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THE QUENCHING OF THE TRIPLET STATES OF AROMATIC CARBONYL COMPOUNDS BY TRIETHYLAMINE: SOLVENT EFFECTS ON CORRELATIONS WITH THE FUNCTION $\{^3\Delta E_{0,0} + E(A^-/A)\}$

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Summary

Rate constants have been determined for the quenching of a series of aromatic carbonyl triplets by triethylamine in acetonitrile, benzene and cyclohexane. These data together with half-wave reduction potentials have allowed the examination of solvent effects on correlations of log k_q with the function $\{^3\Delta E_{0,0} + E(A^-/A)\}$. A dramatic improvement is observed as the polarizability of the medium decreases and this is attributed to the resulting decrease in the overall reaction probability.

1. Introduction

It is currently accepted that amines quench the triplet states of aromatic ketones via an encounter complex which is stabilized by charge-transfer interaction; this complex then breaks down to products. Such processes have been reviewed [1].

In order to demonstrate the involvement of electron donation from the quencher, a method based on a treatment designed by Weller [2, 3] for the interaction of aromatic hydrocarbon singlet states with amines has been employed. In particular it has been proposed by Guttenplan and Cohen that the relation of the following equation can be applied to the reaction of carbonyl excited states with electron donors when such reactions are endothermic by more than 5 kcal mol^{-1} [4]:

$$-\log k_q \propto \Delta G_e \approx \text{IP}_Q - \{\Delta E_{0,0} + E(A^-/A)\} + C \tag{1}$$

In this equation k_q is the quenching rate constant, $\Delta E_{0,0}$ the electronic energy of the excited state, IP_Q the ionization potential of the donor (quencher) and $E(A^-/A)$ the reduction potential of the acceptor in its ground state. Thus for a given excited state with various donors a linear relation

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between $\log k_q$ and IP_Q should be observed. Correlations of this type have met with varying degrees of success [4 - 7]. For a given donor with various excited states a linear relation between $\log k_q$ and $\{\Delta E_{0,0} + E(A^-/A)\}$ is indicated and an excellent correlation has been reported for the quenching of aromatic carbonyl triplets by triethylamine[†] (TEA) [5]. We have ourselves experienced minimal success in obtaining such correlations for the quenching in benzene of a series of aromatic carbonyl triplets by quenchers suspected to be of the charge-transfer type. We have therefore re-examined the quenchings of such triplets by TEA.

The literature half-wave reduction potential data for aromatic carbonyl compounds are highly unsatisfactory in that experimental conditions vary considerably and often no confident choice between several published values can be made. We have therefore determined the half-wave reduction potentials of the compounds investigated under standardized conditions [9]. Quenching rate constants were determined by kinetic absorption spectrometry of triplet states produced by absorption of the 2.5 ns light pulse of a nitrogen laser (337 nm).

2. Experimental

2.1. Materials

Acetonitrile was passed down a column of activated alumina, refluxed over potassium borohydride for 4 d and distilled. Benzene and cyclohexane (AnalaR) were subjected to sulphuric acid, bicarbonate and water treatment and were distilled from phosphorus pentoxide. TEA was distilled from calcium hydride. Benzophenone (48 - 49 °C, EtOH), benzil (95 - 96 °C, EtOH), fluorenone (80 - 80.5 °C, EtOH$-H_2O$) and 2-naphthaldehyde (50 - 51 °C, H_2O) were recrystallized. 2-Acetonaphthone (Aldrich) was used as supplied. Acetophenone and m-methoxyacetophenone were distilled.

2.2. Determination of rate constants

Degassed solutions of carbonyl compound (optical density at 337 nm ≈ 1.0) containing various amine concentrations were subjected to the 2.5 ns light pulse of a Lamda Physik 1 MW nitrogen laser. Transient triplet states were monitored by kinetic absorption spectrometry and stored oscilloscope traces were photographed. The data were digitized by means of a D-MAC digitizer under the control of a DEC PDP-11/45 computer and were transferred on magnetic tape to the Manchester Regional Computer Centre CDC 7600/ICL 1906 A system. Analysis was carried out by means of an iterative programme developed by Dr. C. W. Gilbert of the Christie Hospital and Holt Radium Institute, Manchester. This gave the best parameters for the exponential $OD_t = A(e^{-k't} + B)$.

[†]A strong correlation has also been reported between the rate constants for gas phase quenching of aromatic singlet states by butadienes and the estimated electron affinities of the aromatic compound [8].

2.3. Half-wave reduction potentials

These were determined in 50% aqueous ethanol at pH 12.65 as described in ref. 9.

