The Photoreaction of Aromatic Carbonyl Compounds with Amines: Evidence for Electron Transfer from Tertiary Aromatic Amines to Triplet Benzophenone

By **R. F. Bartholomew**, **R. S. Davidson**,* and **P. F. Lambeth**, Department of Chemistry, The University, Leicester LE1 7RH
J. F. McKellar and **P. H. Turner**, Imperial Chemical Industries Limited, Dyestuffs Division, Hexagon House, Blackley, Manchester M9 3DA

Triphenylamine and tri-*p*-tolylamine quench the photoreduction of benzophenone by diphenylmethanol and in the case of triphenylamine, the quenching effect is substantially increased by a change of solvent from benzene to acetonitrile. Flash photolysis of nitrogen-flushed acetonitrile solutions of tri-*p*-tolylamine containing benzophenone, produced the amine radical cation and the radical anion of the ketone. When oxygenated solutions of either the amine alone or amine plus benzophenone were flash-photolysed, only the radical cation of the amine was observed. The lifetime and concentration of the radical cation is increased as the concentration either of oxygen or of benzophenone is increased. One of the modes of decay of the radical cation appears to be reaction with tri-*p*-tolylamine and a rate constant of $3{\cdot}5 \times 10^3$ l mol^{-1} s^{-1} was determined for this process. Nitrogen-flushed acetonitrile solutions of triphenylamine gave, on flash photolysis, an intermediate ($\lambda_{max.}$ 610 nm) identified, from previous work, as a cyclisation product, whereas when benzophenone is present in solution, the amine radical cation is produced. These results support the conclusion that tertiary aromatic amines can donate an electron to triplet benzophenone, and lend some credence to the previous postulate that amines react with triplet ketones by an electron-transfer process.

THERE is substantial evidence for the formation of exciplexes by interaction of singlet excited aromatic hydrocarbons with tertiary amines in non-polar solvents.[1a—c] When polar solvents are used, the interaction leads to complete electron transfer and the amine radical cation and hydrocarbon radical anion are formed.[1c] These species have been successfully identified by application of flash photolysis. There appears to be little evidence for the formation of triplet exciplexes between triplet aromatic hydrocarbons and amines although evidence for radical ion formation by such a process has been presented.[2] In the last few years there have been many reports in which electron transfer from electron donors to singlet[3a—d] excited and triplet[4a—g] ketones has been postulated. Electron transfer from amines has received particular attention. Other systems include interaction of triplet ketones with sulphides,[5] phosphines,[3c,d] and phosphites.[3c]

Emission from exciplexes formed between triplet ketones and amines has not been observed. There is a recorded example of a tertiary amino-group enhancing the phosphorescence lifetime of a carbonyl group; an explanation was not given.[4e] The only evidence for exciplex formation by ketones has been kinetic. Thus the high rate-constants for reaction of triplet ketones with amines has been taken as indicative of exciplex formation.[4a] More recent evidence includes the quenching action of aniline and substituted anilines, 1,4-diazabicyclo[2,2,2]octane, and diphenylamine upon the reduction of fluorenone by triethylamine.[4b] Exciplex formation is also implicated in the reaction of diphenylamine with benzophenone.[4d]

If amines can react with triplet ketones to give exciplexes and/or radical ions, amines which do not contain abstractable hydrogen atoms should act as physical quenchers of the triplet ketone. Examples of such amines acting as quenchers have been reported by Bäckström and Sandros[6] who found that biacetyl phosphorescence is quenched by triphenylamine. More recently the singlet excited state of biacetyl has been shown to be quenched by the amine.[3a,c]

RESULTS AND DISCUSSION

(a) *Quenching Studies*.—The effect of tertiary aromatic amines which do not contain abstractable hydrogen atoms upon the photoreduction of benzophenone by diphenylmethanol was investigated.[4f] If the amines behave as quenchers, the degree of quenching should be

---

[1] (*a*) D. Rehm and A. Weller, *Z. phys. Chem.* (*Frankfurt*), 1970, **69**, 183; H. Knibbe, D. Rehm, and A. Weller, *Ber. Bunsengesellschaft Phys. Chem.*, 1968, **72**, 257; D. Rehm and A. Weller, *ibid.*, 1969, **73**, 834; *Israel J. Chem.*, 1970, **8**, 259; (*b*) M. G. Kuzmin and L. N. Guseva, *Chem. Phys. Letters*, 1969, **3**, 71; (*c*) H. Leonhardt and A. Weller, *Z. phys. Chem.* (*Frankfurt*), 1961, **29**, 277; A. Weller, *Pure Appl. Chem.*, 1968, **16**, 116.

