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TRANSIENT PHOTOCURRENTS INDUCED BY LASER FLASH PHOTOLYSIS OF AROMATIC CARBONYL COMPOUNDS IN SOLUTION

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Summary

Photocurrents induced by 25 ns laser flashes (λ = 347.1 nm) were measured in order to elucidate the mechanism of the reaction of triplet excited benzophenone (BP) and BP derivatives with unsaturated compounds whose triplet energy E_T is lower than that of BP compounds. It was found that the irradiation of BP compounds alone in various solvents gave rise to the formation of transient currents indicating the existence of exciplexes formed by triplet excited BP compounds and ground state solvent molecules. The quantum yields ϕ(i) of free ions increased with increasing dielectric constant ϵ of the solvent. The highest values of ϕ(i) (about 0.1) were obtained with acetonitrile solutions. Upon addition of unsaturated compounds ϕ(i) was reduced in all cases. If E_T of the added compound was lower than E_T of the BP compound, ϕ(i) decreased steadily with increasing additive concentration (*e.g.* in the case of styrene). If, however, E_T of the unsaturated compound was higher than E_T of the ketones (such as in the cases of methyl methacrylate and acrylonitrile), ϕ(i) was only slightly decreased and levelled off with increasing additive concentration. Thus, it was concluded that free ions were formed stemming from the interaction of unsaturated compounds with triplet excited BP compounds. From this finding it was inferred that exciplexes with CT character are generated which precede the formation of free ions. The following ketones were used: benzophenone (BP), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 3,3',4,4'-tetramethoxycarbonylbenzophenone (TMCB).

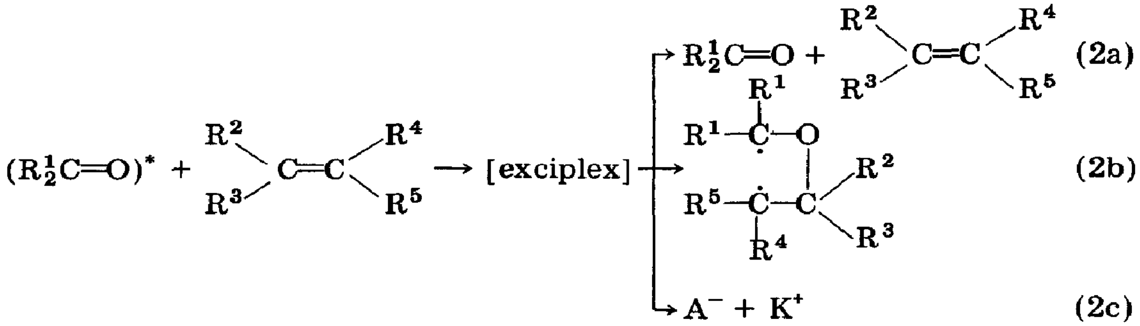
As a standard reaction pertaining to the formation of photocurrents the reaction ^{3}TMCB* + diethylaniline (DEA) was used. Its rate constant was determined as $(7.5 \pm 1) \times 10^9$ M^{-1} s^{-1}.

Introduction

Benzophenone (BP) and several of its derivatives have been used frequently as photosensitizers for the initiation of free radical reactions [1 - 5], especially for the initiation of the free radical polymerization of various unsaturated compounds. Free radicals are generated by the reaction of the triplet excited sensitizer with a hydrogen donor present in the system:

$$^{3}S^{*} + RH \longrightarrow \cdot SH + R\cdot \qquad (1)$$

The application of BP compounds as polymerization sensitizers is, however, limited owing to the high reactivity of many monomers towards triplet excited BP derivatives. Typical rate constants are shown in Table 1. The mechanism of these reactions has been the subject of various publications [6 - 12]. Rate constants pertaining to encounter-controlled reactions ($k > 10^9$ M^{-1} s^{-1}) can be correlated to systems where triplet energy transfer is feasible (E_T(olefin) < E_T(ketone)). In order to interpret smaller but still rather high reactivities as indicated in Table 1 it was assumed [6 - 9] that an exciplex is formed between the excited carbonyl group and the unsaturated compound which is converted to a biradical (reaction (2b)) or deactivated by reforming the starting compounds (reaction (2a)):



It was assumed that the complex possesses substantial charge transfer character and that the olefin is acting as an electron donor [6 - 9].

