**Table II.** Reaction of *tert*-Butyl Hydroperoxide with Acetonitrile in $KO_2$/Pyridine[a]

| pyridine, mL | acetonitrile, mL (mmol) | results[b] |  |
|---|---|---|---|
|  |  | *t*-BuOOH remaining, % | *t*-BuOH + acetone, % |
| 3.95 | 0.05 (1.0) | 95 | 10 |
| 3.79 | 0.21 (4.0) | 69 | 21 |
| 3.48 | 0.52 (10) | 18 | 54 |
| 2.96 | 1.04 (20) | 15 | 61 |
| 1.91 | 2.09 (40) | trace (<2) | 62 |
| 0.00 | 4.00 (76.6) | 0 | 75[c] |

[a] All runs have 1.0 mmol of *t*-BuOOH, 3.0 mmol of $KO_2$, and 0.1 mmol of CE and were treated exactly as described in Table I (with workup) for 30-min reaction times. Temperature was not controlled. [b] Results (percent yield) are in each case based on the initial concentration (from an initial point by GC) of *t*-BuOOH. [c] Worked up after reacting 15 min.

II, there is a direct correspondence between the acetonitrile concentration and the loss of hydroperoxide after neutralization.

From the dramatic difference in *t*-BuOOH stability in the solvents investigated, the effect of KOH, the observation of significant quantities of acetamide, the mixed solvent work, and ample literature precedents, it seems clear that reaction 3 does not occur under the conditions of this or the prior[10] study, but rather that eq 4 and 5 take place, followed by eq 6 in acetonitrile. In an earlier report we had shown that hydroperoxide ion is highly reactive to dimethyl sulfoxide, giving dimethyl sulfone and the corresponding alcohol.[11] Apparently neither $Me_2SO$ nor $CH_3CN$ is an inert solvent in these kinds of systems.

In conclusion, we must comment on the unlikelihood of reaction 2 for superoxide and $H_2O_2$. Neither dialkyl peroxides nor alkyl hydroperoxides act as electron acceptors from $O_2^-\cdot$ (vide supra). The energetics of the $H_2O_2$ molecule are very similar to those of the organic peroxides, and the p$K_a$ of HOOH and *t*-BuOOH are quite close. Indeed, several recent studies fail to observe the occurrence of reaction 2 under conditions in which it might have been an important process. In 1976 McClune and Fee, studying $O_2^-\cdot$ reactions by a stopped-flow method, showed that reaction 2 does not compete with a number of other elementary $O_2^-\cdot$ processes, and it is at best extremely slow.[22,23] They also cite earlier literature on this point that has been generally ignored. Taken together, it would seem that a Haber–Weiss-type process for $O_2^-\cdot$ has not been demonstrated, and that $O_2^-\cdot$ does indeed give solutions that act as if they were strongly basic.

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## Polar Substituent Effects in Triplet Quenching. Excitation Transfer and Cycloaddition

*Sir:*

Rate constants for quenching of sensitizer triplets by excitation acceptors are sensitive to the triplet excitation energy gap, $E_T$(acceptor) − $E_T$(sensitizer), when transfer is endothermic.[1,2] The slope of a plot of log $k_Q$ vs. $E_T$(sensitizer) is roughly the theoretical value of 0.73 decade/kcal, i.e., $(2.3RT)^{-1}$, in favorable cases,[2] which value derives from spectroscopic excitation energies, the assumption of vertical[3] excitation transfer, and the consequent requirement that vertical energy deficits be made up thermally. The quenching of ketone triplets by simple alkenes, however, often leads ultimately to cycloadduct[4] via a polar triplet exciplex[5,6] and a 1,4 biradical, and such rates correlate instead with the energetics of electron transfer.[5–7] Quenching of triplet ketones by amines[8] has also been interpreted on the basis of charge transfer (CT).

Cycloaddition and excitation transfer have only occasionally been observed simultaneously with the same triplet donor–acceptor pair.[9] We now report a study of the kinetics of one such series. We find that, although triplet excitation transfer apparently dominates triplet quenching, sensitizer triplet excitation energies are much inferior to a blend of excitation energy and electron-transfer effects as predictors of rate. The CT contribution to $k_Q$ clearly does not simply correspond to the cycloaddition pathway.