[2] K. H. Grellmann, A. R. Watkins, and A. Weller, *J. Luminescence*, 1970, **1**, **2**, 678.

[3] (*a*) N. J. Turro and R. Engel, *Mol. Photochem.*, 1969, **1**, 142; *J. Amer. Chem. Soc.*, 1969, **91**, 7113; (*b*) S. G. Cohen and J. B. Guttenplan, *Chem. Comm.*, 1969, 2125; L. A. Singer, *Tetrahedron Letters*, 1969, 923; R. A. Caldwell, *ibid.*, p. 2121; (*c*) R. S. Davidson, and P. F. Lambeth, *Chem. Comm.*, 1969, 1099; (*d*) L. D. Wescott, H. Sellers, and P. Poh, *ibid.*, 1970, 586.

[4] (*a*) S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, 1967, **89**, 164; S. G. Cohen and J. I. Cohen, *ibid.*, p. 164; *J. Phys. Chem.*, 1968, **72**, 3782; S. G. Cohen and A. D. Litt, *Tetrahedron Letters*, 1970, 837; (*b*) G. A. Davis and S. G. Cohen, *Chem. Comm.*, 1970, 622; S. G. Cohen and G. Parsons, *J. Amer. Chem. Soc.*, 1970, **92**, 7603; (*c*) G. A. Davis, P. A. Carapellucci, K. Szoc, and J. D. Gresser, *ibid.*, 1969, **91**, 2264; G. Irick and G. C. Newland, *Tetrahedron Letters*, 1970, 4151; A. Padwa and R. Gruber, *J. Amer. Chem. Soc.*, 1970, **92**, 100, 107; C. C. Wamser, G. S. Hammond, C. T. Chang, and C. Baylor, *ibid.*, p. 6362; R. S. Davidson and P. R. Steiner, *J. Chem. Soc.* (*C*), 1971, 1682; *Chem. Comm.*, 1971, 1115; (*d*) C. Pac, H. Sakurai, and T. Tosa, *Chem. Comm.*, 1970, 1311; (*e*) P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, 1969, **91**, 3085; (*f*) R. S. Davidson and P. F. Lambeth, *Chem. Comm.*, 1968, 511; (*g*) R. S. Davidson, P. F. Lambeth, J. F. McKellar, P. H. Turner, and R. Wilson, *ibid.*, 1969, 732; (*h*) W. M. Moore and M. Ketchum, *J. Amer. Chem. Soc.*, 1962, **84**, 1368.

[5] J. B. Guttenplan and S. G. Cohen, *Chem. Comm.*, 1969, 247.

[6] H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, 1958, **12**, 823.

related to the concentration of added amine. From the Stern–Volmer equation[4h] (A) the rate constant

$$
\begin{array}{lll}
 & & \text{Rate} \\
\mathrm{Ph_2CO} \longrightarrow \mathrm{Ph_2CO}(S_1) \longrightarrow \mathrm{Ph_2CO}(T_1) & (1) & \mathrm{I} \\
\mathrm{Ph_2CO}(T_1) + \mathrm{Ph_2CHOH} \xrightarrow{k_r} 2\mathrm{Ph_2\dot{C}OH} & (2) & k_r\,[\mathrm{Ph_2CHOH}][\mathrm{Ph_2CO}(T_1)] \\
\mathrm{Ph_2CO}(T_1) + \text{Amine} \xrightarrow{k_r} \text{Exciplex} & (3) & k_q\,[\text{Amine}][\mathrm{Ph_2CO}(T_1)] \\
\text{Exciplex} \longrightarrow \mathrm{Ph_2CO} + \text{Amine} & (4) & \\
\mathrm{Ph_2CO}(T_1) \xrightarrow{k_d} \mathrm{Ph_2CO}(S_0) & (5) & k_d\,[\mathrm{Ph_2CO}(T_1)] \\
2\mathrm{Ph_2\dot{C}OH} \longrightarrow \begin{array}{c}\mathrm{Ph_2COH} \\ | \\ \mathrm{Ph_2COH}\end{array} & (6) &
\end{array}
$$

k = Rate constant for indicated reaction.

