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Communications

Carbanion Photochemistry. 5. Electron-Transfer Quenching of Carbanion Photoreactivity by Condensed Aromatic Hydrocarbons

Summary: Irradiation of dimethyl sulfoxide solutions of triphenylmethyl anion in the presence of condensed aromatic hydrocarbons leads to efficient quenching of the electron-transfer photochemistry, while addition of tetrahydrofuran induces a change in mechanism from nonchain $S_{RN}1$ to S_{ET}.

Sir: The area of electron-transfer photochemistry continues to be a rich source of new reactions and photophysical phenomena. The use of photoexcited species as donors and electron acceptors as fluorescence quenchers has allowed a much more convincing demonstration of the absence of rate inversions predicted by the Marcus theory in the extremely exoergonic region. Our discovery that resonance-stabilized carbanions readily photoreduce dimethyl sulfoxide (Me_2SO) through a single electron transfer mechanism[2] prompted us to our own investigation of electron-transfer quenching, since the extremely high potentials necessary for Me_2SO photoreduction expand the range of potentials available in the high exoergonic region. Thus we felt that an investigation of electron-transfer quenching for these systems might provide a new framework for further investigations into the Marcus,[3] Rehm and Weller,[4] and Scandola, Balzani, and Schuster[5] models for the mechanism of electron transfer. Additional insight might be provided by the fact that Me_2SO acts as both solvent and acceptor. Thus the lack of necessity for solvent reorganization prior to electron transfer might provide an additional refinement of current models for electron transfer. We now report (1) the ready quenching of triphenylmethyl anion photochemistry by condensed aromatic hydrocarbons and (2) an unusual inverse relationship between acceptor concentration and quantum yield. This photochemistry of triphenylmethyl anion involves formation of 1,1,1-triphenylethane (TPE) as the major product along with diphenyltolylmethane (DTM) through the electron transfer induced decomposition of dimethyl sulfoxide (see Eq 1).[2] The relevant mechanistic steps are outlined in Scheme I.

$$Ph_3C:^- + CH_3SOCH_3 \xrightarrow{h\nu} \underset{TPE}{Ph_3CCH_3} + \underset{DTM}{Ph_2CHC_6H_4CH_3} + CH_3SO^- \qquad (1)$$

Scheme I. Mechanism of Triphenylmethyl Anion Photomethylation

(a) $Ph_3C:^- \xrightarrow{h\nu} Ph_3C:^{-}{}^*$

(b) $Ph_3C:^{-}{}^* \xrightarrow{k_d} Ph_3C:^-$

(c) $Ph_3C:^{-}{}^* + CH_3SOCH_3 \xrightarrow{k_{et}} Ph_3C\cdot + CH_3SOCH_3^{-}\cdot$

(d) $Ph_3C:^{-}{}^* + CH_3SOCH_3 \xrightarrow{k_{d'}} Ph_3C:^- + CH_3SOCH_3$

(e) $CH_3SOCH_3^{-}\cdot \xrightarrow{k_{dec}} CH_3\cdot + CH_3SO^-$

(f) $CH_3\cdot + Ph_3C:^- \xrightarrow{k_{ra}} Ph_3CCH_3^{-}\cdot$

(g) $Ph_3CCH_3^{-}\cdot + Ph_3C\cdot \xrightarrow{k_{rr}} Ph_3CCH_3 + Ph_3C:^-$

(h) $Ph_3C:^{-}{}^* + Q \xrightarrow{k_q} Ph_3C:^- + Q$

Two features of this mechanism deserve comment. The first is that the ready reduction of dimethyl sulfoxide (Me_2SO) indicates the carbanionic excited state has a very large negative oxidation potential (<−3.0 V). Thus molecules with very negative reduction potentials, e.g., aromatic hydrocarbons, should be efficient electron-transfer quenchers. The second feature concerns the nature of the electron-transfer event itself. It may be a dissociative electron transfer yielding methyl radicals directly, or it may involve formation of $k_q\tau$) radical anion of finite lifetime.

