

concentration. For this purpose, an O<sub>2</sub>/N<sub>2</sub> mixture (gas mixer: Brooks Instruments Division, Hatfield, PA) was bubbled into the solution, and the O<sub>2</sub> concentration was calculated using Henry's law and 2.2 mM as the O<sub>2</sub> concentration in air-saturated benzene.<sup>23</sup>

The amount of triplet 6 produced at  $\lambda^{\text{exc}} = 700$  nm and laser fluence = 4.3 mJ·cm<sup>-2</sup> in 12  $\mu$ M benzene solutions with 0–1.9 M bromobenzene was estimated from the  $\Delta A_T$  value extrapolated to zero time.

The rate constant of quenching of triplet 7 by 6 was determined from the triplet decay of 12  $\mu$ M 7 in degassed solutions with 0–49  $\mu$ M 6.

In laser-induced optoacoustic spectroscopy (LIOAS)<sup>30</sup> N<sub>2</sub>-saturated benzene solutions, with  $A_{640} = 0.04$ – $0.16$ , of 7 and of a calorimetric reference, I<sub>2</sub>,<sup>39</sup> were excited by a dye laser ( $\lambda^{\text{exc}} = 640$  nm). The effective acoustic transit time,  $\tau'_a$ , was 760 ns, and the laser fluence was kept below 15  $\mu$ J. In experiments with 6 ( $\lambda^{\text{exc}} = 700$  nm), the dependence of the signal amplitude on the O<sub>2</sub> concentration was analyzed. An air-saturated solution of I<sub>2</sub> ( $A_{700} = 0.205$ ) was used as the reference,  $\tau'_a$  was 229 ns, and the laser energies were below 2  $\mu$ J. For the adjustment of ground-state oxygen concentrations in the solution of 6 ( $A_{700} = 0.205$ ) vide supra.

The instrumental set-up for the time-resolved NIR phosphorescence detection from O<sub>2</sub>(<sup>1</sup> $\Delta_g$ ) has already been described.<sup>60</sup> The solutions were excited either at 355 nm (Nd:YAG frequency-tripled) or at 666 nm (DCM pumped by the second harmonics of the Nd:YAG laser). The emission was monitored at  $\lambda > 1050$  nm (silicon cutoff filter, Glen Creston, thickness 2 mm); its decay in air-saturated benzene solutions of 7 was biexponential. The shorter-lifetime term, with a time constant of  $< 3$   $\mu$ s, was due to the response of the detector to fast sample fluorescence and light scattering. The longer-lifetime term was the O<sub>2</sub>(<sup>1</sup> $\Delta_g$ ) phosphorescence and yielded the O<sub>2</sub>(<sup>1</sup> $\Delta_g$ ) lifetime in benzene.

Quantum yields of O<sub>2</sub>(<sup>1</sup> $\Delta_g$ ) formation,  $\Phi_\Delta$ , in benzene were obtained by the comparative method<sup>27</sup> from the amplitude of the longer-lived signal extrapolated back to zero time,  $I_0$ . Air-saturated benzene solutions of 5 ( $\Phi_\Delta = 0.36 \pm 0.05^{2a,19b}$ ) and ZnPC dipyrindyl complex ( $\Phi_\Delta = 0.50 \pm 0.06^{27}$ ) were used as references at  $\lambda^{\text{exc}} = 355$  and 666 nm, respectively. The laser fluence was  $< 1.3$  mJ·cm<sup>-2</sup>.

The rate constant for the quenching of O<sub>2</sub>(<sup>1</sup> $\Delta_g$ ) by 8 was determined by conventional Stern–Volmer experiments<sup>60</sup> using ZnTPP ( $A_{532} = 0.4$ ) as a sensitizer in air-saturated solutions. The laser fluence ( $\lambda^{\text{exc}} = 532$

nm) was  $< 0.2$  mJ·cm<sup>-2</sup>. An additional band-pass filter at 1270 nm (Spectrogon) reduced the strong fluorescence before reaching the detector.

Steady-state irradiations (light source: 1000-W Hg–Xe lamp with monochromator, bandwidth 13–14 nm) were carried out (i) with 2-methyltetrahydrofuran solutions of 7 ( $A_{790}$  ca. 0.07,  $10^{-5}$  M) at several temperatures from 302 to 193 K ( $\lambda^{\text{exc}} = 435$  nm) (see Results, Irradiation Experiments, for further experiments in liquid solution at room temperatures) and (ii) with 6 (sublimation at 493 K) and 7 (sublimation at 473 K) in Ar matrices at 10 K [several  $\lambda^{\text{exc}}$  values from  $> 695$  nm (cutoff filter) to 253 nm; for a description of the matrix isolation set-up see ref 61]. Product analysis was performed with FTIR and UV–visible absorption spectroscopy.

