

Quenching of excited uranyl ion during its photochemical reduction by triphenylphosphine: Part V—Effect of covalently bonded and ionic halides

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Electron absorption spectroscopy has been used to measure bimolecular photophysical deactivation constant by exploiting photochemical reduction of uranyl ion with triphenylphosphine. Relative rates of bimolecular quenching follow the order $\text{SCN}^- > \text{Cl}^- > \text{CCl}_4 > \text{CHCl}_3 > \text{CH}_2\text{Cl}_2$ showing that free ionic halide and increasing number of chlorine atoms in covalently bonded alkyl halides increase the bimolecular quenching action. The increased availability of non-bonding electrons on halogen atom facilitate interaction with electron deficient species (excited uranyl ion).

The presence of aromatic molecules triggers off a competition between photochemical reduction of uranyl ion with substrates like triphenylphosphine and photophysical deactivation of excited uranyl ion through non-radiative complex formation with aromatic π -electron cloud¹. This phenomenon has been exploited to measure bimolecular quenching constants using UV-Vis spectrophotometry²⁻⁵. Uranyl ion luminescence quenching with halide ions has been measured from life time measurements and obeys the molecular orbital theory^{6,7}. Halogenated molecules (CH_2Cl_2 , CHCl_3 , CCl_4 and ionic species Cl^- , SCN^-) fail to reduce uranyl ion photochemically in aqueous acetone solution. However, their presence reduces the efficiency of photochemical reduction of uranyl ion.

Experimental

Dichloromethane, chloroform, carbon tetrachloride, uranyl acetate, triphenylphosphine, sulphuric acid, sodium chloride, ammonium thiocyanate, ammonium chloride and acetone (all A.R. grade reagents) were used as such. Experimental details are described in our earlier publications^{2,3}.

Results

Prolonged irradiation of solution containing uranyl ion and species under investigation, failed to

produce photochemical reduction of uranyl ion. However, their presence lead to diminishing of the quantum yield for uranium(IV) formation during photochemical reduction of uranyl ion with triphenylphosphine (Fig. 1). A decrease in optical density at 650 nm corresponds to a decrease in quantum yield for uranium(IV) formation. It is a function of the concentration of the quencher (Eq. 1)^{2,3}.

$$\phi_R^\circ/\phi_R = \text{OD}^\circ/\text{OD} = 1 + k_q\tau[\text{Q}] = 1 + K_{sv}[\text{Q}] \dots (1)$$

where ϕ_R° and ϕ_R are quantum yields for uranium(IV) formation in the absence and in the presence of quencher respectively. Linear Stern-Volmer type plots are given in Fig. 2. and

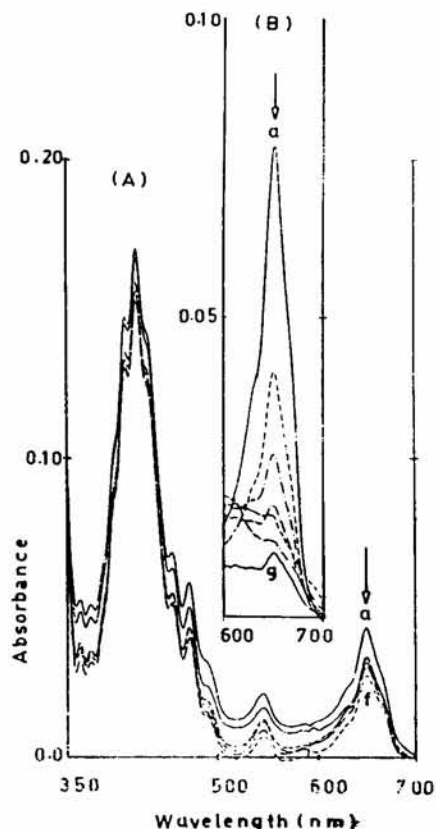


Fig. 1—Electronic spectral changes after irradiation for 7 min by sunlight of solutions containing $[\text{UO}_2^{2+}] = [\text{PPh}_3] = 0.01 \text{ mol dm}^{-3}$ and varying amount of quencher [(A) quencher = carbon tetrachloride (a) 0.00, (b) 0.0025, (c) 0.0050, (d) 0.0100, (e) 0.0130, (f) 0.0180 mol dm^{-3} respectively. (B) quencher = ammonium thiocyanate: (a) 0.00, (b) 0.0025, (c) 0.0050, (d) 0.0100, (e) 0.0130, (f) 0.0180, (g) 0.020 mol dm^{-3} respectively]

