^{2+} ion as a result of the zinc-amalgam reduction of the V(III) starting material. Varying the Zn^{2+} concentration from 0.01 M to 0.41 M at $\mu = 2.5$, $[H^+] = 1$, $[Cl^-] = 1$, using sodium sulfate to maintain ionic strength, gives no detectable change in the quantum yield suggesting that Zn^{2+} is not a more efficient scavenger than hydronium under these conditions although its k_s for reaction with e_{aq} as measured in radiolysis experiments is 1.4×10^{9} M^{-1} s^{-1} [15]. Other ions, however, do have specific effects on the quantum yield when present in high concentrations. Ionic strength variation from $\mu = 1$ to $\mu = 4$ with sodium sulfate as the added salt gives no real effect, however, chloride ion at 4 M gives a small reduction in quantum yield. Perchlorate ion on the other hand exhibits a strong specific negative effect on the

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0020-1693/87/$3.50

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TABLE I. Ionic Strength and Specific Ion Effects on the Quantum Yield for V(II) Photo-oxidation

μ^a	$[So_4^{2-}]$	$[Cl^-]$	[X]	$\phi_{V^{3+}}$
1.25		1.1		0.12(0)
2.00	0.25	1.1		0.12(6)
3.00	0.58	1.1		0.12(0)
3.75	0.83	1.1		0.11(7)
4.75		4.0		0.10(9)
3.00			2.7 M ClO_4^-	0.06(4)
2.40		1.1	1.2 M $CF_3CO_2^-$	0.03(7)
4.4	0.8	1.1	0.8 M Mg^{2+}	0.14(0)

[a] Counter-ion is Na^+; total ionic strength includes contributions from V^{2+} (~0.02 M), Zn^{2+} (~0.01 M) and H^+ (1 M); 22 °C.

quantum yield, Table I. Nearly a 50% reduction in quantum yield is noted if perchlorate is used to replace chloride or sulfate ion in these reactions. Several possible explanations are immediately suggested, but since a similar effect is noted both for the cationic aquo-complexes, Eu^{2+} [11] and V^{2+}, as well as the anionic complex, $CuCl_3^{2-}$ [12], those explanations involving complexation and/or ion-pairing seem unpalatable. Perchlorate is commonly used in many thermal and electrolytic reductions as a supporting counter-ion and specific effects of perchlorate such as noted here have not been previously observed.

Henry [16] reported that a number of anions, including perchlorate, decrease the non-radiative and substitution rate constants of the ^2E state of tris(2,2′-bipyridine)chromium(III) ion. Her explanation considered the decrease in water activity, due to solvation of the perchlorate ion at a concentration of 5 M in water, as important in the formation of a seven-coordinate intermediate formed by addition of a water molecule to the Cr(III) metal center. In the geminate mechanism implied here, perchlorate may be having an altogether different mode of action since the excited state of V(II) more nearly resembles the labile V(III) ion and bulk transfer of water need not be involved. Perchlorate ion, by virtue of its size and charge has a strong effect on the structure of water, causing a notable structure-breaking effect [17]. Since proton transfer from the medium to the geminate-pair and the relative prescribed-diffusional properties of the secondary pair are determinate in the relative scavenging-recombination rates, medium effects due to the chaotropic properties of perchlorate seem to play an important role in the determination of the overall-quantum yield for photo-oxidation of V(II). Supporting this contention, the more strongly structure-breaking ion, trifluoroacetate, has an even more marked effect and addition of the structure-making ion, Mg^{2+}, results in an enhancement of the overall oxidation rate. V(II) photolysis appears to be a sensitive probe for this phenomenon and experiments to delinate specific ion effects are currently being carried out.

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