

## Short Communication

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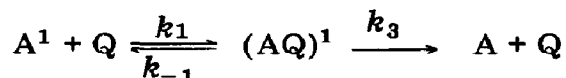
### The role of encounter complexes in singlet quenching

R. C. WHITE and R. E. BUCKLES\*

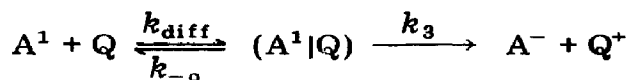
*Department of Chemistry, University of Iowa, Iowa City, Iowa 52242 (U.S.A.)*

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While the existence of exciplexes in photochemical processes has been well established [1, 2], considerable interest is still being directed towards the mechanism of their formation and decay. The change in quantum yield of adduct formation with temperature for some photochemical cycloadditions [3 - 6] led to the suggestion that the intermediate exciplex was being formed reversibly. Subsequent thermodynamic studies [7 - 9] showed that this was indeed the case. In a series of structure-reactivity studies [10, 11] Hammond proposed the following mechanism in which the exciplex is formed directly from the excited state A and the ground state Q, precluding the formation of any encounter complex:



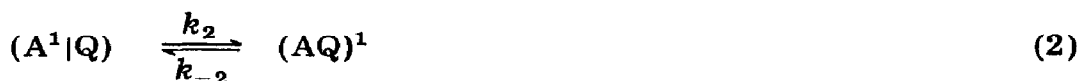
Weller [12] and Ledwith [1] have proposed that the exciplex is formed via a variety of collisional complexes termed encounter complexes in which the components are separated by distances from 5 to 7 Å. Indeed, there has been one report [13] of emission from the encounter complex in the difluoroanthracene-dimethylhexadiene system. Yet, only the Evans mechanism [14] recognizes the encounter complex in a kinetic scheme, but proposes that charge transfer occurs irreversibly from an encounter complex precluding any exciplex as proposed by Weller.



It has been shown [10, 15] that the free energy of the quenching process is related to either the ionization potential or the electron affinity of the quencher, and attempts have been made to show a linear correlation between the logarithm of the quenching rate constant and these two physical properties [7, 8, 12]. In some cases a linear correlation either does not hold or is suspect. A striking example of this is found in a recent report [16] on the triphenylphosphine quenching of a series of substituted anthracenes

with increasing electropositive character. The authors attributed this lack of linearity to a change in the quenching mechanism through the series.

The above quenching mechanisms can be modified to include the reversible formation of an encounter complex which then leads to reversible exciplex formation. Such a mechanism is shown in the following scheme:



A steady state approximation for steps 1 - 3 yields the following Stern-Volmer expression:

$$\Phi_0/\Phi = 1 + k_{q'} \tau [Q] \quad (4)$$

in which the quenching rate constant can be expressed as

$$\frac{1}{k_{q'}} = \frac{1}{k_{diff}} + \frac{k_{-q}}{k_{diff}k_2} + \frac{k_{-q}k_{-2}}{k_{diff}k_2k_3} \quad (5)$$

The right hand terms refer to the free energy differences between the initial reactants and the three possible transition states in reactions (1) - (3). As in the Evans mechanism,  $k_{q'}$  is measured and  $k_{diff}$  can be calculated so that the following expression is obtained:

$$\frac{k_{diff}}{k_{q'}} - 1 = \frac{k_{-q}}{k_2} \left( 1 + \frac{k_{-2}}{k_3} \right) \quad (6)$$

The two right hand terms determine whether the second or third transition state is rate determining. It can thus be seen that the Evans expression is obtained when the second transition state is rate determining and that a deviation will be seen as the third transition state becomes significant.

Therefore, in the case of a series of acceptors and a constant donor, where

$$\Delta G \approx c - \{ {}^1E_A + E(A^-/A) \}$$

if quenching occurs via charge transfer through irreversible exciplex formation from the encounter complex, a plot of  $\ln \{ (k_{diff}/k_{q'}) - 1 \}$  versus  ${}^1E_A + E(A^-/A)$  should result in a straight line, which has been shown by Evans. However, if quenching occurs via charge transfer through reversible exciplex formation from the encounter complex, a deviation from linearity will be seen, the magnitude indicating the degree of reversibility, *i.e.* any deviation from linearity of these plots can be attributed to the formation of a significant amount of the encounter complex.

An example of this is seen in Fig. 1 which shows the data obtained by Weiss and coworkers [16] for the substituted anthracene-triphenyl-

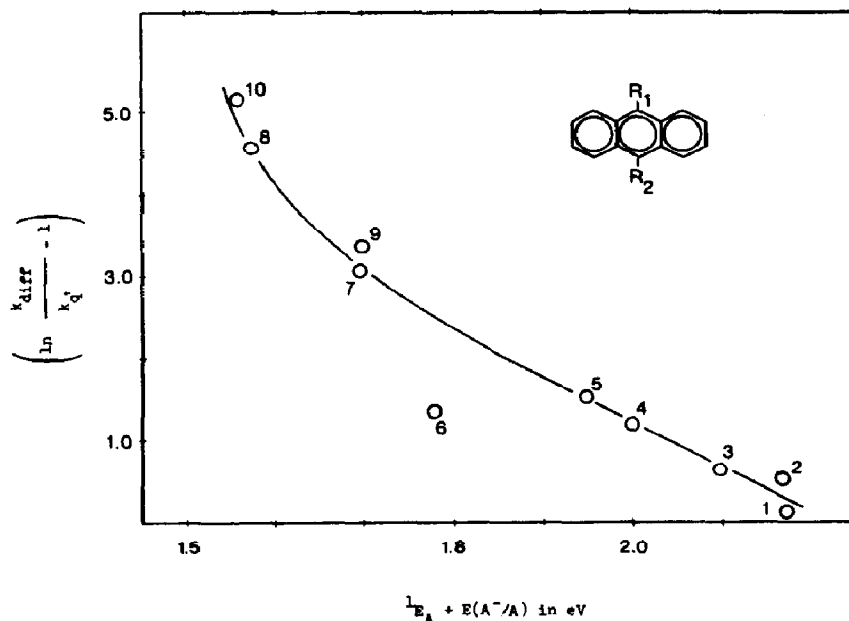


Fig. 1. Fluorescence quenching of anthracenes by triphenylphosphine: (1)  $R_1 = H$ ,  $R_2 = CN$ ; (2)  $R_1 = Br$ ,  $R_2 = Br$ ; (3)  $R_1 = H$ ,  $R_2 = Br$ ; (4)  $R_1 = Cl$ ,  $R_2 = Cl$ ; (5)  $R_1 = H$ ,  $R_2 = Cl$ ; (6)  $R_1 = H$ ,  $R_2 = H$ ; (7)  $R_1 = H$ ,  $R_2 = Me$ ; (8)  $R_1 = Me$ ,  $R_2 = Me$ ; (9)  $R_1 = H$ ,  $R_2 = OMe$ ; (10)  $R_1 = OMe$ ,  $R_2 = OMe$ .

phosphine system. This shows that as the anthracenes become increasingly electropositive the line deviates from linearity. Thus, the attribution to a change in mechanism could well be the conditions stated above.

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