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**Supplementary Material Available:** For 8, tables of detailed information on the crystal structure determinations, final atomic position parameters, final thermal parameters, and interatomic distances and angles (8 pages); listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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## Electron-Transfer Quenching of Excited Diphenylmethyl Radicals<sup>1</sup>

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**Abstract:** The intermolecular reactivity of the excited diphenylmethyl radical (DPM\*) has been studied with particular emphasis on electron-transfer reactions. These studies allow the determination of the rate constants for the reaction of DPM\* with electron acceptors. For example, carbon tetrachloride, methyl benzoate, and benzyl bromide quench DPM\* with rate constants of  $3.3 \times 10^6$ ,  $1 \times 10^6$ , and  $3.6 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup> in acetonitrile. The corresponding carbocation is an observable product of the reaction, leaving no doubt that the reaction involves electron transfer. A kinetic salt effect is observed for the reaction of DPM\* with carbon tetrachloride, where the carbocation yield increases from ca. 61% to ca. 100% with the addition of small concentrations of tetrabutylammonium perchlorate. The lower limits to the rates of back electron transfer (BET) and ion pair escape (ESC) for the product cation and radical anions in acetonitrile solution have been estimated using reductive dehalogenation of aryl halides as clock reactions where the rates of fragmentation have been estimated.

### Introduction

There are very few studies of intermolecular reactions of excited organic free radicals,<sup>3–10</sup> particularly when compared to the volumes of data reported for other excited states. This observation

may be attributed to two factors. First, the ground-state reactivity of most organic free radicals is quite high under normal conditions

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so they must be prepared in situ, usually photochemically. Two-photon photochemistry is then required to study their excited states; the most informative approach involves two-color-two-photon techniques, which have only relatively recently become widely available. Second, the lifetimes of these excited states are quite short,<sup>11</sup> in general less than 100 ns, if they are observable at all. Therefore, only very efficient intermolecular reactions can compete with the deactivation processes, requiring the reactant to be present in high concentrations and limiting the number of useful reactions that can be studied.

The photochemistry of the diphenylmethyl radical (DPM) has been examined in great detail.<sup>4,12-17</sup> The excited doublet has a lifetime of 280 ns in acetonitrile and is produced in high yield within a single 308-nm laser pulse from many precursors, making it a good candidate for the study of these interactions. We have studied the quenching of excited diphenylmethyl radicals (DPM\*) by electron acceptors employing laser flash photolysis techniques. The observation of the characteristic fluorescence from the excited radical in a standard spectrofluorimeter has recently been reported,<sup>15</sup> leading to the expectation that fluorescence quenching studies could possibly be accomplished as well.

Quenching of this excited radical by dienes and oxygen has been reported,<sup>4,18</sup> and the emission from singlet oxygen has been reported.<sup>19</sup> Its increased reactivity, relative to the ground state, toward hydrogen atom donors has also been observed; for example, 1,4-cyclohexadiene and tri-*n*-butyltin hydride quench the excited state<sup>4</sup> and reactions with phenol lead to the corresponding phenoxyl radical.<sup>19</sup> The production of the radical anion from methyl viologen as well as products such as benzhydryl chloride from reaction with CCl<sub>4</sub> implicates an electron-transfer mechanism.<sup>4</sup> Quenching of the excited radical by amines has recently been reported although the quenching mechanism is not certain.<sup>4,7</sup>

Application of the Rehm-Weller equation<sup>20</sup> shows that electron-transfer reactions, with the excited radical acting as a donor, are indeed thermodynamically feasible.

$$\Delta G^\circ = -23.06[E^\circ_{A/A^-} - E^\circ_{D^+/D\cdot}] - e_0^2/E_a - \Delta E_{0,0} \quad (1)$$

The value of  $E_{0,0}$  for DPM\* has been estimated from vibrational structure in the fluorescence spectrum to be 2.38 eV (528 nm).<sup>7,12,14</sup> The oxidation potential of the diphenylmethyl radical has been measured electrochemically to be 0.345 V vs SCE.<sup>21</sup> The Coulombic term is known to be small in polar solvents, estimated at 0.1 eV in acetonitrile. This leads to the expectation that any acceptor with a reduction potential of -1.9 V (vs SCE) or larger will quench DPM\* by electron transfer and that the reaction will become diffusion controlled as the reduction potential of the