The quenching of cyanophenanthrene triplets bearing remote polar substituents by *trans*-β-methylstyrene and by *trans*-anethole (*p*-methoxy-β-methylstyrene) leads to efficient trans–cis isomerization in the four cases that we studied (Table

**Table I.** Rate Constants for Triplet Quenching and Quantum Yields of Triplet Photoprocesses

| quenchee | $E_T$[a] | $E_{1/2}$[b] | *trans*-β-methylstyrene $k_Q$, $M^{-1}\,s^{-1}$ | *trans*-β-methylstyrene $\phi^T_{t\to c}$ | *trans*-β-methylstyrene $\phi^T_A$ | *trans*-anethole $k_Q$, $M^{-1}\,s^{-1}$ | *trans*-anethole $\phi^T_{t\to c}$ | *trans*-anethole $\phi^T_A$ |
|---|---|---|---|---|---|---|---|---|
| 3-methoxy-9-cyanophenanthrene | 58.34 | −2.05 | $9.7 \times 10^7$ | | | $4.12 \times 10^8$ | | |
| 9-cyanophenanthrene | 58.12 | −1.92 | $2.3 \times 10^8$ | 0.45 | 0.015 | $7.7 \times 10^8$ | 0.43 | $<3 \times 10^{-3}$ |
| 3,10-dicyanophenanthrene | 57.07 | −1.57 | $2.79 \times 10^8$ | | | $1.33 \times 10^9$ | 0.43 | 0.05 |
| 3-methoxy-10-cyanophenanthrene | 57.04 | −2.00 | $2.84 \times 10^7$ | | | $1.14 \times 10^8$ | 0.33 | 0.04 |
| 3,9-dicyanophenanthrene | 55.51 | −1.51 | $2.22 \times 10^7$ | | 0.035 | $1.43 \times 10^8$ | | |

[a] ±0.03 kcal/mol, cumene matrix, 77 K. [b] Reference 13.

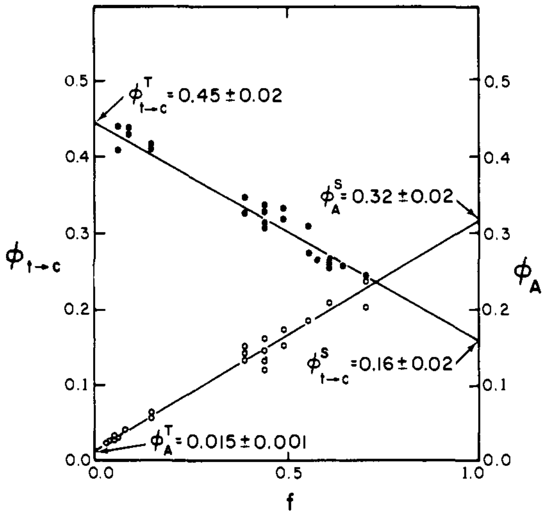

Figure 1. Quantum yield of isomerization of *trans*- to *cis*-β-methylstyrene (O, left ordinate) and of cycloaddition to 9-cyanophenanthrene (●, right ordinate) as a function of *f* (see text).

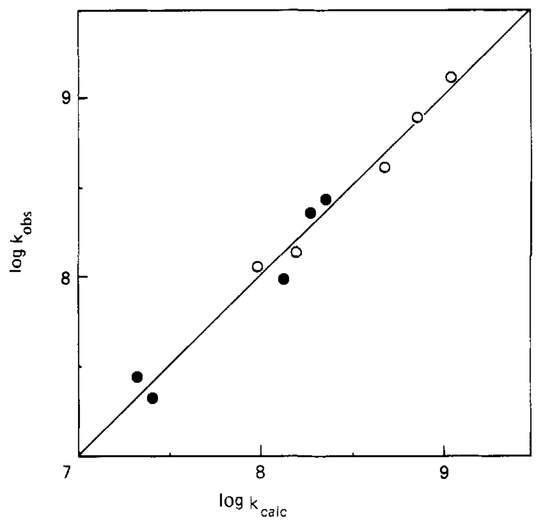

Figure 2. Log $k_Q$(obsd) vs. log $k_Q$(calcd) by eq 1 for *trans*-β-methylstyrene (●) and *trans*-anethole (O).

