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A LINEAR FREE ENERGY RELATIONSHIP BETWEEN σ-VALUES AND RATE CONSTANTS FOR FLUORESCENCE QUENCHING OF SUBSTITUTED ANTHRACENES BY TRIPHENYLPHOSPHINE

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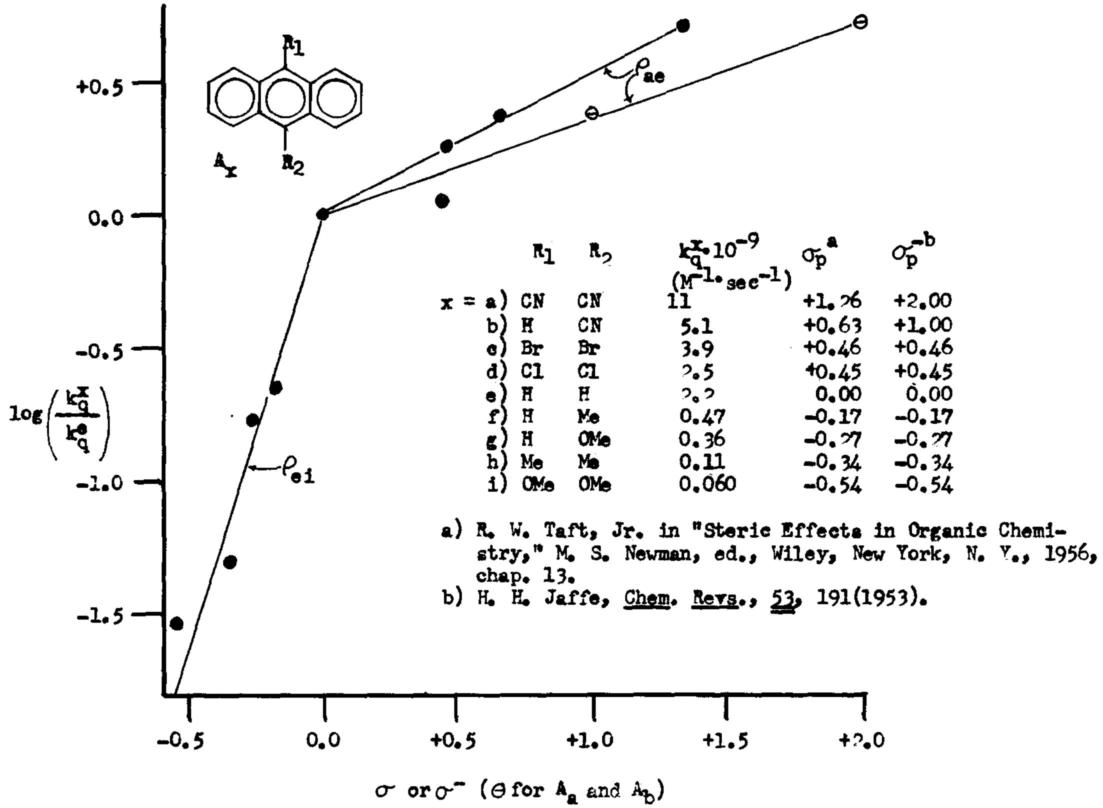
A number of Hammett-type correlations (sigma-rho graphs) for excited state reactions have been reported.[2] For instance, hydrogen abstraction of <u>meta</u>- and <u>para</u>-substituted toluenes by benzophenone triplets yields $\rho = -1.16$ when σ^+ parameters are employed.[3] A $\rho = -1.95$ was obtained for quenching fluorenone triplets by <u>para</u>-substituted anilines. A change in mechanism was suggested to explain why σ, σ^+, and σ^- parameters are required to obtain a linear fit.[4] A $\sigma^{\pm}$ treatment for quenching excited states of biacetyl by phenols and anilines demonstrated that the triplet state is more electrophilic than the excited singlet (for phenols, $\rho_1 = -1.02$ and $\rho_3 = -1.15$; for anilines, $\rho_1 = -0.33$ and $\rho_3 = 0.85$).[5] Quenching of <u>p</u>-dimethoxybenzene fluorescence by <u>para</u>-substituted α-chlorotoluenes and benzylacetates yields $\rho = 0.85$ and 5.2, respectively, using σ parameters only.[6] In all of these cases, charge or electron transfers are thought to be important, and the correlations are made by varying the substituents on the ground state molecules.

It is probable that the Hammett equation cannot be applied generally to excited state molecules. The resonance contributions to σ, especially, should vary significantly from molecule to molecule. In spite of this, we have found what we believe to be the first application of the Hammett equation to excited state molecules: a good correlation is obtained between σ or σ^- and $\log k_q^x$, the logarithm of the rate constants for fluorescence quenching of various substituted anthracenes, A_x, by triphenylphosphine, P.[7] The rate constants were measured by employing a standard Stern-Volmer treatment to the fluorescence intensities. Measurements were performed on degassed, dilute, benzene solutions of A_x and various amounts of P in sealed pyrex tubes. Experimental details will be supplied in a full paper.

The data, summarized in the table and graph, can be accommodated well by two straight lines with $\rho_{ae} = 0.55$ ($r = 0.954$) and $\rho_{ei} = 3.34$ ($r = 0.990$) for σ and $\rho_{ae} = 0.35$ ($r = 0.971$) for σ^-. It is possible that the lower r for the ρ_{ae} may be due to an increased relative importance of steric effects where electronic changes caused by R_1 and R_2 are relatively less important (<u>i. e.</u>, when the rate constants are near the diffusion controlled limit). However, if this were the major factor, k_q of A_c should be less than that of A_d. In any case, it is obvious that the quenching process is more sensitive to modifications in the electron rich anthracenes than in the electron poor ones and that two distinct mechanisms are involved. We prefer not to speculate on the exact meaning of the ρ-values at this time but to emphasize that, at least in certain cases, correlations between ground state σ-values and the reactivity of excited state species should be possible.



	R_1	R_2	$k_q^x \cdot 10^{-9}$ ($M^{-1} \cdot sec^{-1}$)	σ_p[a]	σ_p^-[b]
x = a)	CN	CN	11	+1.26	+2.00
b)	H	CN	5.1	+0.63	+1.00
c)	Br	Br	3.9	+0.46	+0.46
d)	Cl	Cl	2.5	+0.45	+0.45
e)	H	H	2.2	0.00	0.00
f)	H	Me	0.47	-0.17	-0.17
g)	H	OMe	0.36	-0.27	-0.27
h)	Me	Me	0.11	-0.34	-0.34
i)	OMe	OMe	0.060	-0.54	-0.54

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