Tetrahedron Vol 47, No 9, pp 1745-1752, 1991
Printed in Great Britain

0040-4020/91 $3 00+ 00

PHOTOINDUCED SINGLE ELECTRON TRANSFER ACTIVATION OF ORGANOPHOSPHINES: NUCLEOPHILIC TRAPPING OF PHOSPHINE RADICAL CATION

Ganesh Pandey*, Dinah Pooranchand and U T Bhalerao
Organic Division II, Indian Institute of Chemical Technology,
Hyderabad 500 007, India[†]

(*Received in UK* 12 *November* 1990)

Abstract: Photophysical studies show that organophosphines (1-4) form charge transfer stabilized exciplex with excited singlet ^{1}DCN* One electron oxidation of phosphines to corresponding radicalcation via phosphine.. ^{1}DCN* electron donor acceptor pair dissociation is reported Phosphine radical cations are found to react readily with moisture to give phosphine oxides.

Introduction

Photosensitized electron-transfer reactions have recently attracted considerable attention in organic photochemistry. Simultaneously, photoinduced SET initiated generation of radical ions and their synthetic applications is an emerging concept in organic synthesis[1]. Often these are realized by the exciplex dissociation of donor-acceptor pairs in polar solvents. Aromatic nitriles as good electron acceptor in photoinduced electron-transfer reactions have been studied extensively[2] and various types of electron donors have been employed. For example, π-donors such as aromatic compounds[3], ethylene derivatives[4], allyl and benzyl metalloidal compounds[5], n-donors such as amines[6] and σ-donors such as strained hydrocarbons[7]. As a part of our continuing interest in SET initiated reactions, we have developed[6,8] several new reactions of considerable synthetic importance by exciplex dissociation of amine... DCN (1,4-dicyanonaphthalene) pair To broaden the scope of this reaction with different n-donors, we envisaged to investigate systematically the reaction of organophosphines (1-4) (possible n-donors)[9] with singlet excited ^{1}DCN* The present study culminated primarily due to well known similarities and differences of organophosphines with amines. We report herein in detail the fundamental aspects of electron-transfer photosensitization of organophosphines (1-4) with singlet excited ^{1}DCN*.

Results and Discussion

Fluorescence quenching It was found that quenching of DCN fluorescence (λ excit.320nm, emission 395 nm) by 1-4 obeys Stern-Volmer relation (eq 1)

$$I_0 / I = 1 + K_q \tau_f [Q] \qquad (1)$$

Io/I represents the ratio of the fluorescence intensities measured in the absence and presence of quencher Q τ_f is the fluorescence life-time of DCN for Q=o From the slope $K_q \tau_f$ of the straight line (Fig.1), taking τ_f - 10.1 ns[9], the quenching rate constant K_q were calculated (correlation coefficient r > 0.99) and are listed in Table 1. the quenching rate constants are close to diffusion controlled limit (K_{diff} = 2.3 x $10^{10} M^{-1} S^{-1}$). This quenching cannot be attributed to ground or excited state complexation between DCN and organophosphines

---

[†] IICT Communication No 2628

1-4 since the absorption and emission of DCN were unchanged in the presence of the maximum concentration of 1-4. Singlet energy transfer mechanism of fluorescence quenching could also be ruled out on the pretext as singlet excited energy E_s of DCN (79.5 Kcal/mole)[10] is much lower than triphenylphosphine singlet energy (104 Kcal/mole)[11]. Therefore, it is reasonable to assume that fluorescence quenching of DCN by organophosphines 1-4 is via single electron transfer.

Single electron-transfer (SET) mechanism for the fluorescence quenching of DCN by 1-4 is also supported by estimating free energy change associated with this process by Weller equation[12] (Eq...2).

$$-\Delta G_{ET} = E_{1/2}\, D^{+} - E_{1/2}\, A^{-} - E_{0,0} \qquad (2)$$

ΔG_{ET} refers to free energy change associated with electron-transfer phenomenon, $E_{1/2ox}D$ is the half wave oxidation potentials of donor compounds, $E_{1/2red}A$ is the reduction potential of acceptor and $E_{0,0}$ is the excitation energy. Table I lists the ΔG estimated for 1-4 which shows the endoergic (negative) for all compounds. These are also found to be well correlated with those predicted for electron-transfer reactions. Indeed, the SET mechanism in this case is further supported by a correlation plot, log Kq vs oxidation potentials of 1-4 which showed linear relationship (Fig 2).