On certain systems [13 - 15] it has been demonstrated during recent years that the state of charge transfer is strongly dependent on the polarity of the solvent. Thus the completion of charge transfer may be accelerated with increasing solvent polarity in the way that in highly polar solvents free solvated ions are formed as indicated by eqn. (2c). In contrast, from the detection of free ions the existence of CT complexes can be inferred, a possibility which we considered as relevant to the question concerning the mechanism of the interaction of certain unsaturated compounds with triplet excited ketones.

As stated by Mataga *et al.* [13] ionic dissociation is possible if the free energy of the final ionic state is lower than that of the initial dissociative state. Calculated free energy values have led to the understanding of ionic dissociation in various systems such as BP–diethylaniline [14]. Another important conclusion of that work [14] was that the quantum yield of free ion formation may be strongly influenced by processes competing with ionic dissociation. Concerning unsaturated compounds such as those compiled in Table 1, data necessary to calculate free energies were not available. Thus, a prediction concerning the ionic dissociation of the CT complexes of BP deriv-

TABLE 1

Rates of quenching of triplet ketones

Sensitizer	Unsaturated compound	Solvent	$k_q(M^{-1} s^{-1})$	Ref.
3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA)	Styrene	Acetone	7.4×10^9	4
	Vinylpyrrolidone	Acetone	6.5×10^9	4
	Vinyl acetate	Acetone	1.4×10^8	4
	Methyl methacrylate	Acetone	1.1×10^8	4
	Acrylonitrile	Acetone	5.0×10^7	4
Benzophenone (BP)	Styrene	Benzene	3.3×10^9	4
	Methyl methacrylate	Benzene	6.9×10^7	4
	Acrylonitrile	Benzene	3.4×10^7	4
	Isobutylene	Benzene	3.0×10^7	8
	Vinyl acetate	Benzene	5.4×10^6	4
Butyrophenone	Methyl acrylate	Benzene	4.0×10^8	6
	Vinyl isobutyl ether	Benzene	8.6×10^7	6
	Vinyl acetate	Benzene	2.0×10^7	6

atives possibly formed with unsaturated compounds could not be made. We therefore thought that we could contribute empirically to the clarification of the question of CT complex formation by photocurrent measurements.

Experimental part

Materials

The purification of the monomers and of benzophenone (Aldrich 99%) and 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (Aldrich 99%) (BTDA) has been described previously [5]. The 3,3′,4,4′-tetramethoxycarbonylbenzophenone (TMBC) (m.p. 92 °C) was obtained by esterification of BTDA [2]. Diethylaniline (DEA) (Merck, p.a. 99%), pentan-1-ol (Merck, p.a. 99%) and acetone (Merck, p.a.) were distilled under a nitrogen atmosphere via a splitting tube column. Acetone was dried with CaH_2 beforehand. Acetonitrile (Merck, 99.7% was refluxed over P_2O_5 for 18 h and was distilled from K_2CO_3 via a Vigreux column and finally via a splitting tube column [16]. Dichloromethane (Merck, p.a. 99.5% was washed with $NaHCO_3$ solution (5%) and with water. After drying with $CaCl_2$ and CaH_2 it was distilled via a splitting tube column.

