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 ϕ_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 β-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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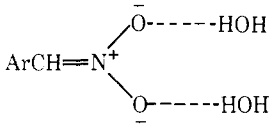
The Nitroalkane Anomaly—Solvent Dependence

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]



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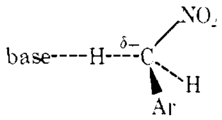

2

The picture we have described[9] allows a prediction: the use of an aprotic solvent will accelerate the reaction and will diminish α. 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 2×10^{-2} M, there were revealed no ion

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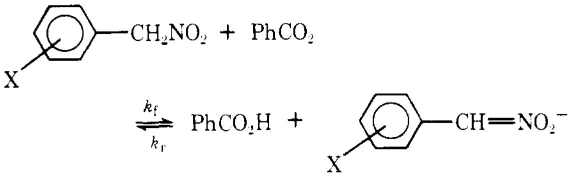
Table I. Kinetic and Thermodynamic Data in Me_2SO (25 °C) for

$$ArCH_2NO_2 + PhCO_2^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} PhCO_2H + ArCH{=}NO_2^-$$

compd	pK_a[a]	k_f, $M^{-1}\,s^{-1}$	k_r, $M^{-1}\,s^{-1}$	K_{eq}	k_f/k_r	k_s, s^{-1} [b]	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal $mol^{-1}\,deg^{-1}$
p-CH_3	12.33 ± 0.05	75 ± 4	979 ± 171	0.0295	0.076	8.42		
H	12.03 ± 0.03	133 ± 1	2450 ± 390	0.0590	0.0540	9.11	13.5 ± 0.5	−3.4 ± 1.8
p-Br	11.11 ± 0.15	1055 ± 268	2290 ± 680	0.490	0.460	9.81		
m-NO_2	10.04 ± 0.04	8560 ± 169	1150 ± 100	5.76	7.44	13.28		
p-CN	9.31 ± 0.09	13000 ± 745	360 ± 80	30.9	36.3	16.64		
p-NO_2	8.62 ± 0.11	16240 ± 1300	65 ± 16	151	250	17.21	6.9 ± 0.2	−16.0 ± 1.5
3,5-$(NO_2)_2$[c]	8.56 ± 0.06	221000 ± 1800	1930 ± 125	174	114			

[a] Calculated relative to pK_a = 10.8 for benzoic acid: C. D. Ritchie, "Solute-Solvent Interactions", Vol. 2, J. F. Coetzee and C. D. Ritchie, Eds., Marcel Dekker, New York, 1976, Chapter 12. [b] The k_s values are computed as small differences between large numbers and are of low precision. [c] We thank Mr. Donald Lamons for assistance in the preparation of this compound.


(1)

pairing or ionic strength effects. Special precautions toward oxygen or atmospheric moisture were unnecessary.

Kinetic data were obtained by stopped-flow spectrophotometry. The data fit eq 2, no evidence being found for more complex terms nor for lyate and lyonium ion catalysis. A primary isotope effect, k_H/k_D = 3.5–7.0, was found for 4-nitrophenylnitromethane. The kinetic and equilibrium constants are given in Table I.

$$k_{exptl} = k_s + k_f[PhCO_2^-] + k_r[PhCO_2H] \qquad (2)$$

The results characterize reaction 1 as a normal acid-base process with the proton-transfer step rate controlling.[10] The deprotonation rates (for a given K_{eq}) average ~10^5 faster in Me_2SO than in water. The Brønsted plot (see Figure 1) is linear for all substituents but 4-cyano and 4-nitro (which are markedly slow). The Brønsted slope = α = 0.92. Correspondingly, the reprotonation rates, k_r, show little dependence on the substituent (β near zero), the 4-cyano and 4-nitro compounds again being unusually slow.