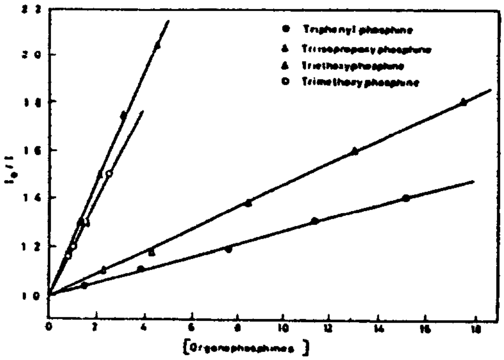


Fig 1 Stern-volmer fluorescence quenching plot of DCN by organophosphines

TABLE: Physical constants Evaluated for Photoinduced SET from Organophosphine (1-4)

Entry	Organo-phosphines	$E_{1/2(ox)}$[a]	ΔG_{ET}[b]	K_{qET}[c] $(\times 10^{10} M^{-1} S^{-1})$	K_{qET}[d] $(\times 10^{10} M^{-1} S^{-1})$	Φdissap[e]
1	Ph_3P	0.98	-23.27	1.38	1.42	0.119 ±0.001
2	$(i.PrO_3)P$	1.45	-16.60	0.45	0.297	0.219 ±0 003
3	$(EtO_3)P$	1.57	-13.84	0.22	0 25	0.211 ±0.005
4	$(MeO_3)P$	1.64	-12.22	0.199	0.257	0.277 ±0 011

a) Referred to saturated calomel electrode (SCE) using 0.1 M $NaClO_4$ as supporting electrolyte in CH_3CN, b) ΔG_{ET} is expressed in Kcal/mole DCN $E_{1/2(red)}$ - 1.28 ev and $E_{o,o}$ = 3 45 ev values were taken as such from ref[10]; c) From fluorescence quenching Stern-Volmer plot; d) From reciprocal plot of Φ vs $[Q]^{-1}$; e) light intensity at 310nm was evaluated by Uranyl oxalate actionometry.

Photoreaction of 1-4 in the presence of DCN: The findings observed above suggested that it might be possible to carry out SET initiated photochemical reaction between organophosphines 1-4 and DCN. To this end, a mixture of triphenyl phosphine (1) and DCN (5) was irradiated by pyrex filtered light (>280 nm) by using 450-W Hanovia medium pressure lamp in dry acetonitrile in complete inert atmosphere, achieved by continuous bubbling of argon. It should be noted here that all light was absorbed by 5 only. Even after 10 h of irradiation no evidence of photoreaction (neither product formation nor starting material loss) was noticed by HPLC analysis. However, similar irradiation in acetonitrile containing 2% water, gave triphenyl phosphine oxides efficiently. No intermolecular reaction product between organophosphine 1 and DCN was noticed. DCN was recovered unchanged (~98%) after photolysis. The triphenylphosphine oxide was characterised by various spectral data and identical HPLC retention time compared with authentic samples. Other phosphines (2-4) underwent similar photoreactions. No dealkylation from 2-4 was noticed, corresponding oxides were the only products identified.

$$R_3P \xrightarrow[CH_3CN:H_2O]{h\nu\,/DCN^*} [R_3P]^* \xrightarrow{H_2O} R_3P{=}O$$

The quantum efficiency (Φ_r) of the photoreaction was appreciably large (Table 1). This indicates that phosphine radical cation formed by one electron transfer reacts efficiently with water to give corresponding oxides. From Table 1, it is apparent that quantum efficiency (Φ_r) increases from 1→4. A probable rationale could be advanced by considering the difference in the dissociation efficiecny of SSIP to FRIP (Scheme 1) with back electron transfer processes Observation of decrease in the fluorescence quenching rate constant (K_{qET}, Table 1) of organophosphines 1→4 seems to support the above explanation. Triphenylphosphine radical cation, generated electrochemically at platinum electrode is also known to react with water to give triphenylphosphine oxide[13].