Irradiations

Solutions of BP, TMCB and BTDA were de-aerated by bubbling with purified argon and irradiated in quartz cells with 25 ns flashes of 347.1 nm light of a frequency-doubled ruby laser (Korad model K1QS2). For transient absorption measurements a xenon lamp (Osram XBO 450 W) was used as light source for the analysing light. For photocurrent measurements a photoconductivity cell made of rectangular Pyrex tubing with 2 mm × 6 mm inner area was used. The platinum electrodes were spaced approximately 4 mm apart. They had small holes to allow the solution to flow through the cell. The platinum plates were placed parallel to the photolysing light beam which irradiated the solution between them. Battery voltages up to 600 V were applied. The load resistor was 470 Ω. The time constant was about 100 ns, the cell constant 1.5 cm^{-1}. Further details have been described elsewhere [17].

Dosimetry

The potassium ferrioxalate actinometer was used [18] ($\phi(\text{Fe}^{2+}) = 1.20$). Normal laser operations yielded about 4×10^{16} photons per flash.

Determinations of quantum yields

Quantum yields $\phi(\text{i})$ of free ions were calculated on the basis of the maximum photocurrent measured after the flash corresponding to an ion concentration c_i (in M):

$$c_\text{i} = \frac{\Delta U}{2\,K\,\mu} \tag{3}$$

with $K = U_\text{B}R_\text{L}F/10^3k_\text{c}$, where ΔU is the signal voltage (V), U_B is the battery voltage (V), R_L is the load resistor (Ω), k_c is the cell constant (cm^{-1}), and $F = 96\,500$ A s. Equal mobility μ ($\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$) and equal concentrations of positive and negative ions (of one charge per ion) were assumed. If the absorbed dose D_abs is expressed in einstein l^{-1}, the quantum yield is $\phi(\text{i}) = c_\text{i}/D_\text{abs}$. The ion yield measured with the system BP–DEA was used as a standard value for the determination of $\phi(\text{i})$ values during the other experiments. The quantum yield of free ions for this system was taken as 1.0 [14]. It was assumed that all ions considered in this work have about the same mobility.

Results

TMCB(BP)–DEA–CH_3CN

Measuring transient absorption spectra Mataga *et al.* [14] found that ionic dissociation occurs with a quantum yield of about 1 upon irradiating the system BP–DEA–CH_3CN with 347 nm laser flashes. We found that a large photocurrent is generated after irradiating acetonitrile solutions of TMCB or BP (7×10^{-4} M) and DEA. The decay of the absorption of TMCB or BP triplets is correlated to the increase of the photocurrent. Following the decay of the absorption at 535 nm and the increase of the photocurrent a rate constant for the reaction

$$^3\text{TMCB}^* + \text{DEA} \xrightarrow{k_\text{DEA}} \text{K}^+ + \text{A}^- \xrightarrow{k_{\text{A}^- + \text{K}^+}} \text{products} \tag{4}$$

$k_\text{DEA} = (7.5 \pm 1) \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$ was evaluated. The photocurrent was found to decay according to a second order law. The rate constant $k_{\text{A}^- + \text{K}^+} = (3 \pm 1) \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$ was evaluated at 25 °C. The ion concentration corresponding to the maximum photocurrent after the flash was estimated by assuming an ion mobility of 4×10^{-4} cm^2 V^{-1} s^{-1}. With the latter value a quantum yield of free ions of about 1 was obtained.

As acrylonitrile was added to acetonitrile solutions of BP and DEA the photocurrent decreased. Figure 1 shows the ratio of the maximum photocurrents measured in the absence and presence of acrylonitrile as a function of the acrylonitrile concentration. From the slope of the straight line $k_q\tau$ = 25 M^{-1} was obtained. The lifetime of BP triplets in a solution containing DEA amounts to 830 ns (obtained from the decay of the absorption at 535 nm). Thus

$$k_q(^3\mathrm{BP}^* + \mathrm{AN}) = 3 \times 10^7\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$$

This value agrees very well with the one reported recently [4] (compare Table 1) which was derived from the dependence of BP triplet lifetimes on the AN concentration in benzene solutions.