$$\frac{\phi\text{Act}}{\phi\text{React}} = 1 + \frac{k_q/k_r[\mathrm{Q}]}{k_d/k_r + [\mathrm{Ph_2CHOH}]} \qquad \text{(A)}$$

ϕAct = Quantum yield of unquenched reaction; ϕReact = quantum yield of quenched reaction.

for quenching can be obtained. Quenching by triphenylamine and tri-*p*-tolylamine of the reduction in benzene and of the reduction in acetonitrile solution by triphenylamine was investigated. Values for k_q of $7{\cdot}6 \times 10^8$, $8{\cdot}4 \times 10^9$, and $1{\cdot}4 \times 10^{10}$ l mol^{-1} s^{-1} respectively were obtained for these systems.[7] The greater efficiency of tri-*p*-tolylamine may be due to its lower ionisation potential[8] although there is the possibility that since its triplet energy (67·1 kcal mol^{-1}) is sligtly lower than that of benzophenone (68·9 kcal mol^{-1})[9] that quenching was a result of triplet energy transfer. This process cannot occur with triphenylamine since its triplet energy (70·1 kcal mol^{-1}) is greater than that of the ketone[9] (68·5 kcal mol^{-1}).[10]

The quenching of the singlet excited states of aromatic hydrocarbons by electron donors becomes more efficient as the polarity of the solvent is increased.[1b,11] A similar effect was found for the quenching by triphenylamine of the reduction of triplet benzophenone by diphenylmethanol; k_q for quenching in acetonitrile solution is higher than that for quenching in benzene solution. Turro and Engel have reported that the quenching of biacetyl phosphorescence by tertiary amines, becomes more effective as the polarity of the solvent increased.[3a] This solvent effect is compelling evidence for tertiary amines quenching triplet ketones by an electron-transfer mechanism.

(b) *Flash-photolysis Results*.—To gain positive evidence for the electron-transfer mechanism a system was sought in which radical ions of reasonable stability would be formed so that they could be easily detected by flash photolysis. Such a system was found to be the reaction of benzophenone with tri-*p*-tolylamine in acetonitrile solution.[4g] This amine is known from polarography to give a relatively stable radical cation.[8]

The absorption spectra of the intermediate produced on flash photolysis of (*a*) nitrogen-flushed acetonitrile solution of tri-*p*-tolylamine containing benzophenone,

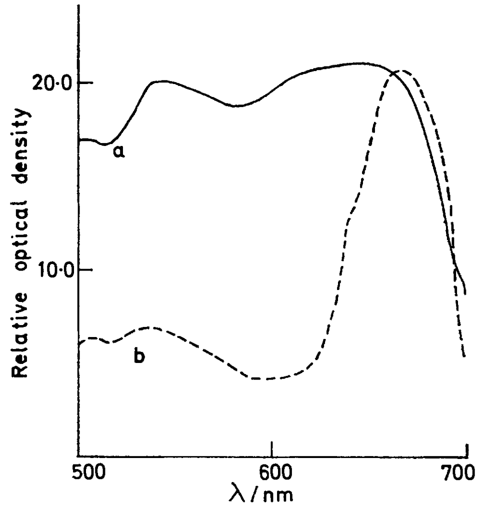


FIGURE 1 Absorption spectra of intermediates present 25 μs after flash photolysis of acetonitrile solutions of tri-*p*-tolylamine and benzophenone: a, nitrogen-flushed solutions; b, air-saturated solutions

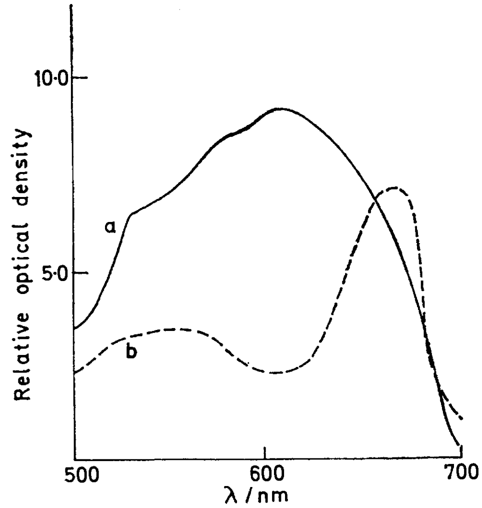


FIGURE 2 Absorption spectra of intermediates present 25 μs after flash photolysis of acetonitrile solutions of tri-*p*-tolylamine: a, nitrogen-flushed solution; b, air-saturated solution