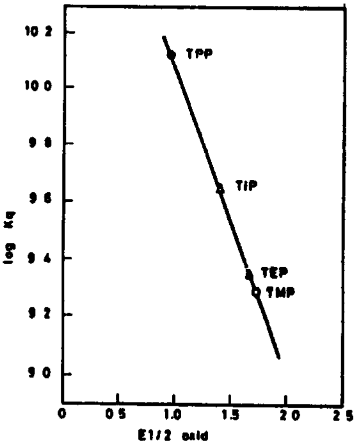
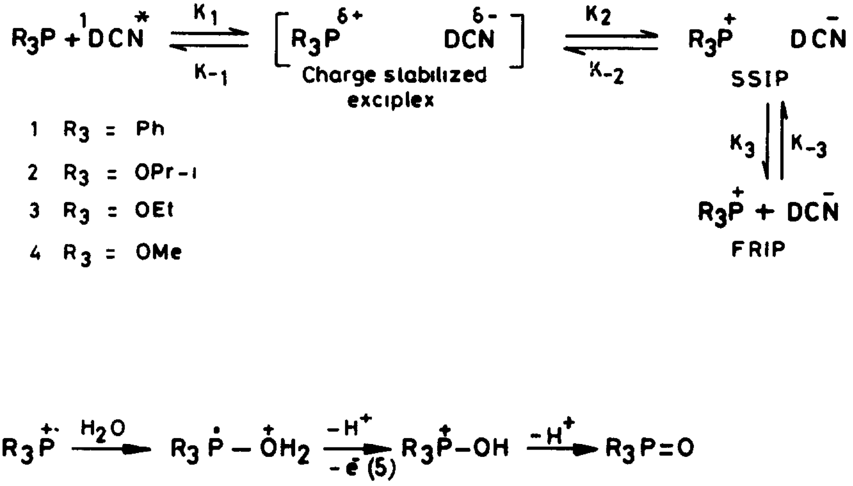


Fig 2 Correlation plot of log Kq vs E 1/2 oxid of organophosphine

Mechanism of Photoreaction: Apparently the present results provide evidence that photochemical reaction proceeds by SET from 1-4 to $^1DCN^*$ In order to correlate the mechanism of fluorescence quenching of DCN and photoreaction, it is concceived that an exciplex with partial charge transfer character is formed between $^1DCN^*$ and organophosphines. In the medium of high dielectric constants, the exciplex is expected to dissociate into solvent separated ion pair (SSIP) which further gets transformed into free radicalion pairs. The phosphine radical cation is stabilized in solvent cage and reacts with water to give corresponding oxides as shown in SCHEME I. In solvents of low polarity the chances of SSIP being transformed to the contact ion pair are usually strongly favoured and back electron transfer competes with the dissociation of SSIP to free ion pairs[14] In the absence of any fast chemical deactivation pathways available for phosphine radical cation formed in dry CH_3CN, possibly it undergoes back electron transfer processes. Intermolecular reaction between phosphine radical cation and DCN^- could be ruled out due to energy considerations



Scheme 1

A quantitative description of the above aspects are obtained by correlating the fluorescence quenching and reaction quantum yield measurements. If Q is quencher (organophosphines) and K_{et} is the rate constant for electron transfer to singlet excited DCN, the life-time of which is τ, and the radical ion pair thus formed reacts to the observed products with the rate constant K_r or unproductively decays to the starting materials, K_d, the quantum efficiency of the reaction could be represented as

$$\Phi_r = \frac{K_r}{K_r+K_d} \quad \frac{K_{et}\,[Q]}{K_{et}\,[Q]+1/\tau} \qquad (3)$$

Or in the inverse form

$$\frac{1}{\phi_r} = \frac{K_r+K_d}{K_r} \quad 1 + \frac{1}{K_{et}\tau[Q]} \qquad (4)$$

Thus a double reciprocal plot of quantum yield vs donor concentration, ϕ_r^{-1} vs Q^{-1} indeed resulted a straight line (Fig.3). The ratio of intercept/slope corresponds almost to the same quantity $K_{et}\tau$ obtained from the Stern-Volmer fluorescence quenching analysis (Table 1). Further evidence of charge transfer stabilized exciplex formation in this reaction is found from the work of Marcondes et al,[15] where they have also suggested the formation of similar complex formation in the fluorescence quenching of anthracenes bearing electron withdrawing groups by triphenyl phosphine.

In conclusion, it is demonstrated that organophosphines efficiently form charge transfer stabilized exciplex which dissociates into free phosphine radical cation in polar solvents similarly as noted in the case of amine ..... $^1DCN^*$ pairs[16].

