Diazonium salts in photochemistry. I. Quenching of triplet photosensitizers[1]

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Aromatic diazonium tetrafluoroborates have been shown to be excellent triplet quenchers. Typical rate constants obtained using laser flash photolysis are in the $1-10 \times 10^9\ M^{-1}\ s^{-1}$ range in acetonitrile at 300 K. With most sensitizers the interaction leads to the dediazoniation reaction, via either energy transfer or electron transfer mechanisms. In the case of anthracene, where the rate constant for benzenediazonium tetrafluoroborate is $(5.4 \pm 0.3) \times 10^9\ M^{-1}\ s^{-1}$, the reaction involves the transfer of an electron, leading to the formation of anthracene radical-cation, which has been characterized by absorption spectroscopy. High energy sensitizers, such as benzophenone, are believed to lead to aryl cations and nitrogen; the process may involve some degree of charge transfer, since it is somewhat faster when electron donating substituents are present in the diazonium salt.

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On montre que les tétrafluoroborates de diazonium aromatiques sont d'excellents pièges à triplet. Les constantes typiques de vitesse obtenues en utilisant la photolyse flash au laser sont de l'ordre de 1 à $10 \times 10^9\ M^{-1}\ s^{-1}$ dans l'acétonitrile à 300 K. Avec la plupart des sensibilisateurs, l'interaction conduit à une réaction de perte d'une molécule d'azote par l'intermédiaire de mécanismes de transfert d'énergie ou de transfert d'électrons. Dans le cas de l'anthracène, où la constante de vitesse du tétrafluoroborate de benzènediazonium est de $(5,4 \pm 0,3) \times 10^9\ M^{-1}\ s^{-1}$, la réaction implique le transfert d'un électron et conduit à la formation d'un cation radicalaire anthracène, que l'on a identifié par la spectroscopie d'absorption. On pense que les sensibilisateurs à haute énergie, tels la benzophénone, conduisent à des cations aryliques et à l'azote; la réaction peut impliquer un certain degré de transfert de charge puisqu'elle est en quelque sorte plus rapide quand des substituants électrodonneurs sont présents dans le sel de diazonium.

[Traduit par le journal]

Introduction

The involvement of diazonium salts in photochemical reactions has been the subject of a number of studies (1–22); however, many fundamental aspects remain, at best, obscure. For example, we find that, while photosensitized processes have been examined in several systems (8, 10–12, 14, 17, 19, 21–23), only in the case of singlet pyrene have a few rate constants been determined (12).

We have recently started work on a project involving the study of the mechanism and kinetics of a wide range of photoreactions of diazonium salts. We find that the total lack of knowledge of quenching rates, particularly in the case of the triplet state, makes any serious analysis of reaction mechanisms virtually impossible. Most photosensitizers induce the loss of molecular nitrogen from the diazonium salt; however, several mechanisms can lead to this result. For instance, energy transfer can lead to an heterolytic mechanism involving the intermediacy of aryl cations. On the other hand, electron transfer can lead to homolytic pathways via diazenyl radicals which decompose to give phenyl radicals and nitrogen. The photoreduction of diazonium salts can take place via a direct electron transfer from the excited sensitizer in the primary photochemical step, or through the involvement of photogenerated radical intermediates. For example, with sensitizers such as benzophenone (21), it is necessary to establish whether the primary photoprocesses involve the solvent (in cases such as methanol) or a direct interaction of the triplet sensitizer with the diazonium salt.

This study was undertaken in order to examine the kinetics of the interaction of a variety of triplet sensitizers, covering a range of molecular structures and triplet energies, with a few diazonium tetrafluoroborates having representative ring substituents. Rate constants were measured using nanosecond laser flash photolysis techniques. In a few cases we have also been able to gather some information concerning the detailed nature of the interaction; while mechanistic aspects are still poorly understood, our experiments provide a glimpse at some of the details, and perhaps complications, that can be expected in these systems.