It may be concluded that (a) the addition of AN does not cause an additional photocurrent because of its reaction with ^{3}BP* and (b) AN and DEA are competing for BP triplets:

$$^3\mathrm{BP}^* + \mathrm{AN} \longrightarrow \text{products} \qquad (5)$$

$$^3\mathrm{BP}^* + \mathrm{DEA} \longrightarrow [\text{complex}] \longrightarrow \cdot\mathrm{A}^- + \cdot\mathrm{K}^+ \qquad (6)$$

BP, TMCB and BTDA in different solvents

The irradiation of dilute solutions of BP, BTDA and TMCB in solvents of different polarity yielded photocurrents in all cases except in dichloromethane. A typical oscilloscope trace demonstrating rise and decay of the photocurrent in an acetonitrile solution of TMCB is shown in Fig. 2. The formation of ions occurred according to a first order law. The half-life of ion formation increased with increasing polarity of the solvent as shown in Table 2, column 5. The rate of ion formation was several times faster than the rate of decay of ketone triplets as measured by following the decrease of the T–T absorption at 535 nm (see Table 2, column 6).

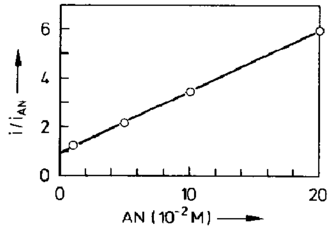
The ion yield is strongly dependent on the dielectric constant ϵ as shown in Table 2, column 4. In the case of dichloromethane no free ions could be detected within the error limit. If free ions are generated at all in this case, $\phi(\mathrm{i})$ is certainly smaller than 10^{-3}. With increasing values of ϵ the ion yield increases to $\phi(\mathrm{i}) = 0.1$ in the cases of BTDA and TMCB.

In Fig. 3 it is shown that $\log\{1/\phi(\mathrm{i}) - 1\}$ is proportional to $1/\epsilon$. Thus, the following empirical equation holds for these results:

$$\log\left(\frac{1}{\phi(\mathrm{i})} - 1\right) = \frac{p}{\epsilon} + q \qquad (7)$$

A dependence of $\phi(\mathrm{i})$ on ϵ according to eqn. (7) was found originally by Mataga *et al.* [10, 13] for several systems such as pyrene–dicyanobenzene and pyrene–N,N-dimethylaniline.

With BP the dependence of $\phi(\mathrm{i})$ on ϵ is less pronounced than with TMCB and BTDA. The highest ion yield obtained in this case is only about 0.01.



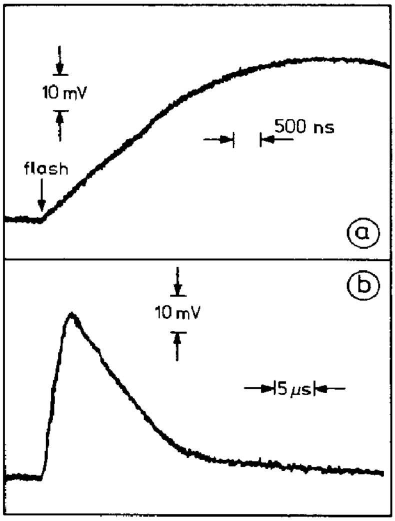


Fig. 1. Ratio of the maximum photocurrents measured in the absence and presence of acrylonitrile *vs.* the acrylonitrile concentration: solvent, oxygen free acetonitrile at 25 °C; [BP] = 7×10^{-4} M, [DEA] = 1×10^{-4} M; absorbed dose per flash, 7.5×10^{-5} einstein l^{-1}.

Fig. 2. Oscilloscope traces demonstrating rise and decay of photocurrents in acetonitrile containing 7×10^{-4} M TMCB: absorbed dose per flash, 5.7×10^{-5} einstein l^{-1}.