Experimental

Extra pure solvents were used for fluorescence measurements Organophosphines 1-4 were purchased from Aldrich Chem Co and were purified before use. DCN was synthesized and purified by following the reported procedure[17] Acetonitrile was purified by being dried over phosphorus pentaoxide followed by distillation Fluorescence spectra were recorded using a Spex Fluorolog-2 spectrofluorimeter with excitation wavelength 320 nm, excitation and emission slit 1.5 nm. Analytical GC was carried out on a Hewlett-Packard HP-5890 machine with hydrogen flame ionization detector using 6' x 1/8" column packed with 10% Apiezon-L coated on chromosorb-W, 100-120 mesh. The HPLC analysis was performed on Hewlett-Packard HP 1090 liquid chromatograph using reverse phase μ-bondpack, C_{18}, 2 5 cm x 2.5 m eluting with acetonitrile-water (8:2) solvent system and monitoring at 250 nm utilizing variable wavelength detector The redox potentials were recorded using cyclic voltametry with PAR 175 universal programmer and PAR RE 0074 XY recording employing calomel reference electrode and glassy carbon rod as working electrode with 0 1 M $NaClO_4$ as supporting electrolyte

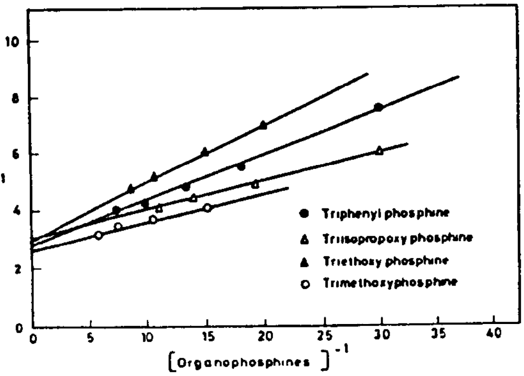


Fig 3 Double reciprocal plot of ϕ_r^{-1} vs $[Q]^{-1}$

and values were compared with the reported ones[18]. Irradiations were performed either using 450-W Hanovia medium presssssure lamp in quartz water jacketed immersion well in combination with pyrex filter or in Rayonet reactor using RPR-3000 Å lamps.

Fluorescence Quenching Experiments: Quenching of the DCN fluorescence was carried out by using compounds 1-4 as quenchers in complete inert atmosphere. Relative fluorescence intensities of DCN at 395 nm were measured in CH$_3$CN solutions containing DCN (1x10^{-4}) and the quenchers at various concentrations (1.5x10^{-4} M to 1.5x10^{-3}M for 1, 2.17x10^{-3}M to 1.3x10^{-2}M for 2, 1.8x10^{-2}M to 4.8x10^{-2}M for 3, 0.75x10^{-2}M to 2.5x10^{-2}M for 4 upto 50% of the intensity was quenched) The Stern-Volmer relation $I_0/I = 1+K_q\tau[Q]$ was obtained where I_0 refers to the fluorescence intensity without quencher and I refers to fluorescence intensity at different concentrations. The quenching rate constant K_q were calculated from the quenching constant K_q and the fluorescence life-time τ_f of DCN 10.1 ns (Table 1).

Quantum yield measurements: The samples for quantum yield determination were degassed by bubbling dry argon for 30 minutes and sealed in pyrex ampules. Usually, 5 mL of sample solution was pipetted into the ampules and were irradiated in Rayonet reactor consisting of only two RPR 3000 Å lamps in merry-go-round apparatus. Irradiations were carried out only for short intervals of time to bring about 8-10% conversion. Uranyl oxalate actinometry was used to monitor the intensity of the exciting light[19]. Quantitative loss of phosphine 1 was carried out by HPLC (C$_{18}$ reverse phase column CH$_3$CN : H$_2$O; 8 2 as eluent, flow rate 1 mL/min), whereas for compounds 2-4 GC (column 10% Apiezon-L, 6'x1/8") was utilized. The quantum yield of the reaction was measured at a donor concentration (1-4) of 1.5x10^{-3}M, 3.4x10^{-2}M, 4.12x10^{-2}M, 6 45x10^{-2} respectively, and DCN concentration of 1x10^{-4}M

Irradiation Procedure of 1-4 in the presence of DCN: General irradiation procedure is illustrated by taking 1 as representative example.