**Table I.** Rate Constants and Cation Yields for Quenching of the Excited Diphenylmethyl Radical in Acetonitrile

quencher	$10^{-8}k_q$ (M <sup>-1</sup> s <sup>-1</sup> )	cation yield (%)
trifluoroacetic anhydride	1.4 ± 0.4	25
acetic anhydride	n/r	
<i>m</i> -dicyanobenzene	43 ± 8	7
<i>p</i> -dicyanobenzene	160 ± 30	9
carbon tetrachloride	3.3 ± 0.3	61
chloroform	≤0.002	
methyl benzoate (MB)	0.01 ± 0.01	
<i>p</i> -Cl MB	0.03 ± 0.01	11
<i>m</i> -Cl MB	1.13 ± 0.08	20
<i>p</i> -Br MB	1.27 ± 0.09	10
<i>m</i> -Br MB	2.3 ± 0.1	15
<i>p</i> -CN MB	52 ± 4	36
<i>p</i> -CF <sub>3</sub> MB	42 ± 3	34
<i>p</i> -NO <sub>2</sub> MB	130 ± 10	38
dimethylterephthalate	2.0 ± 0.1	18
benzyl chloride	0.013 ± 0.01	
benzyl bromide (BB)	0.036 ± 0.01	7
<i>p</i> -Br BB	0.86 ± 0.07	10
<i>p</i> -F BB	0.090 ± 0.006	7
<i>m</i> -F BB	1.05 ± 0.09	18
<i>p</i> -CN BB	52 ± 2	40
<i>p</i> -NO <sub>2</sub> BB	170 ± 8	43

acceptor becomes more positive than -1.5 V (vs SCE).

One of the unique features of excited doublet chemistry is that the spin evolution of the system does not determine the rate of back electron transfer (BET), unlike the case of triplet-derived products. The rate of BET may be unusually large when compared to those of other systems with similar driving force. In addition, the promotion of the electron does not increase the electron affinity of the excited doublet state, a situation that is in contrast with the excited states derived from singlet ground states. For this reason, the transfer distances between the acceptors and the donors may be larger than normal, leading to unusually rapid rates of escape (ESC) for the cation-anion radical pair from the solvent cage. In order to gauge the rates of BET and ESC, we have used related acceptors, in particular substituted methyl benzoates and benzyl bromides. The absolute rates of BET and ESC are estimated by using the reductive dehalogenations as clock reactions. Here, the fragmentation of the acceptor will compete with BET, and the increased product yields will reflect this competition.

## Experimental Section

The 1,1-diphenylacetone (Aldrich) used as the photochemical source of diphenylmethyl radicals was recrystallized from hexane/ethanol before use. The acetonitrile used (Aldrich, BDH) was passed through activated alumina (Fisher Scientific) twice immediately prior to use. The substituted methyl benzoates were either purchased (Aldrich or Lancaster Synthesis) or synthesized from the substituted acids (Aldrich) by refluxing in methanol with catalytic amounts of HCl added, followed by aqueous workup and recrystallization from methanol. Characterized by <sup>1</sup>H NMR and IR spectroscopy and melting points, all materials compared favorably with literature values. The substituted benzyl bromides (Aldrich or Lancaster Synthesis) were purified by low-temperature recrystallizations from hexane prior to use. All other quenchers were used as received (Aldrich). The tetrabutylammonium perchlorate (Eastman) was recrystallized three times from 10% hexane in ethyl acetate and dried under vacuum prior to use.

The laser flash photolysis (LFP) experiments were carried out on one of two similar LFP systems.<sup>4,22,23</sup> Briefly, 2-ml aliquots of 10<sup>-3</sup> M solution of diphenylacetone in dry acetonitrile were placed in sealed, matched 7 × 7 mm quartz cuvettes. Dry nitrogen was bubbled through the samples for 15 min to remove oxygen prior to photolysis. The samples were irradiated with 308-nm pulses from a Lumonics EM510 excimer laser (XeCl mixture, ~8-ns pulse width, ~30 mJ/pulse). The transient signals were captured by a Tektronix 7912-AD digitizer that was interfaced to a PDP 11/55 computer for data storage, processing, and hard-copy output. The quenchers were all degassed neat or in acetonitrile solution to facilitate addition of the appropriate concentration using only