Simple steady-state treatment of the transients involved, along with the assumption that bimolecular reactions between transients do not contribute substantially to the overall kinetics,[2] produces the general equation for the quantum yield given by eq 2. This equation reduces to

$$\phi_r = \frac{k_{et}[Me_2SO]}{(k_d + k_{et})[Me_2SO] + k_d + k_q[Q]} \qquad (2)$$

the more familiar expression for a sensitized reaction, i.e., the decomposition of dimethyl sulfoxide without quencher (Eq 3) and the Stern–Volmer expression for the relative quantum yield of the quenched reaction (eq 4). Here k_{dt}

$$\frac{1}{\phi_r} = \frac{k_{d'} + k_e}{k_{et}} + \frac{k_d}{k_{et}}[Me_2SO]^{-1} \qquad (3)$$

$$\frac{\phi_{r_0}}{\phi_r} = 1 + \frac{k_q[Q]}{k_{dt}} = 1 + k_q\tau[Q] \qquad (4)$$

is the total rate of decay of the reactive intermediate or excited state, i.e., $k_{dt} = k_d + (k_{et} + k_q)[Me_2SO]$, ϕ_{r_0} is the quantum yield in neat Me_2SO, and ϕ_r is the quantum yield in the presence of varying acceptor and quencher concentration. Commonly, the quantities $1/\phi_{r_0}$ and ϕ_{r_0}/ϕ_r are plotted vs. $[Me_2SO]^{-1}$ and [Q], and the quantities k_d/d_{et} and $k_q\tau$ determined from the slopes. In the case of eq 3, the inverse of intercept at infinite Me_2SO concentration in principle gives $k_{et}/(k_{et} + k_d)$, the limiting efficiency of forward (electron transfer) reaction and quenching. Equation 4 is in fact a more general one, and the lifetime τ so determined is the lifetime of whatever species is intercepted, i.e., the inverse of its decay rate constant. It should be pointed out that the rate constants for electron transfer represented by k_{et} and $k_{d'}$ are composite rate constants including solvent reorganization and diffusion[4,5] which will remain constant as long as diffusion out of the encounter cage is not rate limiting.

Solutions of triphenylmethyl anion in dimethyl sulfoxide were irradiated in the presence of condensed aromatic

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[1] For our previous paper, see Tolbert, L. M.; Siddiqui, S. *Tetrahedron* **1982**, in press.

[2] Tolbert, L. M. *J. Am. Chem. Soc.* **1980**, *102*, 6808.

[3] (a) Marcus, P. A. *J. Chem. Phys.* **1956**, *24*, 966; (b) *Ann. Rev. Phys. Chem.* **1964**, *15*, 155.

[4] Rehm, D.; Weller, A. *Israel J. Chem.* **1970**, *8*, 259.

[5] Scandola, F.; Balzani, V.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 2519.

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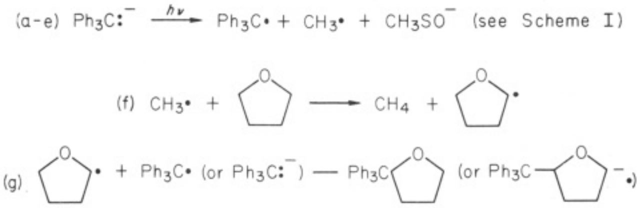
Table I

quencher	$-\epsilon_{1/2}$, V	$10^{-3}\ k_q$
biphenyl	2.70	5.7
naphthalene	2.50	4.1
picene	2.5	7.0
p-terphenyl	2.33	6.9
chrysene	2.30	4.9
anthracene	1.96	5.4
fluoranthene	1.77	4.0

