Carbocation Photochemistry. Electron Transfer Mechanism for the Pyrylium Salt Sensitized Photo-oxidation of Leuco Crystal Violet

By Franklin D. Saeva* and George R. Olin

(*Xerox Corporation, Webster Research Center, Webster, New York* 14580)

Summary The photo-excited cation (pyrylium salt) sensitized oxidation of Leuco Crystal Violet occurs by a sequential electron, proton, and electron transfer process which is facilitated by molecular oxygen acting as an electron transfer species.

THE photochemical behaviour of carbocations is a relatively unexplored area. Pioneering research in this area by van Tamelen,[1,2] Cole[3] and Childs[4,5] has dealt primarily with photoisomerisations[1,3-5] and the reaction of the photo-excited triphenylmethyl cation with oxygen.[2] However, intermolecular reactions of photochemically excited carbocations with electron donor molecules in non-acidic media have received little attention.[5,6]

We report on the mechanism of the photo-oxidation of tris (*p*-dimethylaminophenyl)methane (I, Leuco Crystal Violet) to Crystal Violet (II) sensitized by 2,4,6-tri-*p*-tolylpyrylium tetrafluoroborate (III).

The electrochemical properties of (I) [$E^{\text{red}}_{1/2} = -0\cdot466$ V *vs.* S.C.E. (reversible)] and (III) [$E^{\text{ox}}_{1/2} = +0\cdot738$ V *vs.* S.C.E. (irreversible)] at 25 °C in MeCN indicate that an electron transfer from (I) to (III) is a thermodynamically unfavourable process, *i.e.*, $\Delta F = +27\cdot8$ kcal mol^{-1}. Also, no evidence was found for ground-state charge transfer complex formation between (I) and (III) in MeCN by either spectroscopic or electrochemical methods.[7] Consistent with these observations, solutions of (I) and (III) (*ca.* 10^{-4}M) in dry MeCN are stable in the absence of light, *i.e.*, the presence of (II) could not be detected spectrophotometrically even after several months.

Weller *et al.*[8] have reported a quantitative relationship between the kinetics of luminescence quenching (k_q) and the free energy change, ΔF_q, for an electron-transfer process between some donor–acceptor pairs, where k_q is diffusion controlled when $\Delta F_q < ca.\ -5$ kcal mol^{-1}.

Using the electrochemical data for (I) and (III) in combination with either the singlet or triplet energy for (III), $\Delta F_q < -25$ kcal mol^{-1} is obtained,† indicating that

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† ΔF_q was calculated from the equation $\Delta F_q = E^{\text{red}}_{1/2} - E^{\text{OX}}_{1/2} - {}^1\Delta\text{E}_{0,0} + \text{C}$ (see ref. 8) which includes the oxidation potential of the donor ($E^{\text{OX}}_{1/2}$), reduction potential of the acceptor ($E^{\text{red}}_{1/2}$), the singlet energy (${}^1\Delta E_{0,0}$) or the triplet energy (${}^3\Delta E_{0,0}$), and a Coulomb electrostatic term (C).

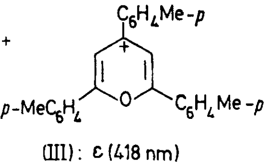
electron transfer from (I) to either the singlet or triplet state of (III) is a thermodynamically favourable process. A Stern–Volmer analysis of the fluorescence quenching of (III) by (I), with $\tau(s_1) = 5$ ns[9] in the absence of (I), was linear and provided a quenching rate constant, $k_q = 2{\cdot}5 \times 10^{10}$ l mol^{-1} s^{-1}, which indicates the process is diffusion controlled.[10]

