

Short Communication

Encounter complexes in singlet quenching

II: Quenching of 2,6-dimethoxynaphthalene by benzyl chlorides

R. C. WHITE and R. E. BUCKLES

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242 (U.S.A.)

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In an earlier paper [1] we discussed the role of encounter complexes in singlet quenching, showing that the formation of the encounter complex may or may not be the rate determining step in the quenching process. This was based on the observation that non-linear correlations often exist between the logarithm of the quenching rate constant and the electronic properties of the quencher [2]. The non-linearity of these plots is predictable from the kinetics for the mechanism in scheme 1. This communication deals with our efforts to support this mechanism further by studying the fluorescence quenching of 2,6-dimethoxynaphthalene (DMN) by a series of benzyl chlorides in acetonitrile.

Scheme 1



Experimental

Relative fluorescent intensities were measured on a Hitachi Perkin-Elmer MPF 2A fluorescence spectrophotometer. Absorption spectra were recorded with a Cary model 118 spectrophotometer. The benzyl chlorides were either purchased or prepared by standard methods and were doubly distilled under reduced pressure, except for *p*-cyanobenzyl chloride which was purified by repeated crystallization. DMN was crystallized three times and sublimed twice under reduced pressure. In variable temperature studies, samples were allowed to equilibrate for 30 min prior to measure-

ments. The absorption spectra showed the absence of ground state complex formation between the benzyl chlorides and DMN.

Results and discussion

The data for the fluorescence quenching of DMN are given in Table 1, which shows that the quenching rate constants increase with quencher electron affinity giving a linear Hammett correlation (Fig. 1). Compounds

TABLE 1
Quenching of DMN fluorescence by p -XC₆H₄CH₂Cl

Compound	X	$E_{1/2}^a$ (V)	$10^9 k_q'$ (M ⁻¹)	ΔH^b (kcal mol ⁻¹)	ΔS (cal mol ⁻¹ K ⁻¹)
1	Me	-2.25	0.08	-1.0	-24
2	H	-2.20	0.15	-1.9	-27
3	F	-2.25	0.22	-2.3	-27
4	Cl	-2.08	1.22	-2.7	-26
5	CN	-1.61	11.62	+0.7	-10

^a Half-wave reduction potentials in DMF versus the dropping mercury electrode in 0.2 N tetrabutylammonium perchlorate as supporting electrolyte.

^b Taken from the slopes of the Stern-Volmer plots at four temperatures from 10 °C to 50 °C and corrected for change of solvent density with temperature.