A Hammett plot of log K_a vs. σ^- is linear for all substituents. The slope, ρ, is +2.65 (three times larger than in water). Log k_t is *not* linear either with σ^- or σ, but the dual substituent parameter method[11] could be applied to the rate and equilibrium data for the 4-substituted members of the series. The results are given in eq 3, 4, and 5. The results are in agreement with the proposition that resonance stabilization of the nitronate anion by aryl rings is important in Me_2SO,[12] but that such an interaction in the transition state is (relatively) weak.

$$\log (K_a{}^X/K_a{}^H) = 2.85\sigma_R + 3.27\sigma_I;\ \rho_R/\rho_I = 0.79 \qquad (3)$$

$$\log (k_f{}^X/k_f{}^H) = 1.19\sigma_R + 2.55\sigma_I;\ \rho_R/\rho_I = 0.47 \qquad (4)$$

$$\log (k_r{}^X/k_r{}^H) = -1.26\sigma_R - 0.70\sigma_I;\ \rho_R/\rho_I = 1.79 \qquad (5)$$

There remains to be explained a new "anomaly". The 4-cyano and 4-nitro members of the series do not fit the rate-equilibrium relationship defined by the other five members. The deviant pair belongs to a separate Brønsted family. We argue that the especially strong resonance interaction which stabilizes the nitronate anion in these two cases is absent in the (pyramidal) transition state; hence a proportional enhancement of log k_f is not forthcoming. A similar argument explains the small values of k_r for these two compounds.

Summary. The present results show that deprotonation of nitroalkanes is subject to a large kinetic solvent effect; that strong mesomeric electron-withdrawing groups do not accelerate proton transfer for arylnitromethanes to the extent anticipated from their effect on K_a; and that the "nitroalkane anomaly" is largely a consequence of experiments done with protic solvents.

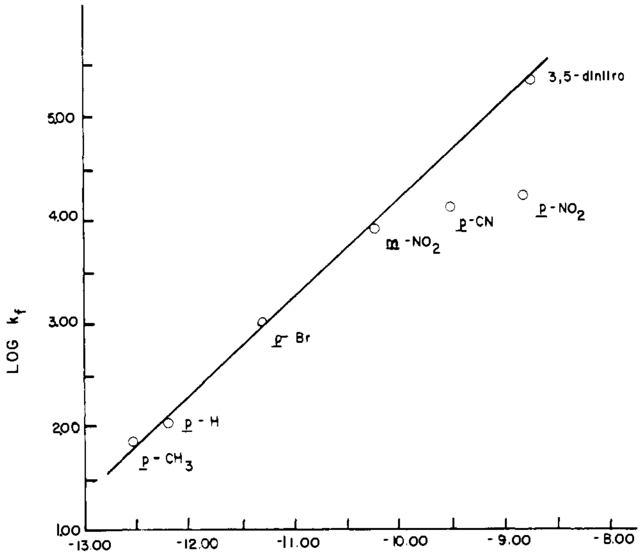


Figure 1. Brønsted plot of log k_f vs. log K_a; slope = α = 0.92

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Excited-State Photochemistry in the Tris(2,2′-bipyridine)ruthenium(II)–Sulfite System

Sir:

We have previously noted that, in many respects, the chemistry of the luminescent excited state of tris(2,2′-bipyridine)ruthenium(II) ($^*Ru(bpy)_3{}^{2+}$) is as well characterized as that of many ground-state metal complexes:[1] $^*Ru(bpy)_3{}^{2+}$ is relatively inert to substitution,[2] but, being both a strong reductant[3-5] and oxidant,[6] readily undergoes outer-sphere electron-transfer reactions with redox quenchers to produce $Ru(bpy)_3{}^{3+}$ and $Ru(bpy)_3{}^{+}$. In this communication the analogy between this excited molecule and ground-state metal complexes is further extended to include charge-transfer photochemistry; in the presence of sulfite ion the use of high intensity visible light[7] effects the sequential two-photon photolysis of $Ru(bpy)_3{}^{2+}$ to yield $Ru(bpy)_3{}^{+}$.