(*b*) air-flushed acetonitrile solution of tri-*p*-tolylamine containing benzophenone, (*c*) a nitrogen-flushed acetonitrile solution of tri-*p*-tolylamine, and (*d*) an air-flushed acetonitrile solution of tri-*p*-tolylamine are shown in Figures 1 and 2. The kinetics of the decay

---

[7] A value of 9×10^6 l mol^{-1} s^{-1} was used for k_r; P. J. Wagner, *Mol. Photochem.*, 1969, **1**, 71.

[8] E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, and R. N. Adams, *J. Amer. Chem. Soc.*, 1966, **88**, 3498.

[9] These values were obtained for the ketone and amine in ether–isopentane–ethanol (5 : 5 : 2) at 77 K. They may well be different in hydrocarbon solvents; R. F. Bartholomew and P. H. Turner, unpublished results.

[10] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1964, **86**, 4537.

[11] H. Leonhardt and A. Weller in 'Luminescence of Organic and Inorganic Materials,' eds. H. P. Kallman and G. M. Spruck, Wiley, New York, 1962, p. 74.

of the tri-*p*-tolylamine radical cation, generated by flash photolysis of aerated acetonitrile solutions of the amine in the presence and absence of benzophenone, were investigated and the results are collated in the Table.

Kinetics of the decay of the tri-*p*-tolylamine radical cation generated by flash photolysis of aerated acetonitrile solutions of tri-*p*-tolylamine in the presence and absence of benzophenone

$[Ph_2CO]/\text{M}$	$[\text{Amine}]/\text{M}$	Air/O_2	Kinetics	Half-life/ μs	D
	6×10^{-4}	Air	Complex	570	0·3
	1×10^{-3}	Air	Complex	510	0·5
	3×10^{-3}	Air	Complex	940	0·5
	1×10^{-2}	Air	Complex	670	0·6
1×10^{-4}	1×10^{-4}	Air	Complex	237	0·8
1×10^{-4}	3×10^{-4}	Air	Complex	420	1·0
1×10^{-4}	1×10^{-3}	Air	Complex	775	1·3
1×10^{-4}	3×10^{-3}	Air	Complex	800	1·6
3×10^{-4}	1×10^{-4}	Air	Complex	316	0·5
3×10^{-4}	3×10^{-4}	Air	Complex	712	1·0
3×10^{-4}	1×10^{-3}	Air	Complex	750	1·4
3×10^{-4}	3×10^{-3}	Air	Complex	850	1·8
1×10^{-3}	1×10^{-4}	Air	Complex	750	1·0
1×10^{-3}	3×10^{-4}	Air	Complex	3750	1·9
1×10^{-3}	1×10^{-3}	Air	1st order	170,000	>2
1×10^{-3}	3×10^{-3}	Air	1st order	76,000	>2
3×10^{-3}	1×10^{-4}	Air	Complex	900	0·9
3×10^{-3}	3×10^{-4}	Air	Complex	5000	1·9
3×10^{-3}	1×10^{-3}	Air	1st order	160,000	>2
3×10^{-3}	3×10^{-3}	Air	1st order	230,000	>2
	1×10^{-3}	O_2	Complex	2250	1·1
	1×10^{-2}	O_2	Complex	2500	1·1

D = Optical density at zero time as obtained by extrapolation.

The tri-*p*-tolylamine radical cation has an absorption at 670 nm[12] and Figure 2b shows that flash photolysis of aerated acetonitrile solutions of the amine produced an intermediate with a similar absorption spectrum. This absorption spectrum is much stronger when benzophenone is present in solution (see Figure 1b). We assign the absorption spectrum to that of the amine radical cation.