3. Results and discussion

The reactions summarized in the following equations take place after triplet formation:

$$^3A* \xrightarrow{k_d} A \tag{2}$$

$$^3A* + A \xrightarrow{k_{sq}} A + A \tag{3}$$

$$^3A* + Q \xrightarrow{k_q} A + Q \text{ (or products)} \tag{4}$$

The first order decay constant k' is given by the following relation

$$k' = k_d + k_{sq}[A] + k_q[Q] \tag{5}$$

where k_d, k_{sq} and k_q are respectively the rate constants for natural triplet decay in the medium, self quenching by carbonyl compound (A) and quenching by amine (Q). Plots of k' versus amine concentration gave straight lines of slope k_q, and such a plot is shown in Fig. 1 together with a typical experimental trace.

The quenching process under discussion is thought to involve charge-transfer interaction and we have therefore determined rate constants in three solvents, namely acetonitrile, benzene and cyclohexane, to accommodate the possibility that the quality of the correlation with the function $\{^3\Delta E_{0.0} + E(A^-/A)\}$ depends on the solvent polarizability. Quenching rate constants
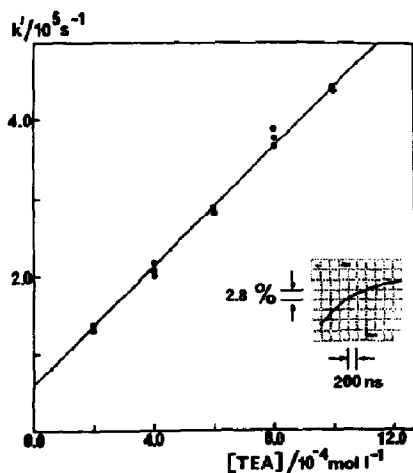

Fig. 1. Dependence of the first order constant for decay of the benzil triplet in cyclohexane on the TEA concentration. Inset: time dependence of benzil triplet decay monitored at 490 nm after absorption by benzil of a 2.5 ns light pulse (337 nm) in cyclohexane containing benzil (1.5×10^{-2} mol l^{-1}) and TEA (10^{-3} mol l^{-1}).

TABLE 1

Triplet energies $^3\Delta E_{0,0}$, half-wave reduction potentials $E(A^-/A)$ and rate constants k_q for quenching of aromatic carbonyl triplets by TEA

Carbonyl compound	$^3\Delta E_{0,0}$ (kcal mol^{-1})	$-E(A^-/A)$ (eV (kcal mol^{-1}))		k_q (l mol^{-1} s^{-1})			
		This work [9]	Previously used [5]	CH$_3$CN	C$_6$H$_6$	C$_6$H$_{12}$	Previously used [5]
Valerophenone (1)	74.6[a]	—	1.99 (45.9)[b]	—	—	—	4.2×10^9 [e]
Acetophenone (2)	73.6 [10]	1.66 (38.3)	—	—	1.9×10^9	—	—
m-Methoxyacetophenone (3)	72.4 [11]	1.74 (40.1)	—	2.3×10^8	4.3×10^7	8.1×10^7	—
Benzophenone (4)	68.5 [10]	1.55 (35.7)	1.73 (39.9) [13]	3.8×10^9	1.7×10^9	1.4×10^8	2.3×10^9 [e] 5.4×10^7 [f]
p-Aminobenzophenone (5)	67.0 [12]	—	1.99 (45.9)[c]	—	—	—	—
2-Naphthaldehyde (6)	59.5 [10]	1.34 (30.9)	1.71 (39.4) [14][d]	6.1×10^7	1.3×10^7	7.5×10^6	8.0×10^6 [g]
2-Acetonaphthone (7)	59.3 [10]	1.72 (39.7)	1.90 (43.8)[c]	3.0×10^5	2.1×10^5	1.2×10^5	6.0×10^5 [g]
Biacetyl (8)	54.9 [10]	1.03 (23.8)	1.46 (33.7)[c]	—	—	—	5.0×10^7 [e]
Benzil (9)	53.7 [10]	0.71 (16.4)	—	1.2×10^9	2.9×10^8	8.8×10^8	—
Fluorenone (10)	53.3 [10]	1.21 (27.9)	1.36 (31.4) [15][d]	4.7×10^8	1.6×10^7	1.0×10^7	3.2×10^7 [f]

