Short Communication

Quenching of biacetyl singlets by olefins: dependence on the solvent acceptor number

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Quenching of excited states by mechanisms involving total or partial participation of charge transfer (CT) states is very common for both singlet and triplet electronic excited states. Typical examples of these processes are the quenching of aromatic hydrocarbons and carbonyl excited states by aromatic compounds [1], olefins [2] and amines [3 - 6]. In most of these systems the participation of CT structures is supported by a strong dependence of the quenching rate constant on both the ionization potential (IP) of the donor and the reduction potential of the acceptor. Simple considerations regarding the change in energy along the reaction path suggest that the rate of these processes should increase when the dielectric constant ϵ and the polarizability of the solvent increase [7, 8], and that this dependence can be employed as a measure of the amount of charge separation at the critical configuration [9]. Nevertheless, quenching by this mechanism involves several partially (or totally) reversible steps which the solvent can modify in such a way that a simple correlation does not emerge [4, 8]. In this way it has been found that an increase in the solvent dielectric constant increases [6, 10, 11], decreases [12], leaves unchanged [4, 5, 9] or changes erratically [13, 14] the rate of quenching in reactions which are considered to occur by CT interactions.

The quenching of biacetyl singlets by diolefins is among those reactions that are considered to occur by a charge transfer mechanism and whose rate is solvent dependent [15]. The sensitivity of this reaction to the stability of the CT complex is emphasized by the relationship observed by Monroe *et al.* [15] in benzene as solvent between log k_Q (where k_Q is the rate constant for quenching) and the IP of the olefin. The data of Fig. 1 show that a similar strong dependence (a change in rate by a factor of 10^3 for a change in IP of 1 eV) is obtained in dichloromethane, a solvent where the rate is considerably faster than in benzene. In order to characterize the property of the solvent which determines the quenching rate, we have measured the rate of quenching by 2,5-dimethyl-2,4-hexadiene and 2,3-dimethyl-2-butene in several solvents
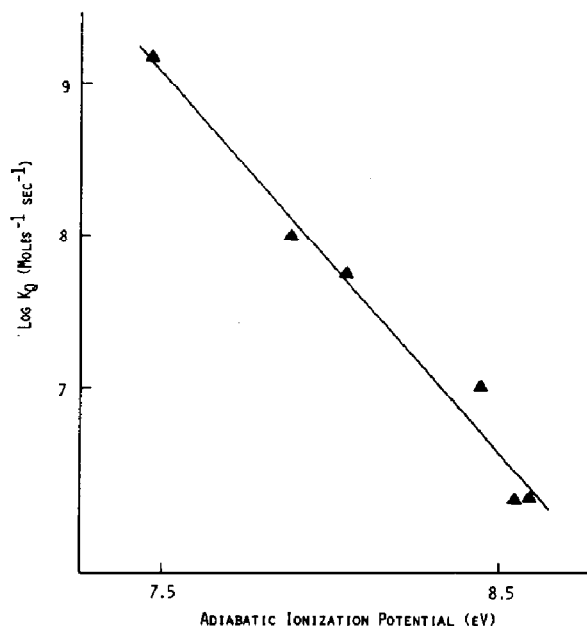
Fig. 1. A plot of log k_Q vs. olefin adiabatic ionization potential in dichloromethane solution.

and solvent mixtures. These olefins were chosen since their rates can be measured in a wide range of solvents. The results obtained are given in Table 1. The k_Q values given in this table were derived from the slope of Stern—Volmer plots for the fluorescence quenching and the biacetyl singlet lifetime τ_s. The values of τ_s, when not available in the literature, were derived from the relative fluorescence quantum yields and integrated absorption bands in the solvent considered and in a reference solvent where τ_S is known. Benzene and cyclohexane ($\tau_S = 10$ ns and $\tau_S = 13$ ns respectively [15]) were employed as references for solvents of low dielectric constant and acetonitrile ($\tau_S = 8.2$ ns [15]) was employed as a reference for solvents and solvent mixtures of high dielectric constant. The values of τ_S have been found to be only slightly sensitive to the solvent [15]. In agreement with this, the values of τ_S obtained by the present method generally differ by less than a factor of 2. The only large discrepancy was obtained with dimethylsulphoxide, for which a lifetime of 2.2 ns was obtained. The short lifetime obtained in this solvent is probably due to quenching by impurities, but this would not modify the evaluated quenching rate constant.