l). In several cases, formation of the head-to-head [2 + 2] cycloadduct was observed,[10] but never with $\phi^T > 0.05$. Figure 1 illustrates our separation of the isomerization quantum yield $\phi^T_{t\to c}$ and the cycloaddition quantum yield $\phi^T_A$ for the triplet component from the corresponding singlet components $\phi^S_{t\to c}$ and $\phi^S_A$ via the equations $\phi(\text{obsd}) = \phi^T + f(\phi^S - \phi^T)$, where $f = 1 - I/I_0$ for the fluorescence of the substituted phenanthrene. The parameter *f* is thus the fraction of phenanthrene singlet quenched, increasing as the styrene concentration increases. Even in the case most predisposed to charge transfer (as measured by $E_T + E^K_{1/2}$, vide infra), 3,10-dicyanophenanthrene triplet quenched by *trans*-anethole, $\phi_{t\to c}$ is very high, far out of line with the thermodynamic control expected for a biradical isomerization mechanism, but quite consistent with expectations based on a triplet transfer mechanism. In the latter case $\phi_{t\to c} = \alpha\phi_{isc}$, $\alpha = 0.5$,[11] and $\phi_{isc} = 0.82 \pm 0.05$ based on $\phi_{isc} = 1 - \phi_f$ and a preliminary estimate of $\phi_f = 0.18 \pm 0.05$. The quenching of more conventional sensitizers in the 53–60-kcal/mol range by *trans*-β-methylstyrene has already been determined to proceed by vertical triplet excitation transfer,[11] and we are confident that this mechanism also dominates the present results.

Rate constants $k_Q$ (Table I) for quenching of the cyanophenanthrene triplets in benzene were measured by kinetic absorption spectrophotometry at 500 nm, at or near the T-T absorption peaks, following excitation by the 8-ns pulse of a nitrogen laser. Plots of $\tau_T^{-1} = k_1 + k_Q[Q]$ vs. [Q] were linear, with $r > 0.991$ in all cases, typically 0.995. Phosphorescence spectra of the cyanophenanthrenes were determined in cumene matrix[12] at 77 K. A calibrated Jarrell-Ash ¼-m monochromator permitted wavelength determination to ±2 Å and consequent calculation of $E_T$ from the 0–0 maximum to ±0.03 kcal/mol. In view of the small range of $E_T$, it was deemed necessary to redetermine the values previously reported[10] in EPA, both to increase precision and to utilize a matrix as similar as possible to the reaction solvent.

The $k_Q$ values give poor correlations as functions of $E_T$ alone. For *trans*-β-methylstyrene, log $k_Q = -8.63 + 0.29E_T$ ($r = 0.64$); for *trans*-anethole, log $k_Q = -3.38 + 0.21E_T$ ($r = 0.51$). Inspection of Table I shows that increases of $k_Q$ are not even monotonic with $E_T$.

Qualitatively, we noted that remote methoxy substituents appears to produce unexpectedly slow rates, while remote cyano substituents caused rate enhancements. Thus, for each styrene, 3,10-dicyanophenanthrene shows an order of magnitude rate enhancement relative to 3-methoxy-10-cyanophenanthrene even though there is almost no difference in $E_T$. The availability of polarographic reduction potentials[13] for the five phenanthrenes permits fits[14] of the form log $k_Q = aE_T + b(E_T + E^K_{1/2}) + C$. The quantity $E_T + E^K_{1/2}$ is the proper measure of reducibility of the triplet,[8a] where $E^K_{1/2}$ (kcal/mol) $= 23.05E_{1/2}$ (volts). Quite good correlations result (eq 1 and 2); the results are plotted in Figure 2. Even better correlations, with no significant difference in the parameters, result when the $E_T$ values in EPA are used.

$$\log k_Q^{\beta MS} = -27.971 + 0.600E_T + 0.102(E_T + E^K_{1/2}),\quad R^2 = 0.950 \qquad (1)$$

$$\log k_Q^{t\text{-}An} = -23.678 + 0.535E_T + 0.107(E_T + E^K_{1/2}),\quad R^2 = 0.978 \qquad (2)$$

Sensitivity to $E_T$ is high, as expected for vertical excitation transfer. For *trans*-stilbene as an acceptor, with sensitizers of $E_T$ such that $1.3 \times 10^7 < k < 9.6 \times 10^8\ M^{-1}\,s^{-1}$, i.e., comparable with ours, we calculate a corresponding slope of 0.701 (cf. $1/RT$ = 0.73 decade/kcal) from published data.[2] Our numbers are slightly lower, but far from the values of 0.22–0.26 which we calculate from published data for the "nonvertical" acceptors *cis*-stilbene and the 1,2-diphenylpropenes.[2] Note that the *total* $E_T$ dependence in eq 1 and 2 is actually $a + b$ = 0.702 and 0.642, respectively. By ignoring the electron-transfer term, we would have observed a much lower sensitivity to $E_T$, inconsistent with the previously suggested[11] vertical transfer.

Sensitivity to $(E_T + E^K_{1/2})$ is only 17-20% of the sensitivity to $E_T$ but, since the variation in $E^K_{1/2}$ is large, is responsible for quite substantial rate effects. We believe that such charge-transfer effects may in principle be observable generally[7] in systems where only excitation transfer occurs, but in practice will be seen most clearly when, as in the present case (a) the range of $E_T$ is restricted, (b) $E_{1/2}$ varies substantially, and (c) structural variation is minimal within the series, so that steric effects, orbital overlap effects, etc., cancel out.