Laser flash photolysis (λ 530 nm, pulse length Δt = 20 ns, photons in at least tenfold excess over $Ru(bpy)_3{}^{2+}$)[8] provides a convenient technique for the production of $^*Ru(bpy)_3{}^{2+}$. When solutions containing $Ru(bpy)_3{}^{2+}$ (5×10^{-5} M) and a reductant (0.01–1.0 M) such as $Eu_{aq}{}^{2+}$ or sodium ascorbate (HA^-) are subjected to laser flash photolysis, the product $Ru(bpy)_3{}^{+}$ (monitored by absorbance changes at 500 nm where $Ru(bpy)_3{}^{2+}$ and $^*Ru(bpy)_3{}^{2+}$ have the same molar absorptivity) is seen to form predominantly in the second of three well-resolved stages. (1) During the laser pulse, ground-state $Ru(bpy)_3{}^{2+}$ is excited (eq 1, $^*k_1 = 2.3 \times 10^3\, I_0\epsilon_1\phi_1$, where I_0 is the laser intensity in einstein $cm^{-1}\,s^{-1}$, ϵ_1 = 850 $M^{-1}\,cm^{-1}$, the molar absorptivity of $Ru(bpy)_3{}^{2+}$ at 530 nm, and ϕ_1 is the quantum yield for $^*Ru(bpy)_3{}^{2+}$ formation at 530 nm[9]). (2) On the 0.1–1-μs time scale $Ru(bpy)_3{}^{+}$ formation by reaction of $^*Ru(bpy)_3{}^{2+}$ with $Eu_{aq}{}^{2+}$ or HA^- (eq 2, $k_q = 2.8 \times 10^7\ M^{-1}\,s^{-1}$ [10] and $2 \times 10^7\ M^{-1}\,s^{-1}$, respectively) parallels $^*Ru(bpy)_3{}^{2+}$ disappearance via eq 1 ($k_{-1} = 1.7 \times 10^6\ s^{-1}$) and eq 2. (3) On a much longer time scale ($t_{1/2} \geq 20$ μs for Q = $Eu_{aq}{}^{2+}$ and HA^-) back-reaction of the photoproducts (eq 3) regenerates $Ru(bpy)_3{}^{2+}$ and Q ($k_t = 2.7 \times 10^7$ and $1 \times 10^9\ M^{-1}\,s^{-1}$ for $Eu_{aq}{}^{3+}$ [10] and HA^-, respectively). The above description applies over the range of light intensities investigated (10^0–10^2 einstein $cm^{-2}\,s^{-1}$ or $^*k_1 = 2 \times 10^6\ s^{-1}$ to $2 \times 10^8\ s^{-1}$).

$$Ru(bpy)_3{}^{2+} \underset{k_{-1}}{\overset{^*k_1}{\rightleftharpoons}} {}^*Ru(bpy)_3{}^{2+} \tag{1}$$

$$^*Ru(bpy)_3{}^{2+} + Q \xrightarrow{k_q} Ru(bpy)_3{}^{+} + Q^+ \tag{2}$$

$$Ru(bpy)_3{}^{+} + Q^+ \xrightarrow{k_t} Ru(bpy)_3{}^{2+} + Q \tag{3}$$

By contrast, when solutions containing $Ru(bpy)_3{}^{2+}$ (5×10^{-5} M) and Na_2SO_3 (0.1–1.0 M, 25 °C) are flash photolyzed at moderate to high light intensities (10^1–10^2 einstein $cm^{-2}\,s^{-1}$), $Ru(bpy)_3{}^{+}$ is seen to form in *both* of the first two stages—that is both during and after the laser pulse. The relative amount formed during the pulse rises steeply with laser intensity. Formation of $Ru(bpy)_3{}^{+}$ in the second ("slow") stage is observed at all intensities and its rate of formation is, within experimental error, the same as that for $^*Ru(bpy)_3{}^{2+}$ disappearance. Thus the "slow" contribution may be attributed to dynamic quenching according to eq 2 with $k_q \sim 3 \times 10^5\ M^{-1}\,s^{-1}$.[11] (Back-reaction is very slow, with $k_t \leq 10^6\ M^{-1}\,s^{-1}$.) The additional $Ru(bpy)_3{}^{+}$ is produced during the laser pulse in yields which are a sensitive function of laser intensity.