Results

All the experiments reported herein have been carried out in deaerated solution, using the pulses from a nitrogen or, occasionally, an excimer laser for excitation. In each system a complete transient spectrum (usually 300 to 760 nm) was recorded in the absence of quencher, as well as in the presence

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of sufficient diazonium salt to make decay-via-quenching the predominant decay mode. Kinetic measurements were carried out by monitoring T–T absorptions at or near the corresponding maximum.

A few preliminary experiments with representative sensitizers showed that the tetrafluoroborate anion (sodium salt) is a very poor quencher by comparison with the diazonium salts (*vide infra*). For example, experiments with benzophenone and anthracene in acetonitrile–water at 300 K led to $k_q = (1.5 \pm 0.7) \pm 10^7$ and $< 3.6 \times 10^5 M^{-1} s^{-1}$, respectively. Thus, the rate constants discussed below cannot be attributed to quenching by free tetrafluoroborate anion, with the possible exception of benzil.

When attempting to carry out experiments on a variety of substituent and solvent effects, it is clear that all possible combinations cannot be examined, and little would be gained by trying to do so. Our systems were selected so that the quenching of all sensitizers used by the "parent" substrate, benzenediazonium tetrafluoroborate, was examined. The sensitizers used were mostly the same employed in other studies from this laboratory (24, 25); this should make the comparison of diazonium salts with other quenchers readily available. Substituent effects were examined mostly using benzophenone and anthracene as sensitizers. Acetonitrile was used as a "base" solvent, with a few experiments in other media. Experiments were carried out either using a flow system or static samples; the former are definitely more accurate, but they are also far more time consuming.

The measurement of the rate constant for benzophenone triplet quenching by benzenediazonium tetrafluoroborate in acetonitrile at 300 K is the only one described in detail here; the same approach was followed in all other systems. A 0.014 *M* solution of benzophenone in acetonitrile was examined in the laser photolysis system using the nitrogen laser; the choice of laser was based on the favorable ratio of extinction coefficients at 337.1 nm, which makes selective excitation of benzophenone possible. The transient spectrum (at 5 nm intervals) recorded immediately following the laser pulse was in full agreement with that reported for the benzophenone triplet (26) and which had already been recorded numerous times in our laboratory. When the full laser dose was used for excitation, the decay of the triplet, monitored at 525 nm, followed mixed first and second order kinetics, the latter reflecting triplet–triplet annihilation. Usage of suitable neutral density filters to attenuate the excitation laser dose led to predominant first order decay. The diazonium salts proved to be excellent quenchers, and in their presence the decay of the triplet followed clean pseudo-first order kinetics, with rate constant k_{obs} given by:

$$[1] \quad k_{obs} = \tau_0^{-1} + k_q[DS]$$

where τ_0 is the triplet lifetime in the absence of quencher, k_q is the rate constant for triplet quenching, and [DS] the concentration of diazonium salts. Figure 1 shows a plot according to eq. [1] and the insert a representative decay trace. As in most of the systems examined, the spectrum in the presence of diazonium salt, and after triplet decay was complete, was also recorded. A residual signal was detected at 375 nm. This signal is not due to benzophenone radical-cation and could be due to nitrylium ion (15), but it has not been characterized in detail yet. We note that in most cases these studies are limited to wavelengths at least 10 nm longer than that of the laser used for excitation, since most samples are not transparent at shorter wavelengths.

One exception to the problems mentioned above is the case of xanthone, which is strongly absorbing at 337 nm, but presents a window in the 300 nm region. For example, in the xanthone – *p*-methoxybenzenediazonium tetrafluoroborate system, it is possible to observe the bleaching of the quencher. Figure 2 illustrates this effect; the top part shows the decay of the triplet ketone, while the bottom part shows that the destruction of the diazonium salt is concurrent with the quenching process. At 300 nm the diazonium salt and triplet xanthone have significant absorption.

Another system where it is possible to monitor the bleaching of the diazonium salts is in the case of *p*-diethylaminobenzenediazonium tetrafluoroborate, where the absorption maximum is located at ~380 nm. Experiments with benzophenone showed, as in the case of xanthone described above, that bleaching of the quencher occurs concurrently with triplet decay.