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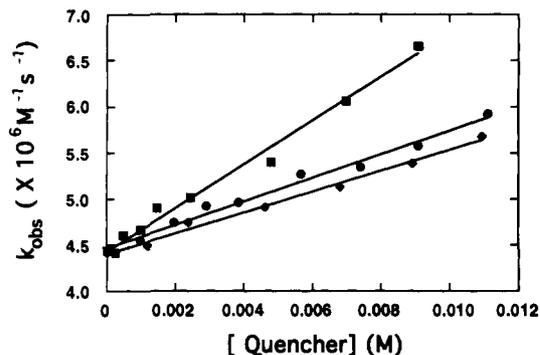


Figure 1. Quenching of the transient absorption of the excited diphenylmethyl radical by (■) methyl *m*-bromobenzoate, (●) methyl *p*-bromobenzoate, and (◆) methyl *m*-chlorobenzoate.

microliter volumes in the additions.

The time-resolved conductivity experiments will be described fully elsewhere.<sup>24</sup> They were accomplished by placing three platinum electrodes (sample, reference, and common) into sample solutions contained in a quartz cell. In general, a 200-V pulse of 4-ms duration was applied across the electrodes with the pulse being applied 1 ms before the laser irradiated the sample. The laser beam was allowed to pass between the sample and common electrodes, and the change in conductivity, measured as a voltage drop between the sample and common electrodes, was differentially amplified by comparison with the voltage applied to the reference electrode. The signal produced was captured on the digitizer and was recorded and stored on the computer as described above.

## Results

The list of quenchers used in this study is presented in Table I. The  $k_q$  values were obtained by observation of the fluorescence decay kinetics (at 520 nm) or the absorbance decay kinetics (at 360 nm) of the excited radical<sup>4,12,13,17,25</sup> for a number of quencher concentrations. The observed pseudo-first-order decay rate constant ( $k_{\text{obs}}$ ) is related to the quenching rate constant ( $k_q$ ) and to the decay rate constant in the absence of quencher ( $k_0$ ) according eq 2.

$$k_{\text{obs}} = k_0 + k_q[\text{Q}] \quad (2)$$

Plots of  $k_{\text{obs}}$  versus quencher concentration are linear with a slope equal to  $k_q$ , the quenching rate constant. Representative examples of the plots obtained are shown in Figure 1. Ideally, as the lifetime of the species in the absence of quencher,  $1/k_0$ , increases, the experimental window in which to measure the rates of quenching will increase. Given the short lifetime of  $\text{DPM}^*$ , quenching studies required moderately high quencher concentrations, and only a 5-fold change in the decay rate was accessible. These limitations are reflected in the error limits of Table I.

For ground-state radicals, the electron configuration consists, in the first approximation, of a HOMO and a LUMO that are equally split by a nonbonding singly occupied orbital, a SOMO. The first excited state, in the case of the diphenylmethyl radical, can be depicted as if the unpaired electron was promoted from the SOMO into the LUMO. This is depicted in Figure 2. At this level of theory, it appears as though an alternative excited-state configuration could be depicted by an electron being promoted from the HOMO into the SOMO. However, at higher levels of theory, the HOMO is stabilized with respect to the SOMO, thus making the latter possibility a much higher energy transition. Using this simple model, it becomes apparent that the promotion of the electron into the LUMO lowers the ionization potential (IP) when compared that of to the ground state but the electron affinity (EA) remains unchanged. Therefore,  $\text{DPM}^*$  will be a much better donor but it is unlikely to be a substantially better acceptor. The electronic configuration produced if  $\text{DPM}^*$  accepts an electron would be that of an excited anion, not a ground state, and the energy of the photon would not be used to advantage. In all of

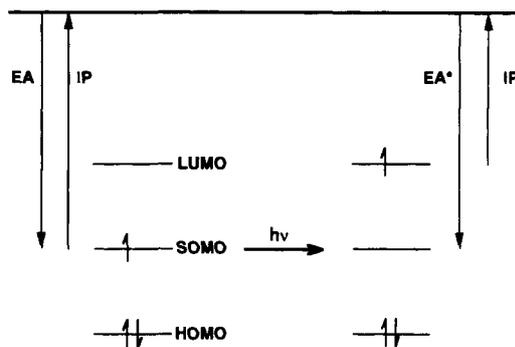
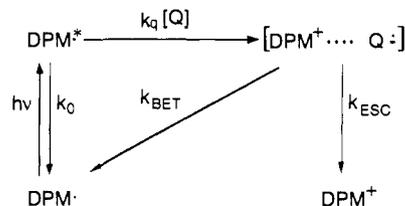


Figure 2. Energy level diagram depicting the ground and first excited doublet states and the effects of excitation on the ionization potential and electron affinity of the diphenylmethyl radical.