Scheme II. Mechanism of 1-(Triphenylmethyl)tetrahydrofuran Formation[11]



hydrocarbons of varying reduction potentials. All of these had the property that ground-state electron transfer would be exoergonic and that energy transfer from the excited state of the carbanion would be energetically prohibitive. Irradiations were carried out on a merry-go-round apparatus to ca. 5% conversion, the reactions quenched with 250 μL of water, and the products analyzed by gas chromatography. In each case, a plot of ϕ_{r_0}/ϕ_r vs. quencher concentration gave good least-squares statistics for best fit to eq 4. The $k_q\tau$ values obtained for each hydrocarbon are listed in Table I, along with the polarographic reduction potentials.[6] Efficient quenching of the photochemistry was obtained at very small quencher concentrations, giving an average $k_q\tau$ value of 4.8×10^3. Making the reasonable assumption that the identical values of $k_q\tau$ mean that electron-transfer quenching is occurring at a diffusion controlled rate, we may approximate k_q by k_{diff} and use the value for k_{diff} calculated from the Hückel–Debye equation and the reported viscosity of Me_2SO.[7] This yields a value of 2.4×10^9, from which we obtain lower limit for τ of 2.0 μs. These experimental observations are remarkably in accord with the results of Walker and coworkers in which solvated electrons were produced in Me_2SO through pulse radiolysis.[8] The electrons produced were rapidly scavenged (14 ns) by Me_2SO to produce a new anionic species. This same anionic species was known to produce methyl radical. Furthermore, Walker noted that the introduction of anthracene to the radiolysis mixture resulted in formation of anthracene radical anions in yields which depended on anthracene concentration to the same extent as our data. Thus the hydrocarbon quenchers have intercepted the dimethyl sulfoxide radical anion ($Me_2SO^{-}\cdot$), and the value of obtained, $1/k_{dec}$, is the lifetime of $Me_2SO^{-}\cdot$. This further indicates that the intermediate quenched by Fox and Owen[9] at a semiconductor electrode during irradiation of dimethyl sulfoxide solutions of fluorenyl anion is presumably the same $Me_2SO^{-}\cdot$ radical anion.

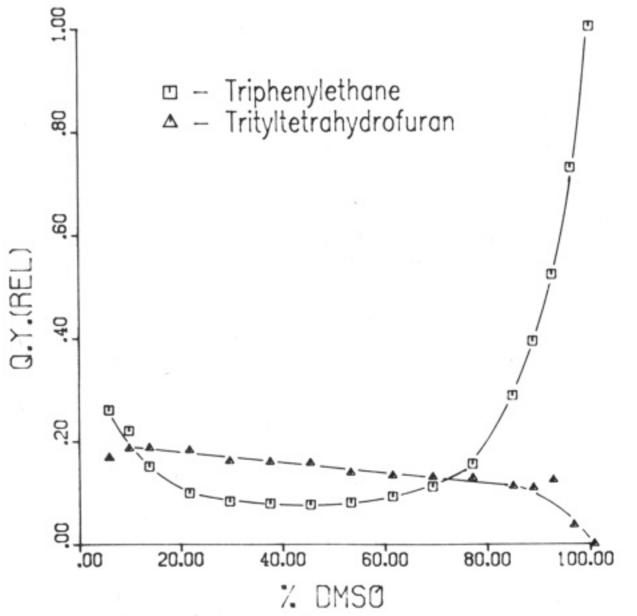


Figure 1. Effect of added tetrahydrofuran on relative yields.

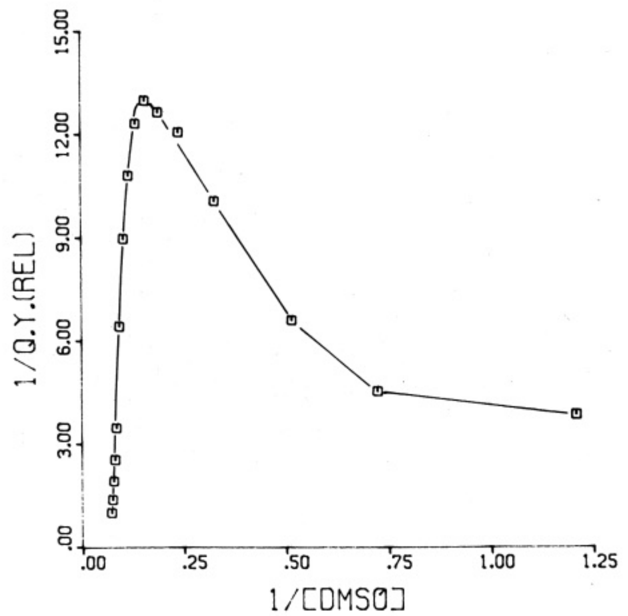
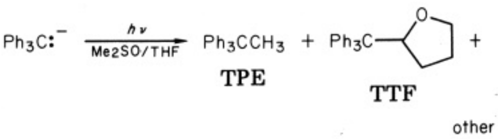


Figure 2. Stern–Volmer plot of $[Me_2SO]^{-1}$.

