Absorption Spectrum and Reaction Kinetics of the Photoreactive State of the Uranyl Ion

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Summary μs and ns excitation of aqueous solutions of uranyl salts produces a short-lived absorption ($t_{\frac{1}{2}}$ *ca.* 1·05 μs) which is systematically quenched on addition of a variety of organic substrates known to photoreduce UO_2^{2+} ion; the isotope effect of 2·76 obtained with CH_3OH and CD_3OH exactly matches that found for quenching of the *fluorescence* of UO_2^{2+} by these substrates, and absolute rate constants have been determined for some photoreactions of UO_2^{2+} for the first time.

SUGGESTED mechanisms of photo-oxidation by UO_2^{2+} have been based largely on product and quantum yield determinations[1] and fluorescence quenching studies.[2,3] The most recent investigations[2,3] have indicated that these data are interdependent and the quenching of uranyl ion fluorescence is chemical in nature, occurring by a photo-redox process, reaction (1), at least in the case of aliphatic substrates. This view has been supported by e.s.r. identification of $\dot{C}R^1R^2\cdot OH$ following the instigation of (1) in matrices

$$R^1R^2CHOH + U^{VI*} \xrightarrow{H_2O} R^1R^2\cdot COH + U^V + H_3O^+ \quad (1)$$

at 77K,[4] although Ledwith *et al.*[5] have succeeded in spin-trapping $CH_3O\cdot$ in the photo-oxidation of CH_3OH by $(UO_2^{2+})^*$.

Flash photolysis of 2×10^{-2}M uranyl perchlorate and nitrate in water, using either a ruby-doubled laser (λ 347·1 nm, flash duration *ca.* 50 ns) or a conventional μs apparatus (flash duration *ca.* 30 μs, 550 *J*) produced the absorptions shown in the Figure (A) with λ_{max} *ca.* 590 ± 10 nm. The

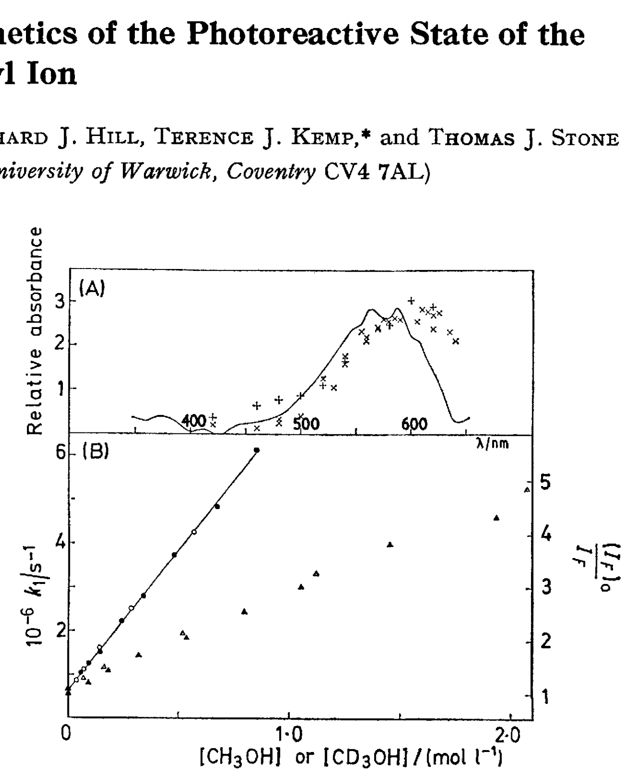

FIGURE (A). *Flash photolysis spectra of aqueous solutions of uranyl salts. Full line—spectrographic recording of absorption from* 2×10^{-2}M *uranyl perchlorate following* μs *flash;* ×—*photo-electrically recorded absorptions on laser flashing* 2×10^{-2}M *uranyl perchlorate,* +—*analogous experiments with uranyl nitrate.* (B). ○—*Pseudo first-order rate constants for disappearance of* 590 nm *transient on laser flash photolysis of aqueous uranyl perchlorate* (0·2M) *in the presence of* CH_3OH, △—*analogous data for* CD_3OH; ●, ▲—*Stern–Volmer plots for the quenching of uranyl ion luminescence by* CH_3OH *and* CD_3OH *respectively in aqueous solution.*

decay in water could be monitored only in the case of the laser flash experiment, *i.e.* with $t_{\frac{1}{2}} = 1{\cdot}05\,\mu\text{s}$, $k = 6{\cdot}57 \times 10^5\,\text{s}^{-1}$ for five half-lives, but in concentrated sulphuric acid k was found to be $7{\cdot}6 \times 10^3\,\text{s}^{-1}$ in conformity with the increased fluorescence lifetime in this medium, $k_F = 7{\cdot}1 \times 10^3\,\text{s}^{-1}$.[6] Systematic addition of a number of organic substrates to aqueous uranyl perchlorate (0·2 M) increased the decay rate of the 590 nm transient and with CH_3OH and CD_3OH in particular, it was possible to ascertain absolute rate constants for the quenching process with some precision, yielding $k_H = (6{\cdot}40 \pm 0{\cdot}08) \times 10^6$, $k_D = (2{\cdot}32 \pm 0{\cdot}10) \times 10^6\,\text{l mol}^{-1}\,\text{s}^{-1}$ and $k_H/k_D = 2{\cdot}76 \pm 0{\cdot}08$. The isotope effect was found to match almost exactly that found for the Stern–Volmer quenching of the fluorescence of the uranyl ion (k^{SV}) by the same substrates under identical reaction conditions, *i.e.* $k_H^{SV}/k_D^{SV} = 2{\cdot}76 \pm 0{\cdot}06$ (Figure). Other approximate values of quenching constants ($k_2/10^6\,\text{l mol}^{-1}\,\text{s}^{-1}$) are: acetic acid (unbuffered) 9·3, acetic acid (pH 5) 4·9, lactic acid (pH 1·5) 9·8, ethanol 42, and $H_2PO_2^-$ 31.

The shortening of the lifetime of the 590 nm transient by added substrates corresponds to photochemical reaction, *i.e.* the state responsible for the absorption is both the photoreactive state of UO_2^{2+} and is that from which emission occurs. No kinetic data for the emission have been recorded in the literature for UO_2^{2+} in pure water (as opposed to H_2SO_4 and H_2SO_4–H_2O media) but $t_{\frac{1}{2}}$ is estimated as $< 10\,\mu\text{s}$[7] and our preliminary results from single photon counting experiments indicate k_1 *ca.* $4{\cdot}7 \times 10^5\,\text{s}^{-1}$. The data with CH_3OH and CD_3OH imply that attack upon a C–H bond by $(UO_2^{2+})^*$ is the principal route of photooxidation of methanol in solution.

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