## Scheme I



the reports of  $\text{DPM}^*$  acting as an acceptor, the products, the diphenylmethyl anion or the radical cations of the donors, have not been observed.<sup>4,7</sup> The usual donors in these reports are amines, with lone-pair electrons, and the rates of quenching of  $\text{DPM}^*$  increase with decreasing solvent polarity,<sup>4</sup> a situation opposite to what is expected for electron-transfer reactions of moderate driving force. These processes are more likely to be nucleophilic, not electron transfer, in nature, and are beyond the intended scope of this report.

The quenchers in this study have been selected so as not to have low-lying singlet or triplet levels into which energy transfer from the excited doublet could occur. None of the quenchers are expected to be efficient hydrogen atom donors. We have no evidence for charge-transfer complexes being formed prior to quenching, as no new absorbances or emissions are detected in the transient spectrum. Observation of the cation growth (or growth of radical anion of the quencher) as a function of quencher concentrations would prove useful to show that the reaction is indeed electron-transfer driven and to give valuable information about the relative rates of BET and ESC. However, the use of optical characterization is hampered, since both the excited radical and the product cation absorb in the same spectral region with comparable extinction coefficients and lifetimes. In addition, many of the radical anions produced are short-lived or absorb in regions masked by the radical or excited radical.

Time-resolved conductivity was employed in order to establish that the cation is present for all of the quenchers used. Cation growth, monitored by time-resolved conductivity measurements, follows closely the excited radical decay monitored optically for the same samples. It is then unlikely that a charge-transfer complex between the excited radical and the quenchers exists. This also proves that the observed cation is a product of the quenching and not a product of two-photon ionization of the  $\text{DPM}^*$ . The proposed reaction sequence is shown in Scheme I, where  $k_q[\text{Q}]$  is the pseudo-first-order quenching rate constant and  $k_{\text{BET}}$  and  $k_{\text{ESC}}$  are the rate constants for back electron transfer and ion pair escape from the solvent cage, respectively. Once the ions have escaped the solvent cage, they will not undergo efficient back electron transfer, at least not sufficiently fast to interfere with the detection of the carbocation, and thus this reaction is not included in the scheme.

The cation yields shown in Table I were obtained by one of two methods. Where possible, the  $\text{DPM}^*$  was quenched to a lifetime of about 50 ns. This allowed for the direct observation of the cation at 440 nm with  $\sim 300$ -ns lifetime, a somewhat shorter lifetime

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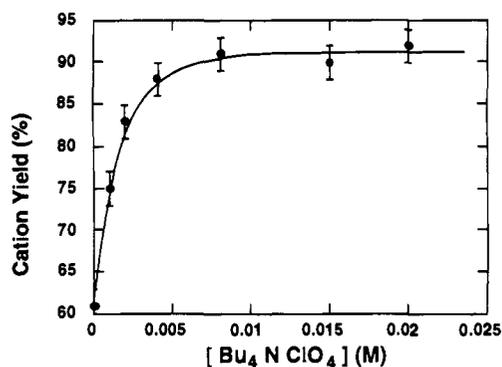
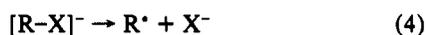
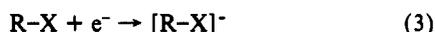


Figure 3. Plot of the effect of the addition of tetra-*n*-butylammonium perchlorate on the observed yields of the diphenylmethyl cation produced from the excited diphenylmethyl radical by reaction with carbon tetrachloride.

than the literature value.<sup>18</sup> The maximum optical density observed at this wavelength, corrected for cation decay, was then used to calculate the concentration of cation produced. In the conversion of optical densities to concentration, we have used 88 000 M<sup>-1</sup> cm<sup>-1</sup> as the  $\epsilon$  of DPM at 330 nm, 80 000 M<sup>-1</sup> cm<sup>-1</sup> for the  $\epsilon$  of DPM\* at 360 nm, and 45 000 M<sup>-1</sup> cm<sup>-1</sup> for the  $\epsilon$  of the diphenylmethyl cation at 440 nm.<sup>4,12,13,17,25</sup> This, along with the lifetime and optical density of the excited state observed at 360 nm, was used to calculate the percent yield of the cation by assuming conditions of complete quenching. The alternative, although a less accurate method, used the permanent bleaching of the radical as an indicator of the cation yield. In these experiments, the radical optical density at 330 nm was measured before and after the addition of quencher; the difference was then attributed to the production of cation. The initial concentration of DPM\* observed before addition of quencher and its lifetime with the quencher added allowed for the calculation of the cation yield, again by assuming conditions of complete quenching. Usually three or more different quencher concentrations were used, and the average yield is reported. When both methods were used, i.e. only for the efficient quenchers, the agreement was usually within 5%. We therefore believe that the cation yields are, at best, accurate to within  $\pm 10\%$ .