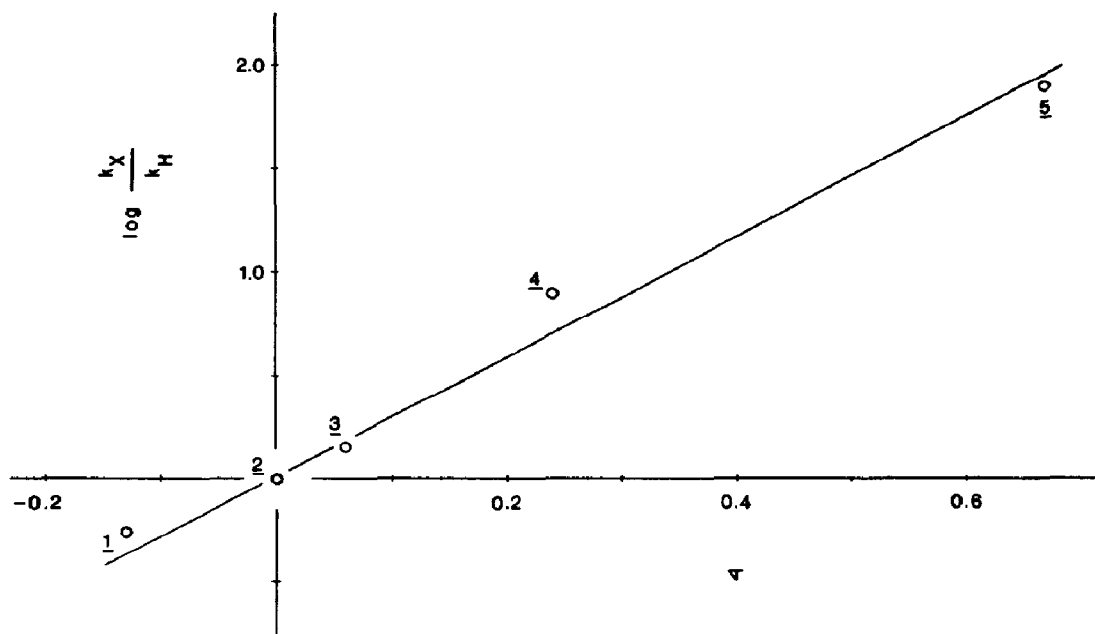


Fig. 1. Hammett plot for the quenching of DMN fluorescence by benzyl chlorides. The compound numbers are the same as those listed in Table 1.

1 - 4 all show a negative temperature dependence suggesting the reversibility of the quenching process [3 - 6]. The decrease in the enthalpy of activation for compounds 1 - 4 correlates with increasing quencher electron affinity reflecting increased exciplex stability. Compound 5 shows a small positive temperature effect and a positive enthalpy of activation. Since the quenching rate constant and the enthalpy of activation are below those expected for an irreversible diffusion controlled process [7], compound 5 can best be described as quenching by a process which is much less reversible than for compounds 1 - 4. The entropy of activation is approximately the same for compounds 1 - 4 suggesting that all four compounds quench from the same transition state, the high negative values being indicative of the restricted geometry of the exciplex. The less negative value for compound 5 shows that quenching occurs from a looser bound transition state nearer the encounter complex on the reaction coordinate. Thus, quenching by compounds 1 - 5 involves two rate determining transition states.

Earlier [1] we proposed that the quenching process includes the reversible formation of an encounter complex which then leads to reversible exciplex formation as shown in scheme 1. A steady state approximation for steps 1 - 3 yields the following Stern-Volmer expression:

$$\frac{\Phi_0}{\Phi} = 1 + k_q' \tau [Q] \quad (4)$$

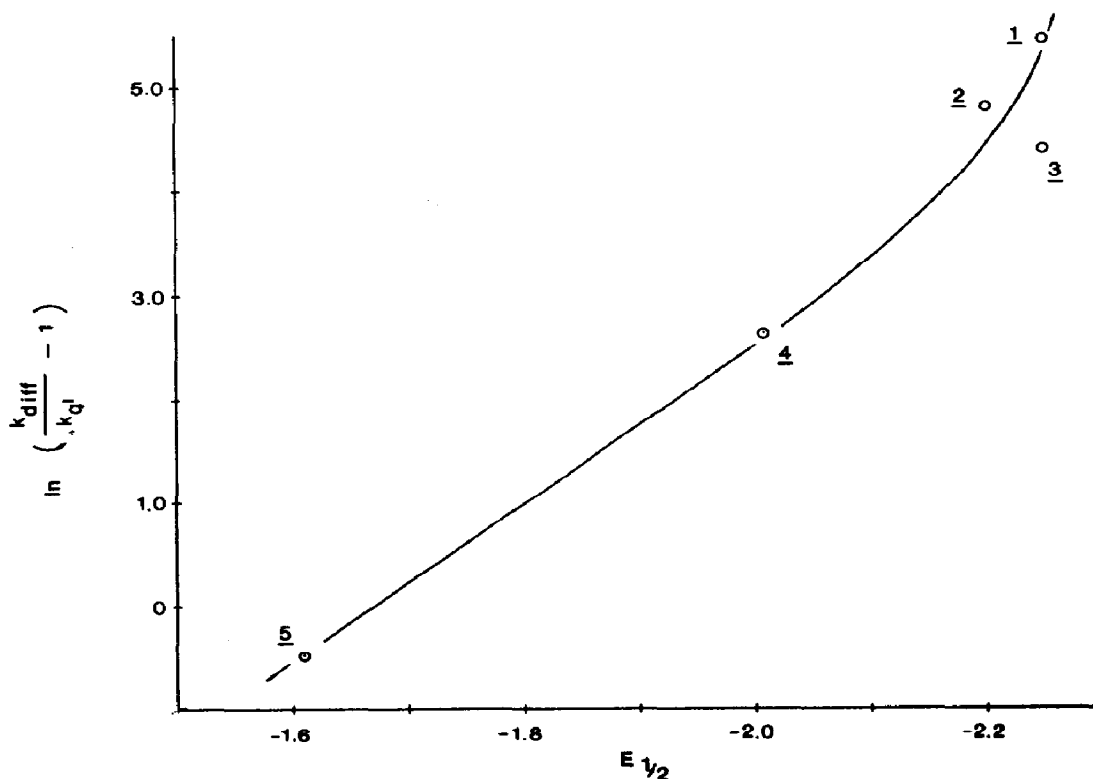


Fig. 2. Correlation of the quenching rate constant with quencher electron affinity.

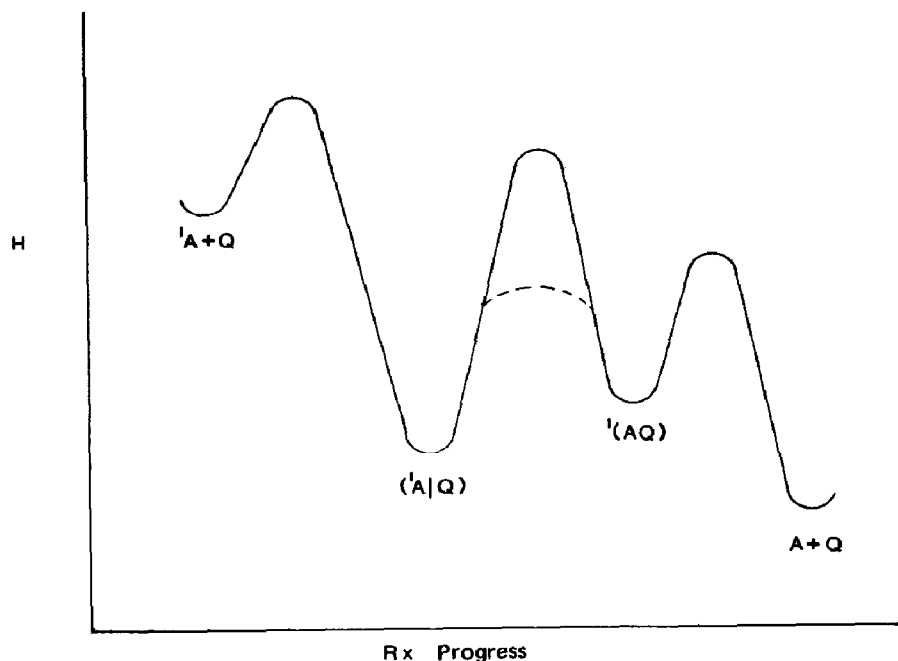


Fig. 3. Possible profile for the singlet quenching process.

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From this the following expression can be derived:

$$\frac{k_{\text{diff}}}{k_q'} - 1 = \frac{k_{-q}}{k_2} \left(1 + \frac{k_{-2}}{k_3} \right) \quad (5)$$

The right-hand terms in eqn. (5) describe whether the second or third transition state of scheme 1 is rate determining.

Hammond [8] notes that, for a constant donor and a series of acceptors, a linear correlation should exist, given by the equation below, so that a plot of $\ln k_q'$ versus $E_{1/2}$ will give a straight line:

$$\ln k_q' = c_1 + c_2 E_{1/2} \quad (6)$$

It can be seen then, that a linear correlation exists when the second transition state is rate determining and that a deviation will be seen as the third transition state becomes significant. Figure 2 shows a plot of $\ln (k_{\text{diff}}/k_q' - 1)$ versus $E_{1/2}$ for the data shown in Table 1. The plot shows that as the quencher electron affinity decreases, the line deviates from linearity.

Therefore, one can construct a graphical representation of the quenching process such as that shown in Fig. 3. This shows the relative enthalpies of activation for the formation of the encounter complex and the exciplex, and for the quenching process. The observed values are dependent upon which transition state is rate determining.

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