Another type of transient phenomena that one can hope to detect in experiments of this type is the transfer of an electron from the sensitizer to the diazonium salt, i.e., reaction [5],

$$[2] \quad S^* \xrightarrow{k_d} S$$

$$[3] \quad S^* + DS \xrightarrow{k_3} S + DS$$

$$[4] \quad S^* + DS \xrightarrow{k_4} S + Ar^+ + N_2$$

$$[5] \quad S^* + DS \xrightarrow{k_5} S^{+\cdot} + Ar^\cdot + N_2$$

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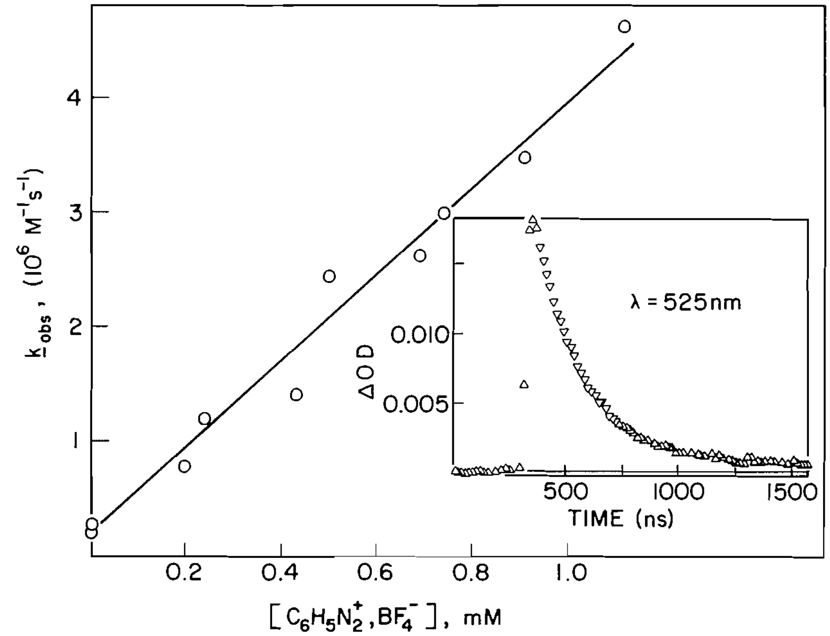

FIG. 1. Quenching of benzophenone triplets by benzenediazonium tetrafluoroborate in acetonitrile at 300 K, according to eq. [1]. *Insert*: Decay of benzophenone triplet monitored at 525 nm in the presence of 1.12 m*M* diazonium salt.

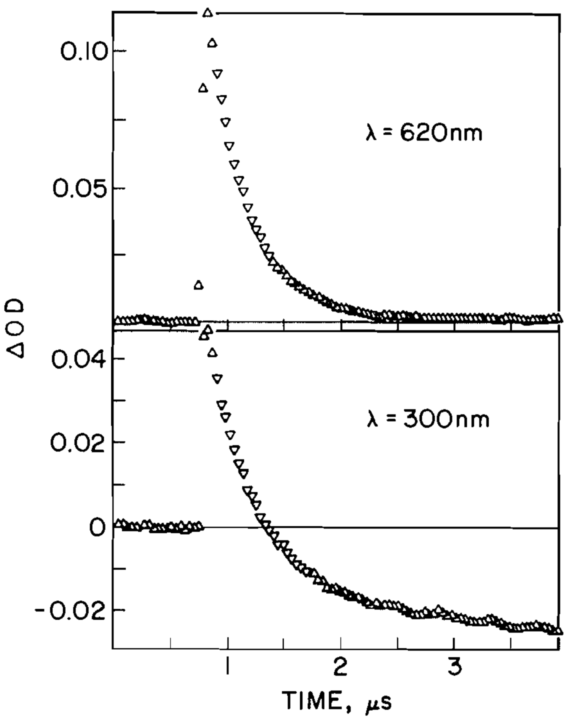

FIG. 2. Transient phenomena observed in the xanthone – *p*-methoxybenzenediazonium tetrafluoroborate (0.26 m*M*), monitored at two different wavelengths. *Top*: Decay of the triplet state. *Bottom*: Triplet decay with concurrent bleaching of the diazonium salt. The slow bleaching at the tail of this trace may be due to relatively minor free radical processes induced in this system.