From the fact that benzophenone enhances the amount of radical cation formed, it is concluded that this species can be produced by reaction of the triplet ketone with the ground-state amine. However, under the experimental conditions employed some direct excitation of the amine occurs which will result in amine radical cation formation. Thus the amount of radical cation formed under the conditions for recording the spectrum in Figure 1b will be the sum of that produced by direct excitation of the amine and that by the benzophenone-sensitised reaction. It could be argued that the benzophenone is not acting as a photochemical sensitiser but is favouring photo-induced electron ejection from the amine by acting as an electron acceptor. The ability of the ketone to facilitate the reaction in this way will be offset by its light-filtering action. Further evidence that benzophenone is acting as a photochemical sensitiser can be gained from the Table. The amount of amine radical cation formed (as judged by the D values) by direct excitation of the amine increases when the oxygen concentration is increased, *i.e.*, when oxygen-saturated rather than air-saturated solutions are used which corresponds to a change from $2 \times 10^{-3}\text{M}$ to $1 \times 10^{-2}\text{M}$-oxygen. The effect of added benzophenone, a much poorer electron acceptor than oxygen, is much more dramatic. Thus a change in concentration of the ketone from $3 \times 10^{-4}\text{M}$ to $1 \times 10^{-3}\text{M}$ in the presence of $1 \times 10^{-3}\text{M}$-amine causes a large increase in the amount of radical cation formed. We therefore conclude that on irradiation of oxygenated solutions of the amine and benzophenone reactions (7)—(12) can occur. As yet, no positive evidence has been obtained for the formation of ground-state complexes between tertiary amines and aromatic ketones[13c] and therefore the extent of participation of such species cannot be ascertained. However, it is known that tertiary amines form complexes with oxygen and from previous work[13b] it seems probable that the amine radical cation formed in the absence of benzophenone is derived from such species.

$$\mathrm{Ph_2CO} \longrightarrow \mathrm{Ph_2CO}(S_1) \longrightarrow \mathrm{Ph_2CO}(T_1) \tag{7}$$

$$\mathrm{Ph_2CO}(T_1) + \mathrm{Ar_3N} \longrightarrow \mathrm{Ph_2\dot{C}{-}\bar{O}} + \mathrm{Ar_3N^{+\cdot}} \tag{8}$$

$$\mathrm{Ph_2\dot{C}{-}\bar{O}} + \mathrm{O_2} \longrightarrow \mathrm{Ph_2CO} + \mathrm{O_2^{-\cdot}} \tag{9}$$

$$\mathrm{O_2^{-\cdot}} + \mathrm{Ar_3N^{+\cdot}} \longrightarrow \mathrm{Ar_3N} + \mathrm{O_2} \tag{10}$$

$$\mathrm{Ar_3N} \xrightarrow{h\nu} \mathrm{Ar_3\overset{+\cdot}{N}} + \mathrm{e} \tag{11}$$

$$\mathrm{e} + \mathrm{O_2} \longrightarrow \mathrm{O_2^{-\cdot}} \tag{12}$$

In the experiments carried out with nitrogen-flushed acetonitrile solutions containing the amine and benzophenone, it was expected that the benzophenone radical anion ($\lambda_{\text{max.}}$ 620 nm) besides the amine radical cation should be formed. The absorption spectrum obtained (Figure 1a) showed species absorbing over the range in which the radical cations and anions absorb. When the spectrum of the radical cation (Figure 1b) was subtracted from the spectrum in Figure 1a, the spectrum shown in Figure 3 was obtained. This spectrum compares very favourably with that reported by Porter and Wilkinson[14] for the benzophenone radical anion. We therefore conclude that in air-free solution both the ketone radical anion and amine radical cation are present. Comparison of Figures 1b and 2b shows that benzophenone enhances the yield of intermediates. If benzophenone had been serving only as a source of triplet energy a spectrum similar to that in Figure 2a, only with increased intensity, would have been obtained. The intermediate formed a flash photolysis of the amine in air-free solution is thought, on the basis of the previous work[15] on triphenylamine, to have the structure

---

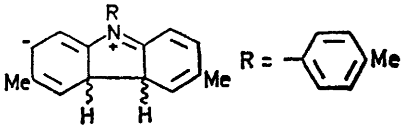
[12] S. Granick and L. Michaelis, *J. Amer. Chem. Soc.*, 1940, **62**, 2241; G. N. Lewis and D. Lipkin, *ibid.*, 1947, **64**, 2801.

[13] (*a*) S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, 1968, **90**, 165; R. F. Bartholomew, R. S. Davidson, and P. F. Lambeth, unpublished observations; (*b*) H. Tsubomora and R. S. Mulliken, *J. Amer. Chem. Soc.*, 1960, **82**, 5966; H. Hori, H. Itoi, and H. Tsubomora, *Bull. Chem. Soc. Japan*, 1970, **43**, 3765.