[a]Value for propiophenone [10]. [b]Value for acetophenone [13]. [c]Estimated. [d]Normalized. [e]Benzene. [f]Cyclohexane. [g]Acetonitrile.
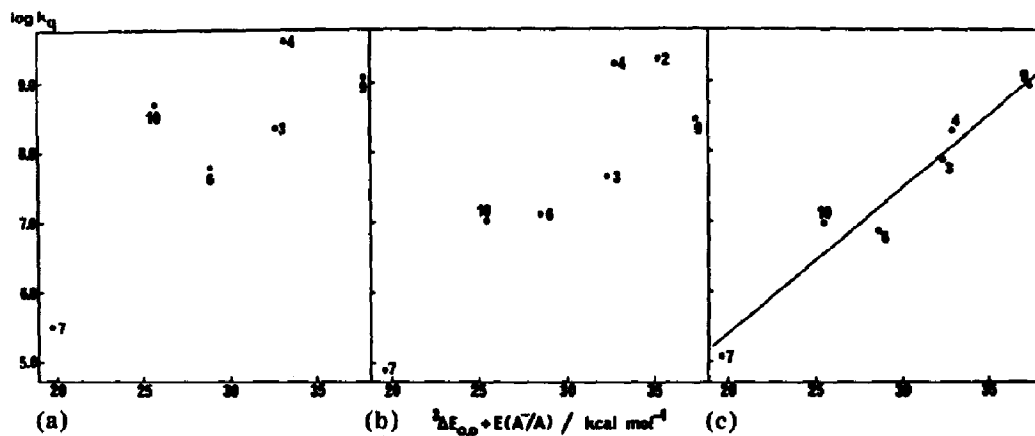
Fig. 2. Plot of log k_q against the function $\{^3\Delta E_{0.0} + E(A^-/A)\}$ for TEA quenching of carbonyl triplets in (a) acetonitrile (b) benzene and (c) cyclohexane. See Table 1 for the triplet identity.

and half-wave reduction potentials are given in Table 1 together with values used previously by Guttenplan and Cohen [5]. In Fig. 2 are shown plots of log k_q versus $\{^3\Delta E_{0.0} + E(A^-/A)\}$ constructed from our data for the three solvents. Interestingly the charge-transfer correlation improves on changing to the less polarizable solvent, the correlation coefficients being 0.82, 0.89 and 0.98 in acetonitrile, benzene and cyclohexane respectively with almost identical slopes of 0.19, 0.20 and 0.21 mol kcal^{-1} respectively. These results raise important questions concerning the value of the correlation published by Guttenplan and Cohen [5] which was constructed from literature rate constants measured in acetonitrile (6 and 7), benzene (1,4 and 8) and cyclohexane (5 and 10) together with half-wave reduction potentials which were either literature values determined under a variety of conditions and normalized or estimated (see Table 1 for details and triplet identities). These data gave a surprisingly excellent correlation coefficient of 0.99 and a slope of 0.28 mol kcal^{-1} (Fig. 3).
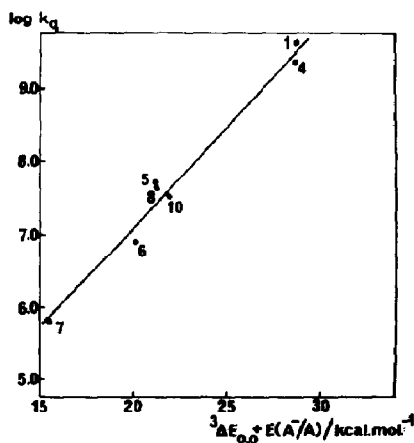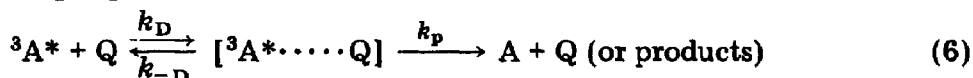

Fig. 3. Plot of log k_q against the function $\{^3\Delta E_{0.0} + E(A^-/A)\}$ for triethylamine quenching of carbonyl triplets according to the data of Guttenplan and Cohen [5]. See Table 1 for the triplet identity.

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It is instructive to consider the observed solvent effect in terms of the following sequence

$$^3A* + Q \xrightleftharpoons[k_{-D}]{k_D} [^3A* \cdots \cdot Q] \xrightarrow{k_p} A + Q \text{ (or products)} \tag{6}$$

in which the formation of an exciplex or charge-transfer stabilized encounter complex between the carbonyl triplet ($^3A*$) and amine quencher (Q) takes place at an essentially diffusion controlled rate. The measured rate constant k_q is given by the equation

$$k_q = \frac{k_p k_D}{k_{-D} + k_p} \tag{7}$$

and for low overall reaction probability, i.e. $k_{-D} \gg k_p$, the following relation should hold

$$k_q = K k_p \tag{8}$$

where K is the equilibrium constant for exciplex formation. Only in such a situation and where k_p is insensitive to the function $\{^3\Delta E_{0,0} + E(A^-/A)\}$ should the relation of eqn. (1) hold. In cyclohexane the lower solvent polarizability should lower the exciplex stability, i.e. increase k_{-D}, and should increase the validity of eqn. (8). A better correlation is therefore understandable.

4. Conclusions

The quenching in cyclohexane of aromatic carbonyl triplets by TEA correlates well with the function $\{^3\Delta E_{0,0} + E(A^-/A)\}$ of the carbonyl compound. As the solvent polarizability increases so does the overall quenching efficiency and a good correlation is no longer observed. This is in agreement with a situation in which the rate constant for exciplex dissociation becomes smaller with respect to further reaction of that complex as the solvent polarizability increases.

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