A more unexpected turn of events occurred when the acceptor dimethyl sulfoxide was diluted with tetrahydrofuran. First, an additional if unsurprising product appeared, 2-(triphenylmethyl)tetrahydrofuran (see eq 5 and Scheme II).[10] Second, at more dilute dimethyl sulfoxide concentrations an inversion in the quantum yield occurred, giving the paradoxical result that when the acceptor was present at lower concentrations, higher yields resulted (see Figure 1). A plot of ϕ_{r_0}/ϕ_r vs. $[Me_2SO]^{-1}$ was linear at high concentrations but not at low concentrations (see Figure 2) and even gave a negative intercept when extrapolated to infinite dimethyl sulfoxide concentration! Additional quenching studies were carried out with *p*-terphenyl as quencher and with tetrahydrofuran added in the amount



TPE **TTF**

other products (5)

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(6) (a) Streitwieser, A., Jr. "Molecular Orbital Theory for Organic Chemists", Wiley: New York, 1961; p 178. (b) Although Me_2SO was *not* used for these polarographic measurements, the relative order in Me_2SO should still be the same.

(7) LeBel, R. G.; Goring, D. A. I. *J. Chem. Eng. Data* **1962**, *7*, 100.

(8) (a) Walker, D. C.; Klassen, N. V.; Gillis, H. A. *Chem. Phys. Lett.* **1971**, *10*, 636. (b) Cooper, T. K.; Walker, D. C.; Gillis, H. A.; Klassen, N. V. *Can. J. Chem.* **1973**, *51*, 2195.

(9) Fox, M. A.; Owen, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 6559.

(10) This product was synthesized independently and gave satisfactory spectral data and elemental analysis: Tolbert, L. M.; Martone, D. P., submitted for publication.

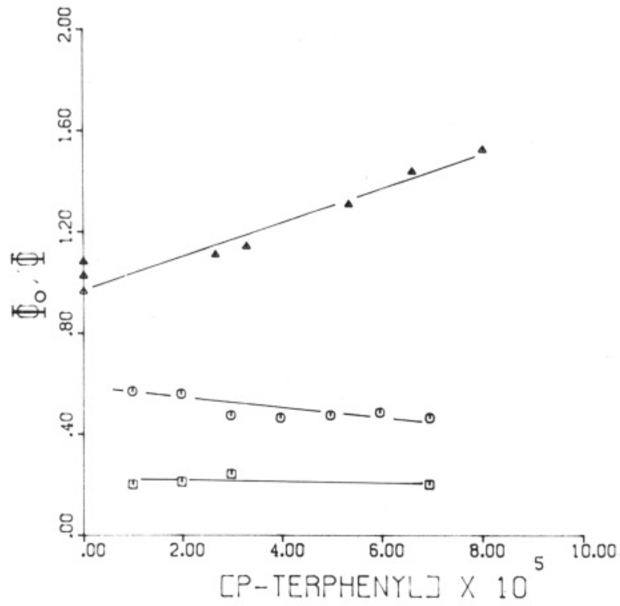

Figure 3. Effect of added tetrahydrofuran on electron-transfer quenching (△, no THF; ○, 5% THF; □, 10% THF).

that reduced the quantum yield by a factor of 2 and 4. When similarly prepared solutions and concentrations of quencher were used, there was no measurable quenching of product formation (see Figure 3), indicating a dramatic change in the Me$_2$SO$^-\cdot$ lifetime. Although the reason for the increased rate of decomposition of Me$_2$SO$^-\cdot$ is obscure, Walker and co-workers[8] have noted a dramatic effect on the lifetime of free electrons and other anionic species upon addition of water to Me$_2$SO.