$(p\text{-}Me_2N\text{-}C_6H_4)_3CH$

(I) : ε(MeCN; 303nm) 7700

$(p\text{-}Me_2N\text{-}C_6H_4)_3C^+$

(II): ε(586nm) 104,000

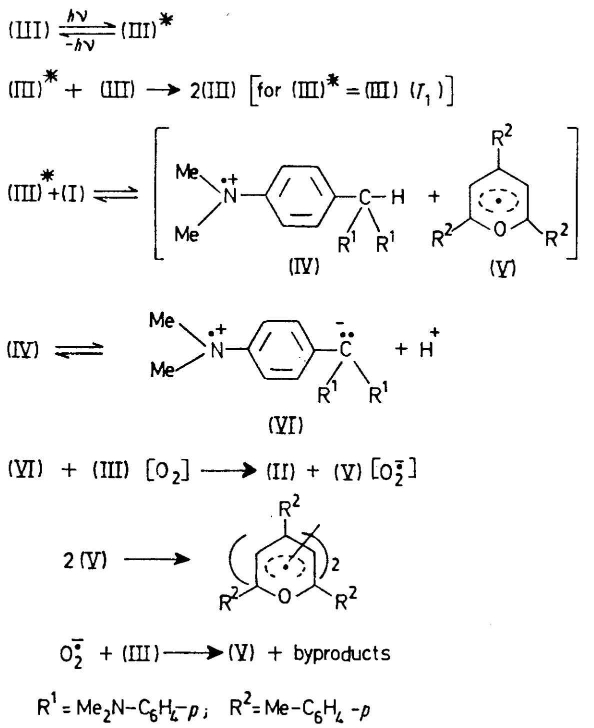


(III): ε(418 nm) 50,200

Three mechanistic pathways must be considered as possibilities for the photo-oxidation process. They are hydride transfer, electron–hydrogen atom transfer and thirdly, electron–proton–electron transfer. A measurement of the relative rate of photo-oxidation of (I) with deuterium and hydrogen on the α-carbon led to a primary deuterium isotope effect k_H/k_D of 3·0 at 25 °C both in degassed and air-saturated MeCN, indicating that hydrogen is lost in a rate-determining step which is not modified by the presence of oxygen. The rate of formation of (II) is *ca.* 30 times greater in air-saturated MeCN than in degassed MeCN, but the ratio of (II) formed to (III) lost remains unchanged at *ca.* 0·50. Also, one mole of acid (measured potentiometrically) is formed for every mole of (II) formed.

The rate of formation of (II) and the rate of disappearance of (III) varies linearly with light intensity and concentration of (I) in degassed and air-saturated MeCN. Increasing the concentration of (III) has an inverse effect on the rate, d[(II)]/dt, in degassed MeCN while not affecting this rate in air-saturated solution. In view of the fact that self-quenching of the singlet state of (III) was not observed over the concentration range studied[9] the inverse rate effect is attributed to the self-quenching of the triplet state.

In the proposed mechanistic scheme, electron transfer from (I) to (III)* forms radical cation (IV) and radical (V). The radical–radical cation pair may undergo reverse electron transfer back to (I) and (III)*. In competition with this process, (IV) can lose a proton to form the radical (VI). The equilibrium nature of this process was demonstrated by the observation of a decrease (by a factor of 4) in the rate of formation of (II) with the addition of HBF_4 (1×10^{-4} M) to the MeCN solution of (I) and (III). The fate of (VI) can be predicted based on its oxidation potential, $E^{ox}_{1/2} = +0{\cdot}8$ V[11] *vs.* S.C.E., indicating the spontaneity of an electron transfer process to any species with a reduction potential, $E^{red}_{1/2} > ca.\ -0{\cdot}8$ V *vs.* S.C.E. Under degassed conditions (III) fulfils this requirement and gives (V). In an air-saturated solution molecular oxygen with $E^{red}_{1/2} = -0{\cdot}8$ V *vs.* S.C.E.[12] can also accept an electron from (VI)$^{\cdot}$ to produce $O_2^{\cdot-}$. Molecular oxygen then facilitates the photo-oxidation process by acting as an electron transfer species. Since the ratio of (II) formed to (III) lost does not vary significantly from 0·5 in either air-saturated or degassed MeCN, $O_2^{\cdot-}$ must react with (III), either by e$^-$ transfer or chemically. The involvement of singlet O_2 ($^1\Delta_g$) was eliminated by its generation in the presence of (I) and (III) by the thermal decomposition of 9,10-diphenylanthracene peroxide[13] in the dark and observing the ratio of (II) formed to (III) lost. This ratio was found to be 2·94 instead of 0·5. Product studies indicate the formation of dimer and a series of polar oxygenated products.



(*Received*, 13*th August* 1976; *Com.* 938.)

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