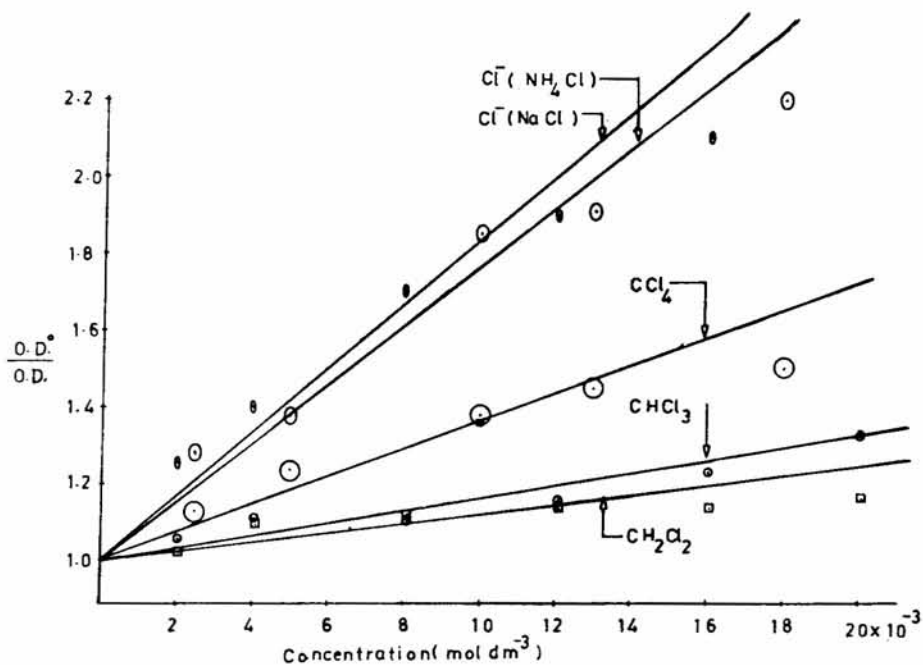


Fig. 2—Stern-Volmer plots $\{[UO_2^{2+}] = [PPh_3] = 0.010 \text{ mol dm}^{-3}, [H^+] = 0.10 \text{ mol dm}^{-3}\}$

Table 1—Stern-Volmer (K_{sv}) and bimolecular quenching constant (k_q) for quenching of the excited uranyl ion with some covalently bonded and ionic halides $\{[UO_2^{2+}] = [PPh_3] = 0.01 \text{ mol dm}^{-3}, [H^+] = 0.1 \text{ mol dm}^{-3}, \text{ at } 25 \pm 5^\circ\text{C}\}$

Quencher	$K_{sv} (\text{dm}^3 \text{ mol}^{-1})$	$k_q (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$
Dichloromethane	12.50	0.84×10^7
Chloroform	16.65	1.12×10^7
Carbon tetrachloride	36.36	2.45×10^7
Chloride ion (NH_4Cl)	76.90	5.19×10^7
Chloride ion (NaCl)	82.75	5.59×10^7
Thiocyanate (NH_4SCN)	333.00	22.50×10^7

values in Table 1. $\tau = 1/\sum k_i$ ($1.48 \times 10^{-6} \text{ sec}$) is a measure of life-time of excited uranyl ion in solution⁶. The bimolecular quenching constant $k_q = K_{sv}/\tau$ for various species can be readily calculated. However, bromo and iodo species failed to form transparent solution.

Discussion

On optical excitation of uranyl ion, an electron jumps from highest occupied molecular orbital (HOMO) comprising uranium $5f/6d$ and oxygen $2p$ atomic orbitals to lowest unoccupied molecular orbital (LUMO) consisting of uranium $5f$ atomic orbital⁸. Consequently, a partial positive charge delocalizes on axial oxygen atoms of uranyl ion and makes it an electron deficient species. A donor-acceptor complex is formed between the

electron deficient (excited uranyl ion) and the electron rich species (alkylhalides/halide ions) in aqueous acetone solution leading to photophysical deactivation of uranyl ion.

Stern-Volmer constant (K_{sv}) or bimolecular quenching constant (k_q) is a measure of quenching action of various species. Quenching constant follows the order thiocyanate > chloride ion > carbon tetrachloride > chloroform > dichloromethane which indicates that increase in number of chlorine atoms in alkyl halide, increases the probability of interaction of electron deficient species (excited uranyl ion) with easily available non-bonding electron pair on chlorine atoms of alkyl halides. Larger k_{sv} values for free chloride or thiocyanate ion in solution, may be due to the ability of anions to undergo multiple optical collision with excited uranyl ion, leading to its photophysical deactivation in a cage of solvent.

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