Electron transfer from excited states is unique when compared to other quenching processes in that the deactivation of the excited state generally reverses the driving force and back reaction often occurs. There are several ways in which back electron transfer may be circumvented;<sup>26</sup> we have tried to induce the fragmentation of the acceptor, thereby making the transfer irreversible. Reductive dehalogenation reactions may be characterized as shown by eqs 3 and 4. In some cases, i.e. alkyl halides, fragmentation



(reaction 4) is so rapid that the fragmentation appears to be, or is indeed, concerted with the electron transfer (reaction 3). This should be the case for carbon tetrachloride although recent theoretical results suggest that a small interaction between the fragments may exist even for simple alkyl chlorides.<sup>27</sup> Since BET will not be able to compete with dehalogenation, all of the excited states that undergo electron-transfer reactions should result in cation formation. Yet the yield of cation observed for carbon tetrachloride is significantly lower than 100%. Given that the cation is known to react with chloride ion,<sup>18</sup> it is possible that the decreased yield of cation reflects losses through in-cage (geminate) reactions with the chloride ion produced from the dissociation of the alkyl chloride. The addition of unreactive ions should therefore stabilize the cation, increase the rate of escape from the solvent cage, and mask the chloride ion, thereby reducing the in-cage

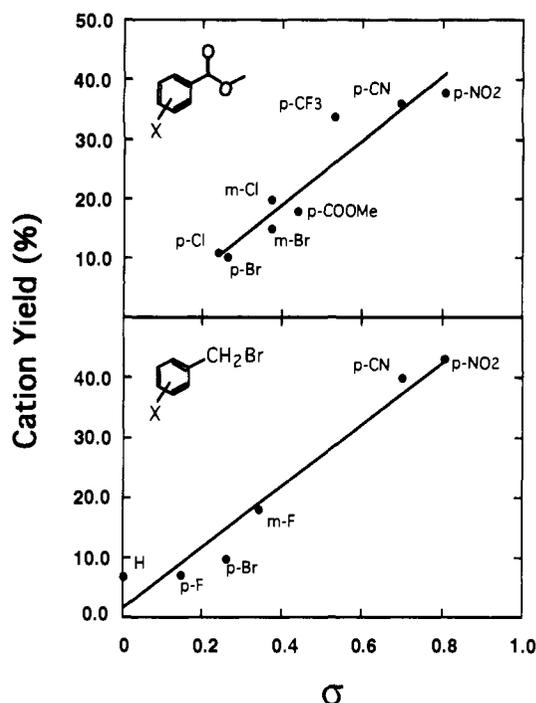


Figure 4. Plots of observed yields of the diphenylmethyl cation as a function of the Hammett  $\sigma$  parameter of the substituent for (top) substituted methyl benzoates and (bottom) substituted benzyl bromides.

reaction rate and increasing the product yields. To test this, we have added tetra-*n*-butylammonium perchlorate, Bu<sub>4</sub>NClO<sub>4</sub>, where the perchlorate ion is a poor scavenger of the cation although it is not completely unreactive. The effect of salt addition on the yield of cation from the quenching of carbon tetrachloride is shown in Figure 3. This plot levels off at close to 100% cation yield, leading to the conclusion that BET does not compete with fragmentation for this quencher, as expected.