where S* stands for triplet sensitizer, and reactions [3]–[5] have been written as a single step for simplicity. In fact, reactions [3] and [4] may involve an electronically excited diazonium salt, while reaction [5] probably involves a diazenyl radical (12, 27), which then loses molecular nitrogen. Further, the aryl cation produced in reaction [4] may not be initially in its ground state since, depending upon substitution, these may have singlet or triplet ground states (28, 29).

Occurrence of reaction [5] should lead to the formation of sensitizer-derived radical-cations. This has been observed in the case of anthracene, where the radical-cation shows a very characteristic absorption band at 720 nm (30). Figure 3 shows the transient spectra recorded before significant triplet decay and after the decay (predominantly via quenching) was complete. Time resolved studies showed that the formation of anthracene$^{+\bullet}$ occurred concurrently with triplet decay. From a knowledge of the extinction coefficients of the triplet state (31) and the radical-cation (30) it is possible to estimate the yield of the latter. From an estimated ratio of extinction coefficients of 4 or 5 (triplet-to-radical-cation, at the corresponding maxima (30, 31)), we estimate that the yields of electron transfer are close to quantitative in acetonitrile at 300 K, for benzene- and *p*-methoxybenzenediazonium tetrafluoroborates. It should be noted that estimates are not quantum yields, but rather, the fraction of quenching events that lead to

TABLE 1. Quenching of triplet sensitizers by diazonium tetrafluoroborates at 300 K

Sensitizer (E_T)[a,b]	Diazonium salt[c]	Solvent	λ_{ex}, λ_{mon}, method[d]	k_q, $M^{-1}\,s^{-1}$[e]
Benzophenone (69)	Benzene	Acetonitrile	337, 525, flow	(3.8±0.5) × 10^9
	Benzene	Acetone	337, 525, flow	(3.0±0.3) × 10^9
	o-Toluene	Acetonitrile	337, 525, flow	(1.6±0.4) × 10^9
	p-Methoxybenzene	Acetonitrile	337, 525, flow	(8.2±1.3) × 10^9
	p-Diethylaminobenzene	Acetonitrile	308, 525, flow	(7.6±2.7) × 10^9
	1-Naphthalene	Acetonitrile	308, 525, flow	(8.4±1.0) × 10^9
Xanthone (74)	Benzene	Acetonitrile	337, 620, flow	(9.8±0.9) × 10^9
	Benzene	Water	337, 620, static	(2.8±0.8) × 10^9
	p-Methoxybenzene	Acetonitrile	337, 620, flow	(6.9±2.0) × 10^9
p-Methoxyacetophenone (72)	Benzene	Acetonitrile	337, 375, static	(1.3±0.4) × 10^{10}
	Benzene	Acetone	337, 400, static	(5.2±1.6) × 10^9
	o-Toluene	Acetonitrile	337, 400, static	(5.4±0.3) × 10^9
Anthracene (42)	Benzene	Acetonitrile	337, 420, flow	(5.4±0.3) × 10^9
	p-Methoxybenzene	Acetonitrile	337, 420, flow	(2.3±0.7) × 10^9
α,α,α-Trifluoroacetophenone (71)[f]	Benzene	Acetonitrile	337, 370, static	(6.7±0.5) × 10^9
Benzil (54)	Benzene	Acetonitrile	337, 475, static	≤2 × 10^6
Phenanthrene (62)	Benzene	Acetonitrile	337, 483, static	(3.3±0.4) × 10^9
Pyrene (48)	Benzene	Acetonitrile	337, 410, static	(6.1±0.8) × 10^8