[14] G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, 1961, **57**, 1686.

[15] K. H. Grellman, G. A. Sherman, and H. Linschitz, *J. Amer. Chem. Soc.*, 1963, **85**, 1881.

(1). It is unlikely to be that of the triplet state of the amine since, from the value of 531 nm for the maximum absorbance of the triphenylamine triplet,[16] the position of maximum absorbance of triplet tri-*p*-tolylamine is probably well below 610 nm.



(1)

The kinetic results showed that amine radical cation formation is favoured (as measured by its concentration after the photolysis flash) by (*a*) an increase in oxygen concentration and (*b*) an increase in benzophenone concentration. The favourable effect of increasing oxygen concentration may be a direct result of either (*a*) increasing the concentration of the ground-state complex between the amide and oxygen, and thereby increasing the number of excited molecules available for electron transfer, or (*b*) the increase in concentration in the electron acceptor which enables the electron-transfer reaction to compete more successfully with the recombination (14) of the amine radical cation and the ejected electron. As discussed earlier, benzophenone may also

$$Ar_3N \xrightarrow{h\nu} Ar_3N^{+\cdot} + e \qquad (13)$$

$$Ar_3N^{+\cdot} + e \longrightarrow Ar_3N \qquad (14)$$

react in this way, but what is more likely is that increasing the benzophenone concentration increases the concentration of the ketone triplets which abstract an electron from the amine.

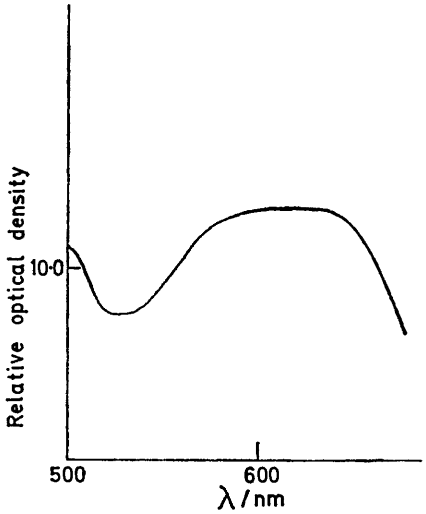


FIGURE 3 Absorption spectrum obtained by subtracting the spectrum in Figure 1b from that in Figure 1a

Although in the majority of cases the kinetics of decay of the radical cation were complex, high amine and benzophenone concentrations resulted in first-order kinetics being observed, *i.e.*, under these conditions the rate of decay of the radical cation is directly proportional to its concentration [equation (15)]. The rate

$$\text{Rate} = k^1[\text{TPTA}^{+\cdot}] \qquad (15)$$

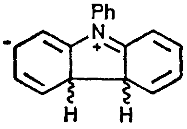
$$\text{TPTA}^{+\cdot} = \text{Radical cation of tri-}p\text{-tolylamine}$$

constant in this expression is a composite rate constant; *i.e.*, it is dependent upon an amine concentration term and this is shown by the fact that it changes in value from 4·0 s^{-1} to 9·1 s^{-1} when the amine concentration is changed from 1×10^{-3}M to 3×10^{-3}M. Thus the expression for the rate of decay becomes (16), which

$$\text{Rate} = k[\text{Amine}][\text{TPTA}^{+}] \qquad (16)$$

implies that the radical cation decays by reaction with the ground-state amine. There are many known examples of amine radical cations reacting in this way.[17,18] In the case of the reaction of the triphenylamine radical cation (generated polarographically) the rate constant for its reaction with triphenylamine has been determined as $2{\cdot}4 \times 10^3$ l mol^{-1} s^{-1}.[18] The bimolecular rate constant for decay of the tri-*p*-tolylamine radical cation came out as $3{\cdot}5 \times 10^3$ l mol^{-1} s^{-1}.