A dilute solution (500 ml) containing a mixture of 1 (0.524 g, 2 mmol) and DCN (0.08 g, 0 45 mmol) in acetonitrile water (8 2) was irradiated in a pyrex vessel by 450-W Hanovia medium pressure lamp using quartz water jacketed immersion well in combination with pyrex filter. A continuous stream of dry argon was bubbled throughout the irradiation. The progress of the reaction was monitored by drawing and analysing by HPLC. On completion of the reaction the solvent was removed by rotary evaporator under reduced pressure. The reaction mixture upon chromatographic separation on silica gel gave a solid (92%) compound, mp. 156-158°C which was characterised as triphenyl phosphine oxide by IR, ^{1}H NMR and mass spectral data which was further confirmed by comparing the identical retention time on HPLC with authentic samples

Similar photoreaction was performed for compounds 2-4 but the irradiation was carried out in Rayonet reactor equipped with RPR 3000 Å lamps.

Acknowledgement

One of us (DPC) is thankful to CSIR, New Delhi, for the award of research fellowship.

REFERENCES

1. Fox, M.A. and Chanon, M., "Photoinduced Electron Transfer Reactions : Organic Substrates Part C, Elsevier Publications, New York, 1988.

2. Davidson, R.S. Adv.Phys.Chem., 1983, **19**, 1.

3. Yoshino, A.; Ohashi, M. and Yonezava, T. **J.Chem.Soc.Chem.Commun.**, 1971, **97**; Yoshino, A.; Yamasaki, K.; Yohezawa, T. and Ohashi, M. **J.Chem.Soc.Perkin Trans. I**, 1975, 735; Lewis, F.D. and Petisce, J.R. **Tetrahedron**, 1986, **42**, 6207.

4. Mattes, S.L. and Farid, S. "Organic Photochemistry", Padwa, A.Ed. 1983, **6**, 233, Vol.5.

5. Mizuno, K.; Ikeda, M. and Otsugi, Y. **Tetrahedron Lett.** 1985, **26**, 461; Mizuno, K.; Terasaka, K.; Yasueda, M. and Otsugi, Y. **Chem.Lett.** 1988, 145.

6. Pandey, G.; Kumaraswamy, G. and Bhalerao, U.t., **Tetrahedron Lett.** 1089, **30** and reference cited therein.

7. Gassman, P.G.; Olson, K.d.; Walter, L. and Yamaguchi, r. **J.Am.Chem.Soc.**, 1981, **103**, 4977

8. Pandey, G.; Lakshmaiah, G.; Kumaraswamy, G. and Bhalerao, U.T. **J.Am.Chem.Soc.**, (Accepted).

9 Electron transfer from Organoselenium Compounds was osberved from our laboratory Pandey, G.; Somasekhar, B. and Bhalerao, U.T. **J.Am.Chem.Soc.** 1990, **112**, 5650.

10. Arnold, D.R.; Wong, P.C.; Maroulis, A.J. and Cameron, T.S. **Pure & Appl.Chem.** 1980, **52**, 2609

11. Ronald, F.Z.; Steven, L. and Zui, D. **J.Chem.Soc.Chem.Commun.**, 1970, 1124.

12. Rehm, D. and Weller, A. **Isr. J. Chem.** 1970, **8**, 259.

13. Schiavon, G.; Zecchin, S.; Cogoni, G. and Bontempelli, G. **J.Electroanalyt. Chem.**, 1973, **48**, 425 (**Chem.Abstr.**, 1974, **80**, 33250m); Matschiner, V.H.; Kravise, L. and Krech, F.

Z.Anorg.Chem. 1970, 373, 1 (**Chem.Abstr.** 1970, **72**, 866479a).

14. Masuhara, H. and Mataga, V.N., **Acc.Chem.Res.** 1981, **14**, 312; Simon, J.D. and Peters, K.S. **J.Am.Chem.Soc.** 1982, **104**, 6142; 1983, **105**, 4875.

15 Marcondes, M.E R.; Toscano, V.G. and Weiss, R.G. **J.Am.Chem.Soc.**, 1975, **97**, 4485, **J.Photochem.**, 1979, **10**, 315, 425

16 Pandey, G.; Kumaraswamy, G. and Krishna, A. **Tetrahedron Lett.**, 1987, **28**, 2649.

17 Krishna, A.; Ph D. Thesis submitted to Osmania University, 1988.

18. Hidenobu, O.; Shiro, N and Masaichiro, M **J.Chem.Soc.Perkin Trans.I**, 1979, 2023.

19 Murov, S.L "Hand Book of Photochemistry", Marcel Dekker, New York, 1973, pp 124-125.