[a] Triplet energy in kcal mol^{-1}, rounded up to the closest unit.
[b] Reference 38.
[c] All tetrafluoroborates, e.g. in the first line: $C_6H_5N_2^+$, BF_4^-.
[d] Excitation and monitoring wavelengths in nanometers.
[e] Only random errors (95% confidence limits) are included.
[f] Reference 39.

complete electron transfer, i.e.,

$$[6]\quad \text{yield of radical-cation} = \frac{k_5}{k_3 + k_4 + k_5}$$

Other systems where the detection of $S^{+\bullet}$ could have been expected to be simple are the cases of phenanthrene and pyrene. For the former we could not detect any significant concentrations of radical-cation, suggesting that reaction [5] is unimportant.

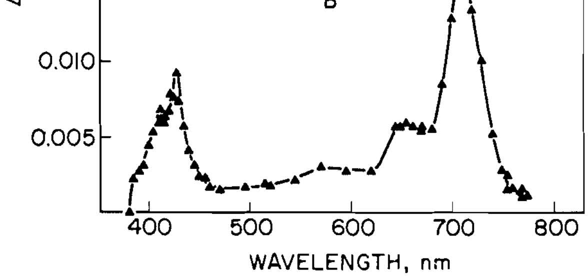

FIG. 3. Transient spectra recorded in the anthracene – *p*-methoxybenzenediazonium tetrafluoroborate (0.88 m*M*) in acetonitrile at 300 K. *Top*: Immediately after laser excitation. *Bottom*: 2.5 μs after excitation.

In the case of pyrene, the radical-cation can be detected, but the problem is complicated by the efficient biphotonic ionization of pyrene (32). This problem can be reduced by working at very low excitation doses, although this leads to a decrease in the signal-to-noise ratio. After a detailed study of the yields of radical cations as a function of laser dose, our conclusion is that pyrene$^{+\bullet}$ is formed rather inefficiently and that some of this radical-cation may in fact be the result of singlet quenching as suggested by Becker *et al.* (14), although overall ion formation is rather inefficient.

We have also carried out a detailed study of the uv–vis spectra of sensitizer – diazonium salt mixtures, since it has been reported that these systems can form electron donor–acceptor complexes (12). Typical equilibrium constants at 293 K in acetonitrile are somewhat below 1 M^{-1} (e.g. for pyrene, anthracene, and phenanthrene). Our studies indicate no complex formation under the conditions of our experiments, typically involving both reagents in millimolar (and occasionally lower) concentrations.

Discussion

The data in Table 1 clearly show that diazonium tetrafluoroborates are, in most cases, excellent triplet quenchers. Our studies using sodium tetrafluoroborate show that this property reflects the

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behaviour of aryldiazonium cations, since the anion, BF_4^-, shows only very inefficient quenching. Our results also indicate a true intermolecular process, since complex formation has been shown to be unimportant in these systems.

The only example where the anion is likely to play a role is the case of benzil, where the quenching process is quite slow. The result is perhaps not surprising; benzil has a tendency to show very peculiar behaviour as a sensitizer (24), and it has been suggested that this may be the result of the dramatic structural differences between the ground and triplet states (24).

While one could be tempted to try to offer a comprehensive explanation for the triplet quenching mechanism, this seems rather difficult in view of the rather contradictory spectroscopic evidence on the triplet level of the diazonium compounds. For example, Zharkov and Kondratenko (33) have studied the absorption spectra of *para*-substituted benzenediazonium salts between 4.2 and 300 K; they claim that the long wave edge of the main absorption band is due to absorption to the lowest triplet level, which is a predissociative state. If this is correct, then one can expect the mechanism of triplet quenching to be similar to that proposed in the case of peroxides (24, 34), involving the transfer of energy to a dissociative state of the acceptor. The spectroscopic evidence does not seem consistent with the observation by Sukigara *et al.* (6) of well defined triplet phosphorescence in the case of the unsubstituted substrate, benzenediazonium tetrafluoroborate, with $\lambda_{max} = 412$ nm (77 K). Our own evidence indicates that if excited triplet diazonium salts are formed at all in solution at room temperature, their lifetimes must be extremely short, probably in the subnanosecond range, since the diazonium salt is bleached concurrently with triplet decay (see Fig. 2) and no new transients are observed following it. This is true of all systems examined, including 1-naphthalenediazonium tetrafluoroborate, where the presence of the naphthalene chromophore could be expected to lead to easily detectable triplets.