TABLE 2

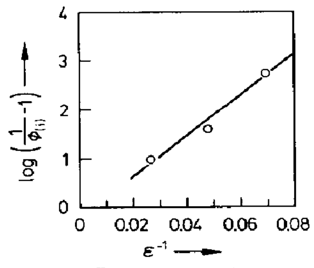
Ion yields obtained with ketones dissolved in different solvents

Solvent	Dielectric constant ϵ of solvent at 25 °C	Ketone	$\phi(i)^{ab}$	Ion formation $\tau_{1/2}$ (µs)	Triplet decay $\tau_{1/2}$ (µs)
Dichloromethane	8.9	TMCB	–	–	1.9
Pentan-1-ol	14.4	TMCB	1.7×10^{-3}	0.3	2.7
Acetone	20.7	TMCB	2.5×10^{-2}	0.4	2.0
Acetonitrile	37.5	TMCB	9.2×10^{-2}	1.6	5.1
Acetone	20.7	BTDA	4.5×10^{-2}	0.2	0.7
Acetonitrile	37.5	BTDA	7.4×10^{-2}	1.7	0.5
Acetone	20.7	BP	1.0×10^{-2}	0.4	2.8
Acetonitrile	37.5	BP	1.5×10^{-2}	0.6	1.5

[TMCB] = 6.0×10^{-4} M; [BTDA] = 7.0×10^{-4} M; [BP] = 7.4×10^{-4} M.
[a] Calculated by assuming $\mu = 4 \times 10^{-4}$ cm^2 V^{-1} s^{-1}.
[b] The error limit amounts to ±20%.

Since the photocurrent depended in all cases on the intensity I of the incident laser light as $i \propto I^1$ it can be inferred that a multiphotonic ionization mechanism is not operative here.

The photocurrent was found to decrease according to a first order law. A typical example is shown in Fig. 4.



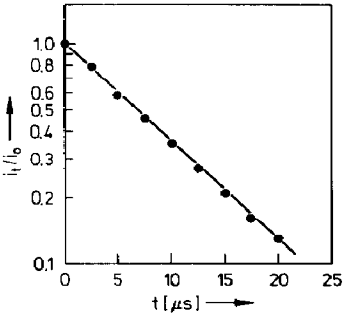


Fig. 3. Plot according to eqn. (7) demonstrating the dependence of the ion yield $\phi(i)$ on the dielectric constant ϵ.

Fig. 4. First order plot of the decay of the photocurrent: TMCB (7×10^{-4} M) in acetonitrile at 25 °C; absorbed dose per flash, 9.3×10^{-5} einstein l^{-1}.

Solutions containing sensitizer and unsaturated compounds

In all cases it was observed that the ion yield decreased upon addition of an unsaturated compound. Figure 5 shows results obtained with acetone solutions containing 6×10^{-4} M TMCB. The strongest diminution was found in the case of styrene. In the cases of AN and MMA the ion yield decreased only relatively weakly and approached a limiting value with increasing monomer concentration, thus indicating the formation of a new species of ions. The photocurrent also decreased according to a first order law when monomer was present in the solution. The lifetime of the decrease differed from the lifetime observed in the absence of monomer (usually the lifetime decreased with increasing monomer concentration). Results found with acetonitrile solutions were similar to those obtained with acetone solutions.

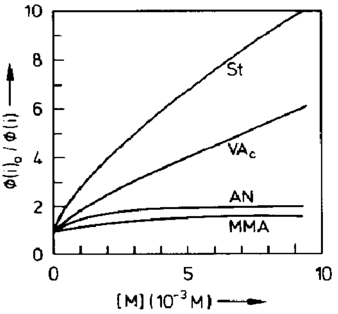


Fig. 5. Relative ion yield obtained in acetone solution as a function of monomer concentration: [TMCB] = 6×10^{-4} M.