The measured cation yields for the substituted methyl benzoate series fall into correlation with Hammett  $\sigma$  parameters for the substituent, as is shown in the top of Figure 4. The rates of dehalogenation for these compounds are known to decrease with increasing Hammett parameter.<sup>28</sup> If the cation yields were dependent upon the dehalogenation rates, the yields would also decrease with increasing Hammett parameter, which is opposite to what is observed. Decarbonylation of the benzoate esters could also occur although these reactions are generally too slow to compete with in-cage BET or escape ( $10^3$ – $10^6$  s<sup>-1</sup> may be expected for the methylbenzoate esters).<sup>29</sup> In the case of aryl halides, the fragmentation rate has been shown to be dependent upon the halogen and the stabilization of the substituent.<sup>28</sup> This leads to the prediction that debrominations will be more rapid than the dechlorinations and the para withdrawing substituents will be stronger than the meta. An estimate of the fastest dehalogenation rate, loosely based on correlations between the quenching rate constants and reduction potentials and comparison with known fragmentation rates,<sup>28,30–38</sup> is  $10^{10}$  s<sup>-1</sup> for *p*-bromobenzoate. BET

(28) Chanon, M.; Hawley, M. D.; Fox, M. A. Introduction In *Photoinduced Electron Transfer*; Fox, Chanon, Eds.; Elsevier: New York, 1988.

(29) Masnovi, J.; Maticic, J. *J. Am. Chem. Soc.* **1988**, *110*, 5189–5191.

(30) There have been numerous studies published that have correlated the reduction potentials of haloaromatics with the rates of dehalogenation,<sup>28,31</sup> and equally as many that have correlated the reduction potentials of related compounds with Hammett parameters of substituents,<sup>28,32</sup> with moderate success. Since the electron-transfer-quenching rate is directly related to reduction potential of the quencher, and therefore to the Hammett parameter, we have used the measured quenching rate constants, and the known reduction potentials where possible to predict the fragmentation rates of our quenchers on the basis of the measured rates of fragmentation for related compounds.<sup>31,34–38</sup> The errors associated with this estimate may be very large, with the largest source being the need to extrapolate from the slow fragmentations, i.e. the only ones that have been experimentally measured, to the those that should be much faster. While this method is not as rigorous as we would like, it produces the only estimate available at this time.

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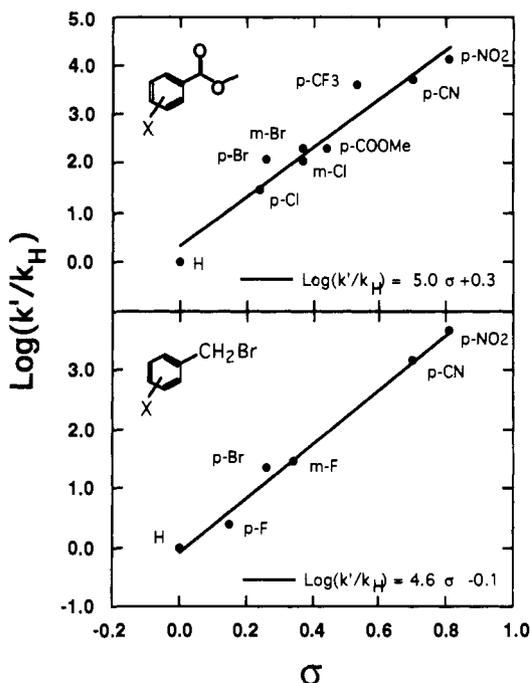


Figure 5. Hammett plots for the rate constants of quenching of the excited diphenylmethyl radical by (top) substituted methyl benzoates and (bottom) substituted benzyl bromides.

must then be significantly faster. This estimate of the BET rate along with the cation yield from Table I leads to an estimate of the ion escape rate. A lower limit of  $10^{10} \text{ s}^{-1}$  for BET in the case of methyl *p*-bromobenzoate leads to a lower limit of  $10^9 \text{ s}^{-1}$  for escape. This escape rate appears to be faster than is usually assumed for ions of this size in acetonitrile<sup>39,40</sup> although no other estimates for cation/radical anion escape rates have been published. The accuracy of the estimates for BET and ESC precludes any rigorous comparison with published rates. However, there is no doubt that both processes must be extremely fast. A possible rationalization for this result is that there will be little attraction between the excited radical and the donor molecules before the electron transfer takes place and the average distance over which the transfer takes place will be larger than in the case of similar singlet-derived reactions. With larger distances separating the ions at conception, the Coulombic term will be substantially smaller for these reactions and cage escape will be facilitated.

The cation yields for the substituted benzyl bromides also correlate with the Hammett  $\sigma$  parameters (Figure 4, bottom), showing that these fragmentations must also be slower than BET. This result may have two possible explanations. The dehalogenation from the low-lying  $\sigma^*$  orbital for these molecules is not a concerted reaction, or the  $\pi^*$  orbital accepts the electron and a slow rate of interconversion prevents the  $\sigma^*$  orbital from being populated.