Our data suggest that electronic effects (see *para*-substituted substrates in Table 1) do not play a major role in determining the rate constants for triplet quenching, while steric effects (see *o*-toluene diazonium data in Table 1) could be of importance. Some small electronic effects are in fact observable; for example, in electron transfer processes, as is the case for anthracene triplet, the rate for benzenediazonium ion is ~2.3 faster than for the methoxy substituted derivative, while in the case of the electrophilic benzophenone triplet the situation is reversed. Solvent effects do not seem extensive; only water seems to reduce significantly the rate constants, at least in the case of xanthone. Futher studies in this area are certainly needed.

While it may be tempting to use free energy relationships to further interpret the data, these may be of very limited applicability in many of these systems. The majority of the rate constants measured are close to diffusion controlled, a fact that will tend to mask substituent effects. Further, some of the more informative substituents (such as nitro) can lead to enough absorption at the excitation wavelength (35) to make selective sensitizer excitation difficult, and ground state complex formation a definite possibility.

In the case of the sensitizers examined, we believe that the most common pathway is probably the fragmentation of the diazonium salt according to reaction [4], which occurs concurrently with the decay of the triplet sensitizer. Figure 2 illustrates this effect.

Full electron transfer from the sensitizer triplet seems to be a less common process, observed as an efficient reaction in the case of anthracene and to some degree in pyrene. It is possible that reaction [5] will be a favoured process for triplets with relatively low triplet energy and substantial electron donor ability. Naturally, anthracene is precisely a good representative of this group.

While electron transfer may not be a common pathway with high energy sensitizers, charge transfer may play a role in the transition state during the quenching process. As pointed out earlier, the reactivity changes observed in the case of benzophenone point in this direction; even the intermediacy of an exciplex is a definite possibility. Many sensitizers can form electron donor–acceptor complexes with the diazonium salts under favorable conditions (14), and this property is expected to be enhanced in the excited state.

Finally, as pointed out above, we have observed residual absorption signals in a number of systems after the quenching event and triplet decay are complete. Benzophenone and xanthone are two examples of this behaviour; these signals are likely to arise from reactions of aryl cations or of transients derived from them. The complete characterization of these species is beyond the scope of this report, but we hope to undertake the detailed study of some of these problems in the near future.

Experimental

Materials

p-Diethylaminobenzenediazonium tetrafluoroborate was an Aldrich product, and was purified by recrystallization from acetonitrile by precipitation with ether. All other diazonium compounds were prepared from the corresponding amines by

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standard procedures (36) and purified as indicated above. The solid samples were stored at −20°C, and freshly prepared solutions were used in the experiments.

Spectra

The uv–vis spectra of the samples were recorded in Varian 219 or Hewlett Packard 8450-A spectrometers.

Laser flash photolysis

The samples (under oxygen-free conditions) were excited with the pulses from a Molectron UV-24 nitrogen (337.1 nm, ∼8 ns, up to 10 mJ) or a Lumonics TE-860-2 excimer (308 nm with Xe/HCl mixtures, ∼4 ns, up to 80 mJ) laser. The samples were contained or flowed through Suprasil cells. In the case of the excimer laser the optical path was 7 mm and a flow system was essential because of its high power. In the case of the nitrogen laser the energy per pulse is considerably less and fresh static samples were, in some cases (see Table 1) regarded as acceptable; in these experiments the optical path was 3 mm. The signal from an RCA-4840 photomultiplier tube was terminated into 93 ohms. Each trace was initially stored in an R7912 Tektronix transient digitizer, and later transferred to a PDP 11/23 computer which controlled the experiment and provided suitable processing, storage, and hardcopy facilities. Further details have been given elsewhere (37).

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