Phenomenological rate constants $k_A$ for triplet-cycloadduct formation may be estimated, if imprecisely, from $k_Q$ and $\phi_A^T$ by assuming $\phi_{isc} \sim 0.8$ for all phenanthrenes: $k_A = \phi_A/\phi_{isc} \times k_Q$. Both 3,10 disubstitutions, remote cyano and remote methoxy, enhance the rate of adduct formation with anethole, while 3,9-dicyanophenanthrene is less reactive than 9-cyanophenanthrene toward $\beta$-methylstyrene as measured by $k_A$. Those values thus accord rather poorly with the charge-transfer term, and both the triplet regiochemistry (head to head) and the $k_A$ values seem to follow better the "most stable biradical" precept. However, the stereochemistry[10] (*endo*-aryl) of the triplet reaction is not in accord with expectations based on a *freely rotating* triplet 1,4 biradical; the anomaly is currently under study.

Several studies[5,15,16] of the reactivity of triplets in cycloaddition to alkenes have suggested that charge transfer, or at least polar exciplex formation, is important. From the $k_A$ estimates above, it is clear that increased charge transfer does not enhance adduct formation from the triplet cyanophenanthrene-styrene pair. We conclude that CT is important in the *binding* of the reactants, not at the transition state for adduct (or perhaps biradical) *formation*, analogous to the situation with singlet-state cycloaddition via singlet exciplexes.[17,18] Our present results point to a triplet exciplex intermediate, bound by both exciton-resonance and CT interactions (though presumably with much less CT than the highly polar singlet exciplexes), which partitions between excitation transfer and collapse to adduct.

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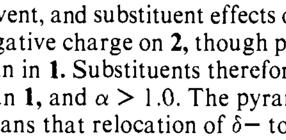
## The Nitroalkane Anomaly—Solvent Dependence

*Sir:*

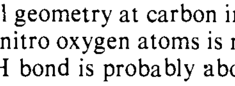
Nitroalkanes are conspicuously strong as C–H acids, but their proton transfer behavior is anomalous in several respects. For example, (1) nitroalkanes are "slow" acids, i.e., rate vs. equilibrium correlations reveal deprotonation of nitroalkanes and protonation of nitronate anions to be slower than for other carbon acid families, let alone for normal N–H and O–H acids;[1] (2) substituent effects within the series $X-C_6H_4-CH_2NO_2$ (arylnitromethanes) are greater on the *rates* of deprotonation ($k_f$) than on the equilibrium acidities ($K_a$). Brønsted's $\alpha = d \log k_f / d \log K_a \simeq 1.5$.[2]

Among reasons given for the slowness of carbon acids in general is the necessity, in most cases, for extensive nuclear reorganization and charge relocation upon proton loss. A recent study concludes that this is the main factor retarding proton transfer involving carbon acids.[3] However, it has been known for some time that C–H acids react much faster (taking $pK_a$ into account) in aprotic solvents than in protic solvents.[4,5] Ritchie argues persuasively that the reorganization of solvent molecules from reactant state to transition state locations is a costly process for C–H acids in protic solvents.[5]

The nitroalkane anomalies cited above were observed for polar, protic media. Both anomalies can be rationalized by assuming that solvent plays an important explicit role, namely, that nitroalkane acidity in protic solvents is enhanced by hydrogen-bonding stabilization of the nitronate anion (**1**), but that similarly effective solvation of the partial negative charge on the pyramidal substrate moiety in the transition state (**2**) does not occur. Thus, stabilization of **1** is borne largely by solvent, and substituent effects on $K_a$ are small ($\rho = 0.83$). The negative charge on **2**, though partial, is more accessible to Ar than in **1**. Substituents therefore affect the stability of **2** more than **1**, and $\alpha > 1.0$. The pyramidal geometry at carbon in **2** means that relocation of $\delta-$ to the nitro oxygen atoms is not well along,[6,7] even though the C–H bond is probably about half-broken.[6-8]



**1**



**2**

The picture we have described[9] allows a prediction: the use of an aprotic solvent will accelerate the reaction and will diminish $\alpha$. We report here rate and equilibrium data for reaction 1 in dimethyl sulfoxide at 25°C.

Equilibrium constants were obtained spectrophotometrically using $PhCO_2^- - PhCO_2H$ buffers. The products are separately solvated, not paired. Using lithium and potassium counterions and total [salt] up to $2 \times 10^{-2}$ M, there were revealed no ion

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