The plots of  $\log(k'/k_H)$  for the substituted methyl benzoates with Hammett constants indicate better correlation with  $\sigma$  than with  $\sigma^-$ . The plot obtained using  $\sigma$  is shown at the top Figure 5. The fact that the  $\rho$  value is 5.0 indicates that the reaction is strongly influenced by substituents and becomes much faster as the electron-withdrawing ability of the substituent increases. Calculations and ESR studies on the radical anions of methyl benzoates have determined that these  $\pi$  radical anions are planar and that there is significant delocalization of the spin and charge onto the aromatic ring.<sup>29,41</sup> This is consistent with the better correlation with  $\sigma$  than with  $\sigma^-$ .

The  $\log(k'/k_H)$  value for substituted benzyl bromides also correlates better with  $\sigma$  than with  $\sigma^-$  and has a slope similar to that of the methyl benzoate plot ( $\rho = 4.6$ ). This plot is shown at the bottom of Figure 5. This similarity in the slopes would not be expected if the highly localized  $\sigma^*$  orbital were the accepting orbital. Instead, the  $\pi^*$  orbital must be accepting the electron, as is the case for the methyl benzoates. The observation of the radical anions of *p*-cyano<sup>36</sup> and *p*-nitrobenzyl bromide<sup>37,38</sup> has been rationalized in terms of intramolecular electron-transfer reactions, and this explanation may also apply here. The lack of a significant increase in the cation yields due to fragmentation may be explained in terms of orbital symmetry and a kinetic control of product formation. Better overlap between the  $\pi$  radical center of DPM\* with the more diffuse  $\pi^*$  orbital of the acceptor, even if the  $\sigma^*$  orbital is thermodynamically lower in energy, would tend to favor the  $\pi^*$  radical anion. Fragmentation would be delayed by solvent reorganization until the localized  $\sigma^*$  orbital could be populated, a process that would have to compete with BET. The reported solvent reorganization energies for dissociative electron transfers<sup>42</sup> have been very high and could be a significant barrier to the fragmentation.

There is no evidence for the formation of an exciplex or charge-transfer complex of any kind, and the  $\rho$  for the reaction is so large ( $\rho = 4.6$ ) that full electron transfer must occur. This conclusion is supported by the fact that cation yields are again proportional to the reduction potential of the quencher (inversely proportional to the driving force for back electron transfer) and the highest yields of ionic species occur when the likelihood of complexation is the largest. This is the opposite of what would be expected if complexation were to be used to explain these results.

## Conclusions

The reactivity of excited diphenylmethyl radical toward electron acceptors has been described. The electron-transfer processes are accompanied by usually fast back-electron-transfer reactions and rapid solvent cage escape of the product ions. These fast reactions may be monitored by using chemical clock reactions in the form of reductive dehalogenations. A surprising result is that the formation of the radical anions of substituted benzyl bromides does not lead to immediate fragmentation but back electron transfer successfully competes with the dehalogenation reactions. This result is explained in terms of the population of a  $\pi^*$  state in preference to the dissociative  $\sigma^*$  state.

**Registry No.** DPM, 4471-17-4; Ph<sub>2</sub>CHCOCH<sub>3</sub>, 781-35-1; CF<sub>3</sub>CO<sub>2</sub>COCF<sub>3</sub>, 407-25-0; *m*-CNC<sub>6</sub>H<sub>4</sub>CN, 626-17-5; *p*-CNC<sub>6</sub>H<sub>4</sub>CN, 623-26-7; CCl<sub>4</sub>, 56-23-5; PhCO<sub>2</sub>Me, 93-58-3; *p*-ClC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Me, 1126-46-1; *m*-ClC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Me, 2905-65-9; *p*-BrC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Me, 619-42-1; *m*-BrC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Me, 618-89-3; *p*-CNC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Me, 1129-35-7; *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Me, 2967-66-0; *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Me, 619-50-1; 1,4-(CO<sub>2</sub>Me)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 120-61-6; PhCH<sub>2</sub>Cl, 100-44-7; PhCH<sub>2</sub>Br, 100-39-0; *p*-BrC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br, 589-15-1; *p*-FC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br, 459-46-1; *m*-FC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br, 456-41-7; *p*-CNC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br, 17201-43-3; *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br, 100-11-8; Ph<sub>2</sub>CH<sup>+</sup>, 709-82-0; CHCl<sub>3</sub>, 67-66-3; Bu<sub>4</sub>N<sup>+</sup>ClO<sub>4</sub><sup>-</sup>, 1923-70-2.

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