Discussion

From the fact that photocurrents were observed with BP, TMCB and BTDA in various solvents it is inferred that associative states (complexes) between ketone and solvent molecules are formed. The possibility of bi- or multiphotonic ionization could be excluded because of the $i \propto I^1$ dependence found in all cases.

$$K + h\nu \longrightarrow K^* \qquad \text{(a)}$$

$$K^* \longrightarrow T \qquad \text{(b)}$$

$$\begin{tikzcd}
 & T + S' \arrow[d, shift right=1.5ex, "k_f^{I}"'] & \\
\text{I} & (T{-}{-}{-}S) \arrow[u, shift right=1.5ex, "k_r^{I}"'] \arrow[r, "k_p^{I}"] \arrow[d, shift right=1.5ex, "k_f^{II}"'] & K + S + \text{energy (or products)} \\
\text{II} & (T^-{-}{-}{-}S^+) \arrow[u, shift right=1.5ex, "k_r^{II}"'] \arrow[r, "k_p^{II}"] \arrow[d, shift right=1.5ex, "k_f^{III}"'] & K + S + \text{energy (or products)} \\
\text{III} & A^- + K^+ \arrow[u, shift right=1.5ex, "k_f^{III}"'] \arrow[d, shift right=1.5ex, "k_f^{IV}"'] & \\
\text{IV} & (A^-{-}{-}{-}K^+) \arrow[u, shift right=1.5ex, "k_r^{IV}"'] \arrow[r, "k_p^{IV}"] & \text{products}
\end{tikzcd}$$

Fig. 6. The reaction sequence.

We think that the results obtained with solutions of ketones can be understood on the basis of the reaction sequence shown in Fig. 6. A series of equilibrium states is assumed which allows the formation of end products or the radiationless deactivation of the excited states via three different routes. After the excitation of ground state ketone molecules K, triplet states T are formed by intersystem conversion within the 25 ns flash. The triplet excited molecules interact with solvent molecules forming complexes I which give rise almost quantitatively to deactivation of T if the solvent is rather unpolar. As the polarity of the solvent increases, the equilibrium state II is reached which possesses CT character and may dissociate into free ions. Evidence for an equilibrium state forming a precursor for free ions is inferred from the finding in all cases studied that free ions were generated much faster than the triplet absorption decayed. Thus it is believed that in the beginning complex I is formed which is partly converted to II. Both the equilibrium concentrations of I and II are rather low compared with the concentration of T. Furthermore, the rate constant k_p^I is relatively large. Thus the probability of the formation of free ions is very low. Unfortunately, the optical absorption of associative states such as I and II appears not to be discriminated from the absorption of T, thus preventing a determination of the various rate constants.

The fact that the photocurrent decayed according to a first order rate law gives evidence for an intermediate state IV whose conversion to products is the rate determining step for the disappearance of free ions.

As far as the interaction of monomer molecules with triplet excited ketones is concerned, the following conclusions can be arrived at by considering the results shown in Fig. 5. The photocurrent is decreased upon adding monomer to the solution in all cases. However, there is a clear distinction between the different monomers.

In the cases of AN and MMA the photocurrent is reduced only weakly. From the fact that a limiting value of $\phi(i)_0/\phi(i)$ at relatively low monomer concentrations is reached it is inferred that, in competition with the formation of the complexes (T---S) and (T^----S^+), complexes such as (T---M) and (T^----M^+) are formed, the latter giving rise to the formation of free ions. Therefore, the photocurrent is not reduced any more by increasing the monomer concentration. Thus, it appears that complex formation plays an important role during the interaction of excited BP and BP derivatives with those unsaturated compounds whose triplet energy is higher than in the case of BP compounds. This conclusion is corroborated by the fact that the curve pertaining to styrene (see Fig. 5) is rather steeply increasing with monomer concentration without approaching a limiting value. Here, triplet energy transfer from excited ketone to the monomer is occurring, thus preventing the formation of complexes I and II and therefore the formation of free ions.

In conclusion it may be stated that photocurrent measurements could be used to obtain evidence for the fact that excited CT states play a certain role during the deactivation of excited triplet states of BP, TMCB and BTDA. The importance of CT states becomes, as expected, greater if the dielectric constant of the solvent increases. Furthermore, evidence could be obtained that certain unsaturated compounds whose triplet energy is higher than those of BP, TMCB and BTDA are deactivated via complex formation.

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