Another system, which was studied in less detail, was the reaction of benzophenone with triphenylamine in acetonitrile solution. When air-saturated solutions of the amine and of amine mixed with benzophenone were flash-photolysed, no intermediate species could be observed. When a nitrogen-flushed solution of the amine was flash-photolysed, an intermediate having maximum absorption at 610 nm was observed (see Figure 4). This intermediate has been previously identified as the zwitterion (2).[15] When nitrogen-flushed acetonitrile solutions containing triphenylamine and benzophenone were flash-photolysed, a much stronger absorption spectrum (Figure 5) than the one in Figure 4 was obtained, *i.e.* the benzophenone cannot have acted as a light filter, but has promoted a photochemical reaction. The spectrum in Figure 5 is similar to the published spectrum for the triphenylamine radical cation,[19] although it appears to be a little distorted by the absorption of the '610' intermediate. Subtraction of the absorption spectrum of this species from the spectrum in Figure 5 leaves a spectrum (Figure 6) which is very similar to that of the triphenylamine radical cation. Unfortunately it is impossible to tell



(2)

---

[16] G. C. Terry, V. E. Uffindell, and F. W. Willetts, *Nature*, 1969, **223**, 1050.

[17] J. F. McKellar, *Proc. Roy. Soc.*, 1965, *A*, **287**, 363; *Photochem. and Photobiol.*, 1967, **6**, 287.

[18] R. F. Nelson and R. N. Adams, *J. Amer. Chem. Soc.*, 1968, **90**, 3925.

[19] T. Shida and W. H. Hamill, *J. Chem. Phys.*, 1966, **44**, 2369.

whether there is any absorption due to the benzophenone radical anion. If this species was present, it would not appreciably distort the spectrum of the amine radical cation.

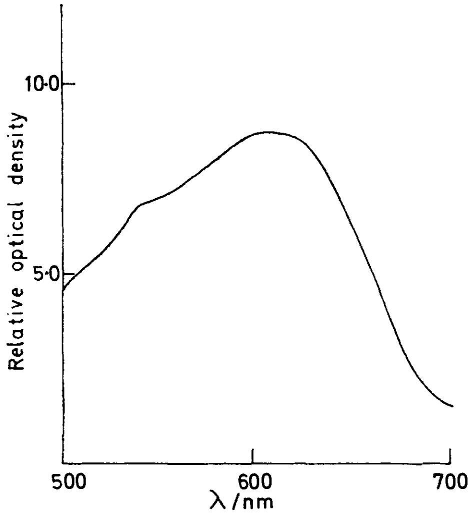


FIGURE 4 Absorption spectrum of intermediates present 25 μs after flash photolysis of triphenylamine in nitrogen-flushed acetonitrile solutions and in the absence of benzophenone

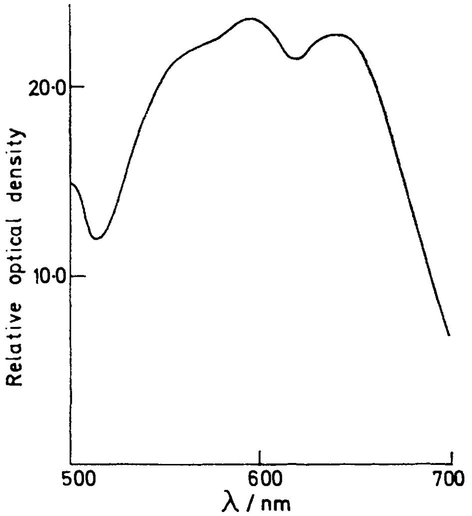


FIGURE 5 Absorption spectrum of intermediates present 25 μs after flash photolysis of triphenylamine in nitrogen-flushed acetonitrile solutions and in the presence of benzophenone

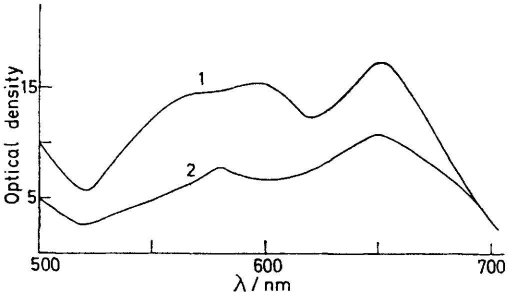


FIGURE 6 Absorption spectra 1, obtained by subtraction of spectrum in Figure 4 from that in Figure 5; and 2, of the triphenylamine radical cation (from ref. 19)

Conclusion.—The reported kinetic and flash results on the photoreactions of benzophenone with tertiary aromatic amines support the view that the triplet ketone and amine can undergo an electron-transfer reaction. For the cases studied, electron transfer appears to go to completion in acetonitrile solution, and radical ions are formed. In less polar solvents, the electron transfer may well not be complete and an ' exciplex ' will be formed.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus and were uncorrected.

