The Quenching of Excited States by Tervalent Phosphorus Compounds and Arylamines

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Summary Triphenylphosphine and triphenylamine have been found to quench n–π^* singlet and triplet and π–π^* singlet excited states, the amine being the more efficient and its efficiency being increased by the use of polar solvents.

WE have previously reported[1] that methyl phenyl sulphide and dimethylphenylphosphine are ineffective sources of hydrogen atoms for excited benzophenone and recently it was shown[2] that the unreactivity of the sulphur compound was due to its acting as a quencher.

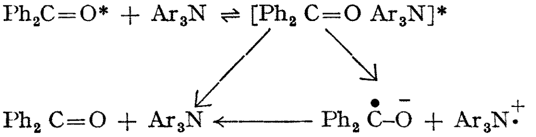
The reactions of tervalent phosphorus compounds with excited carbonyl groups have been further investigated since excited charge-transfer complex and radical-ion formation may well occur, as in the photoreactions of amines with carbonyl compounds. Intramolecular interaction of an excited carbonyl group with a phosphorus atom has been postulated recently[3] to explain the observed photorearrangement of dimethyl β-ketoethyl phosphites to dimethylvinyl phosphates.

The effect of triphenylphosphine and of trimethyl phosphite upon the photoreduction of benzophenone by diphenylmethanol has been investigated. A plot of the reciprocal of the quantum yields for the reaction against the concentration of added phosphorus compound gave a straight line with slope equal to the ratio k_q/k_r where k_q is the bimolecular quenching rate constant and k_r is the bimolecular hydrogen-abstraction rate constant. The results are shown in Table 1. Change of solvent from benzene to acetonitrile has little effect upon the k_q/k_r values. This result contrasts[4] with the solvent-effect observed for the quenching of the same reaction by arylamines. In this latter case, the quenching is believed to be due to excited charge-transfer complex formation, which may be reversible, and the greater efficiency in acetonitrile to be due to dissociation of complex into radical-ions. The formation of the latter has been confirmed by flash-photolysis studies.[5]

TABLE 1

k_q/k_r *Values for the quenching of the photoreduction of benzophenone by diphenylmethanol, by tervalent phosphorus compounds.*

Phosphorus compound	Solvent	k_q/k_r
Triphenylphosphine	Benzene	40
Triphenylphosphine	Acetonitrile	35
Trimethyl phosphite	Benzene	26
Trimethyl phosphite	Acetonitrile	29



In order to elucidate the effect of trivalent phosphorus compounds and arylamines upon n–π^* singlet excited-states, the quenching of the fluorescence of biacetyl was examined. As has been previously shown,[6] triphenylamine quenches the fluorescence in benzene solution. This quenching effect is markedly increased by the use of acetonitrile as solvent (Table 2). Triphenylphosphine was found to be less efficient than triphenylamine when benzene was used as solvent and its quenching ability was not increased by use of acetonitrile as solvent (Table 2).

The photochemistry of fluorenone, in particular its photoreduction by amines, has attracted recent attention.[7a–d] Amines have been shown to quench the fluorescence of the ketone[7c,8,9] and the quenching efficiency is greater in acetonitrile than in benzene solution. Both triphenylamine and triphenylphosphine quench the fluorescence of the ketone and show a similar effect. Once again, the phosphorus compound is the less efficient quencher. The greater quenching efficiency, shown by both compounds in the more polar solvent may well be due to radical-ion formation although doubts as to the validity of this explanation have been expressed. Singer[3] and Cohen[7c] have both shown that fluorenone fluoresces with greater efficiency in acetonitrile than in benzene. From a consideration of the changes in the energies of the excited electronic states of the fluorenone caused by a change in solvent polarity, they have concluded that intersystem crossing between the π–π^* singlet and n–π^* triplet state is relatively inefficient in acetonitrile compared with that in benzene solution. As a result of this varying efficiency, the sum of the unimolecular rates of deactivation of the singlet state will also vary from solvent to solvent and consequently one cannot compare K_q values determined in different solvents.

A further study of the quenching of π–π^* singlets was made by examining the quenching of the fluorescence of anthracene by triphenylphosphine.† The results, shown in Table 2, indicate that some radical-ion formation may occur in acetonitrile but a flash-photolysis study did not support this conclusion. Quenching of the fluorescence of anthracene by triphenylamine could not be studied due to absorption of the latter in the region required for excitation of the hydrocarbon.

TABLE 2

K_q[a] *Values for the quenching of the fluorescence of biacety , fluorenone and anthracene.*

Fluorescer	Quencher	Solvent[b]	$K_q(\text{M}^{-1})$
Biacetyl	Triphenylamine	Benzene	41
Biacetyl	Triphenylamine	Acetonitrile	202
Biacetyl	Triphenylphosphine	Benzene	7
Biacetyl	Triphenylphosphine	Acetonitrile	4
Fluorenone	Triphenylamine	Benzene	45
Fluorenone	Triphenylamine	Acetonitrile	440
Fluorenone	Triphenylphosphine	Benzene	11
Fluorenone	Triphenylphosphine	Acetonitrile	110
Anthracene	Triphenylphosphine	Benzene	21·5
Anthracene	Triphenylphosphine	Acetonitrile	58

[a] $K_q = k_q/k_d$ where k_q = bimolecular quenching rate constant and k_d = sum of the unimolecular decay rate constants.
[b] Solvents were purged with nitrogen for several hours before use.

This work has shown that triphenylamine is a more efficient quencher of n–π^* singlet and triplet and π–π^* singlet states than triphenylphosphine. Evidence for radical-ion formation in the quenching by triphenylphosphine was not obtained and the quenching is believed to occur by excited charge-transfer complex formation. Radical-ion formation probably only occurs in those systems in which the electron donor has a low ionisation potential and in which solvation of the radical-ions is efficient.

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† Anthracene was found to fluoresce with similar efficiency in benzene and acetonitrile solutions (ϕ = 0·25 and 0·28).

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