The presence of a negative intercept for eq 3 is not surprising if one considers that in neat Me$_2$SO, the *effective* concentration of acceptor will already be at its limiting value, since very little diffusion needs to take place prior to electron transfer. Moreover, various aspects of relative product formation indicate that the Me$_2$SO$^-\cdot$ lifetime is *the* factor determining the remaining anomalous quantum yield behavior. We have previously noted that whereas the combination of methyl radical with trityl radical yields exclusively the product of *alpha* attack, TPE, the combination of methyl radical with trityl anion yields both TPE and the product of para attack DTM in a ratio 3:1 that is characteristic of the radical anion process.[2] This additional product may reflect the stability of the intermediate radical anion or the greater delocalization of trityl anion over trityl radical due to electron-electron repulsion.[12] When tetrahydrofuran is added, however, a decrease in DTM yield is noted.[13] Furthermore, the large increase in TPE yield at high THF concentrations is unaccompanied by a similar increase in TTF yield. Both these results indicate that the quantum yield inversion is due not to an increase in free methyl radical concentration, which would increase the yield of all products, but a cage effect dependent upon the competition between Me$_2$SO$^-\cdot$ decomposition and diffusion from the cage. Thus when Me$_2$SO$^-\cdot$ lifetime is short or, equivalently, the electron transfer to Me$_2$SO becomes dissociative, the back electron transfer represented by $k_{d'}$ becomes negligible, and the quantum yield of TPE formation increases. This corresponds in a change from the nonchain S$_{RN}$1 mechanism[14] to the S$_{ET}$ mechanism.[15]

Steady-state treatments of electron-transfer reactions provide good models for observed rate constants when both donors and acceptors are well separated by a nonreacting solvent. At high concentrations of acceptors, and presumably donors, large deviations from linearity and even rate inversions are possible. These anomalies reflect partially the participation of the acceptor in the solvation sphere of the donor and partially the change in partition between the forward reaction and back electron transfer. Although we do not of course understand every aspect of this behavior, we are very excited by the prospect that high concentration studies may provide new details of nature of donor–acceptor interactions and may allow direct determination of the microscopic rate constants for electron transfer which are only now inferred.

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Registry No. Triphenylmethyl anion, 40006-86-8; biphenyl, 92-52-4; naphthalene, 91-20-3; picene, 213-46-7; *p*-terphenyl, 92-94-4; chrysene, 218-01-9; anthracene, 120-12-7; fluoranthene, 206-44-0.

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[11] The involvement of methyl radical in the mechanism is demonstrated by the stability of tetrahydrofuran solutions of trilithium upon prolonged irradiation with no detectable yield of TTF.

[12] House, H. O.; Weeks, P. D. *J. Am. Chem. Soc.* **1975**, *97*, 2785.

[13] As a minor product, the yield of DTM was difficult to quantitate. However, it never exceeded 5% of the product mixture.

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An Efficient Synthesis of Ellipticine

Summary: A synthesis of the antitumor pyrido[4,3-*b*]carbazole alkaloid ellipticine (**1a**) is described in which the key steps are, successively, a highly regioselective acylation of 2-lithio-1-(phenylsulfonyl)indole (**4**) with 3,4-pyridinedicarboxylic anhydride (**3**) and acetic anhydride induced ring closure to give keto lactam **8**. Further manipulation affords ellipticine in 54% overall yield from indole (**2a**).

Sir: The alkaloid ellipticine (**1a**) and its 9-oxygenated derivatives **1b** and **1c** show pronounced anticancer activity toward several experimental[1] and human[2] tumor systems. For example, 9-methoxyellipticine (**1c**) is capable of inducing complete remission in patients with acute myeloblastic leukemia[2] and 2-methyl-9-hydroxyellipticinium acetate has been successfully used to treat certain intractable human cancers unresponsive to other drug protocols.[3,4]

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