Reagents.—AnalaR benzene was dried with sodium and distilled under dry nitrogen before use. Acetonitrile was purified as described.[20] Reagent grade benzophenone (B.D.H.) was used without further purification [recrystallisation from light petroleum (b.p. 60—80°) did not alter its m.p.]. Triphenylamine was recrystallised from ethyl acetate to m.p. 127° (lit.,[21] 127°). Tri-*p*-tolylamine was prepared by the method of Walter [22] and had m.p. (from acetic acid) 114—117°.

*Kinetics of Quenching of the Photoreduction of Benzophenone by Diphenylmethanol by Use of Triphenylamine and Tri-*p*-tolylamine as Quenchers.*—The irradiation apparatus consisted of a 125 W Hanovia medium-pressure mercury lamp contained in a water-cooled Pyrex sleeve. The sleeve fitted into a reaction vessel which contained 150 ml of the solution to be irradiated. Dry, oxygen-free nitrogen was bubbled through the reaction mixture for 30 min before irradiation and throughout the irradiations. The rate of reduction of benzophenone was determined by withdrawing samples of the reaction mixture after known irradiation periods, and measuring the amount of benzophenone by i.r. spectroscopy (a Perkin-Elmer 137 infrared spectrophotometer was used). The concentration of benzophenone was obtained from the height of the carbonyl absorption band at 1675 cm^{-1} by means of a standard reference curve which showed how the height of the band varied with the ketone concentration.

The standard reaction mixture (which was also used as the actinometer solution) was a 0·05M solution of benzophenone in benzene containing 0·1M-diphenylmethanol.

The value of k_d/k_r was determined by the method of Moore and Ketchum.[4h] The ratio of the amount of benzophenone used in the standard reaction to that used in reactions containing diphenylmethanol at several concentrations was determined. A plot of the values of the ratio (*i.e.*, ϕAct/ϕReact) against the reciprocal of diphenylmethanol concentration gave a straight line. The intercept gave the quantum yield for the actinometer (ϕAct = 0·9) and from the slope of the line a value for k_d/k_r was obtained.

Values of k_q/k_r were determined as follows: values of ϕAct/ϕReact for the reduction run in the presence of various amount of the amines were determined. Plots of the ϕAct/ϕReact values against amine concentration gave straight lines. From the slope of these lines values of k_q/k_r were calculated [see equation (A)].

---

[20] J. F. O'Donnell, J. T. Ayres, and C. K. Mann, *Analyt. Chem.*, 1965, **37**, 1161.

[21] J. Piccard and M. Kharasch, *J. Amer. Chem. Soc.*, 1918, **40**, 1074.

[22] R. I. Walter, *J. Amer. Chem. Soc.*, 1955, **77**, 5999.

Flash-photolysis Experiments.—The apparatus was of conventional design and included both photographic and photoelectric attachments for detection of transient species. Both Pyrex and quartz reaction vessels were used. These were 22 cm long and 1·5 cm in diameter. The photolysis and spectroscopic lamps were constructed of quartz and were attached to banks of capacitors of capacitance 10 and 2 μF respectively. The photolysis and spectroscopic lamps were discharged at 9 and 10 kV, and the lifetimes of the flashes at half-peak intensity were *ca.* 45 and 50 μs respectively.

For the photographic technique, the spectra were obtained on a Hilger medium quartz spectrograph, and were recorded on Kodak I.R. E.R. photographic plates, with four exposures. Plate photometry was carried out on a Joyce–Loebl double-beam recording microdensitometer.

A Hilger photo-electric scanning unit (type E720) incorporating an R.C.A. I.P.28 photomultiplier was used for the photoelectric measurements. The signal from the photomultiplier was directly coupled to an oscilloscope and photographed with an oscilloscope camera on Polaroid film. The monitoring light source was a d.c. xenon lamp (150 W). The vertical linearity of the oscilloscope response was checked with neutral density filters, which were calibrated on a Unicam SP800 spectrophotometer.

We acknowledge maintenance grants by the S.R.C. (to R.F.B.) and Ipswich County Borough Council (to P. F. L.) and thank Imperial Chemical Industries Limited, Dyestuffs Division, for laboratory facilities (for R. F. B.) under the S.R.C. CAPS scheme.

[1/1860 *Received, 11th October,* 1971]