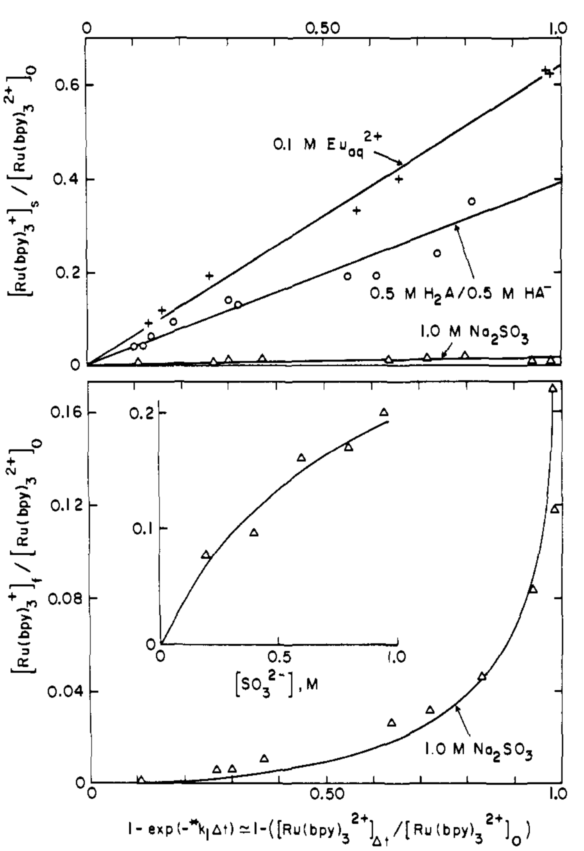

Figure 1. Plot of the yield of $Ru(bpy)_3{}^{+}$ produced after (top) and during (bottom) the 20-ns laser pulse as a function of the quantity ($1 - \exp(-^*k_1\Delta t)$). The solutions are 5×10^{-5} M in $Ru(bpy)_3{}^{2+}$ with concentrations of reducing agent as given in the figure. In the lower major figure the curve drawn is for κ = 0.05. The insert in the lower figure gives the sulfite ion dependence of the yield of $Ru(bpy)_3{}^{+}$ produced during the laser pulse. Error bars on the sulfite data are ±15% of the values shown. The error bars on the other data are ±7%.

The formation of $Ru(bpy)_3{}^{+}$ during the pulse may be explained in terms of a model involving photolysis of an excited state/sulfite ion pair (eq 4) according to eq 5.

$$^*Ru(bpy)_3{}^{2+} + SO_3{}^{2-} \overset{^*K}{\rightleftharpoons} {}^*Ru(bpy)_3{}^{2+}/SO_3{}^{2-} \tag{4}$$

$$^*Ru(bpy)_3{}^{2+}/SO_3{}^{2-} \xrightarrow{^*k_2} Ru(bpy)_3{}^{+} + SO_3{}^{-} \tag{5}$$

(Here $^*k_2 = 2.3 \times 10^3\, I_0\epsilon_2\phi_2$ (ϵ_2 is the molar absorptivity of the $^*Ru(bpy)_3{}^{2+}/SO_3{}^{2-}$ ion pair at 530 nm and ϕ_2 is the quantum yield for production of $Ru(bpy)_3{}^{+}$ from the ion pair.)

This model is supported by the data presented in Figure 1. For both upper and lower major figures the abscissa is the fraction of $Ru(bpy)_3{}^{2+}$ depleted after the laser pulse as calculated from $1 - \exp(-^*k_1\Delta t)$ assuming a 20-ns rectangular pulse and the excess photon limit. In the absence of multiphoton processes and/or very rapid disappearance of $^*Ru(bpy)_3{}^{2+}$, this expression gives the fraction of $Ru(bpy)_3{}^{2+}$ converted to $^*Ru(bpy)_3{}^{2+}$. In the presence of $Eu_{aq}{}^{2+}$ and HA^- (upper portion of figure) this quantity of $^*Ru(bpy)_3{}^{2+}$ may subsequently be converted to $Ru(bpy)_3{}^{+}$ via eq 2 with a yield (Y) determined by the product of the quenching yield ($Y_Q = k_q[Q]/(k_{-1} + k_q[Q])$) and the cage escape yield[12] ($Y_t = 1 -$