The data of Table 1 show a wide range of k_Q values in the different solvents. Furthermore, the data show that the solvent dependence is rather similar for both olefins. The only noticeable difference is the wider range of values obtained employing 2,3-dimethyl-2-butene. This can be partly a consequence of partial diffusion control for the quenching by 2,5-dimethyl-2,4-hexadiene in some solvents but also can be a consequence of the larger selectivity generally associated with a lower reactivity.

TABLE 1

Experimental results

Solvent	ϵ	η	Donor number	Acceptor number[a]	τ_s (ns)	$(k_Q)_{DMH}$[b] $\times$ 10^7 (M^{-1} s^{-1})	$(k_Q)_{TME}$[c] $\times$ 10^7 (M^{-1} s^{-1})
Hexane	1.88	1.37	—	0	14.7	10	
Cyclohexane	2.02	1.43	—	0	13	14	< 0.1
Diethyl ether	4.34	1.35	19.2	3.9	13.5	13	
Tetrahydrofuran	7.58	1.41	20	8.0	10	32	
Benzene	2.27	1.50	0.1	8.2	10	36	1.0
Dioxane	2.2	1.42	14.8	10.8	7.4	39	
Acetone	20.7	1.36	17	12.5	8.1	81	2.8
Pyridine	12.4	1.51	33.1	14.2	5.7	63	
Dimethylformamide	36.7	1.43	26.6	16	7.8	130	4.1
Acetonitrile	37.5	1.34	14.1	19.3	8.2	150	6.3
Dimethylsulphoxide	46.7	1.48	29.8	19.3	2.2	100	
Dichloromethane	9.08	1.24		20.4	11	155 .	5.5
Chloroform	4.81	1.45		23.1	9.7	165	
2-Propanol	19.1	1.38		33.5	7.0	240	15
Ethanol (95%)	24.6	1.36		39.1	7.0	430	26
Methanol	32.7	1.33		41.3	9.0	360	
Acetonitrile–water (9:1)				27.8	7.5	290	
Acetonitrile–water (1:1)				45.7	8.6	690	50
Diethyl ether–dichloromethane (1:1)				14.1	10.2	68	
Acetonitrile–2-propanol (1:1) .				25.1	7.6	210	
Tetrahydrofuran–dichloromethane (1:1)				14.9	8.8	92	
Dimethyl sulphoxide–acetonitrile (1:1)				19.3	4.4	120	

[a]The solvent acceptor number AN in mixtures is obtained by assuming additivity:
$AN_{mixture} = \Sigma X_i (AN)_i$ where X_i is the mole fraction.
[b]Quenching rate constant employing 2,5-dimethyl-2,4-hexadiene.
[c]Quenching rate constant employing 2,3-dimethyl-2-butene.

The data obtained in the present work show only a poor correlation with the dielectric constant and practically no correlation with the refractive index η of the solvent. Particularly remarkable are the large values obtained in dichloromethane and chloroform and the low value obtained in dimethylsulphoxide in spite of its high value of ϵ. Similarly, it must be mentioned that the rates in the alcohols are faster than in acetonitrile, a solvent of higher dielectric constant. This result is rather unique since the rates of quenching in alcohols are lower than those expected on the basis of their polarity [16] in several systems.

Solvent donor and acceptor numbers are among the properties of the solvent that, at a microscopic level, can stabilize or favour the production of zwitterionic structures [17]. The values of these parameters have also been

included in Table 1, where it can be seen that, although the data correlate poorly with the donor number, they correlate fairly well with the solvent acceptor number AN. In particular, a dependence on this factor can explain (1) the large values in dichloromethane and chloroform, (2) the faster quenching in the alcohols than in acetonitrile and (3) the relatively slow rate observed in dimethylsulphoxide.

Some of the values shown in Table 1 for 2,5-dimethyl-hexadiene are close to the values for the diffusion-controlled limit. In order to take this effect into account and to visualize the degree of dependence on the solvent acceptor number, the values of $\log\{k_Q/\eta(k_{\mathrm{diff}} - k_Q)\}$ are plotted against AN in Fig. 2. This figure shows a very good correlation over a 70-fold change in k_Q. The most noticeable deviation from a linear relationship corresponds to methanol, but it has to be considered that the characteristics of the absorption spectra of biacetyl are considerably altered in this solvent, indicating a strong interaction between the donor and the solvent. If methanol is not considered, the correlation coefficient for the data of Fig. 2 is 0.988.

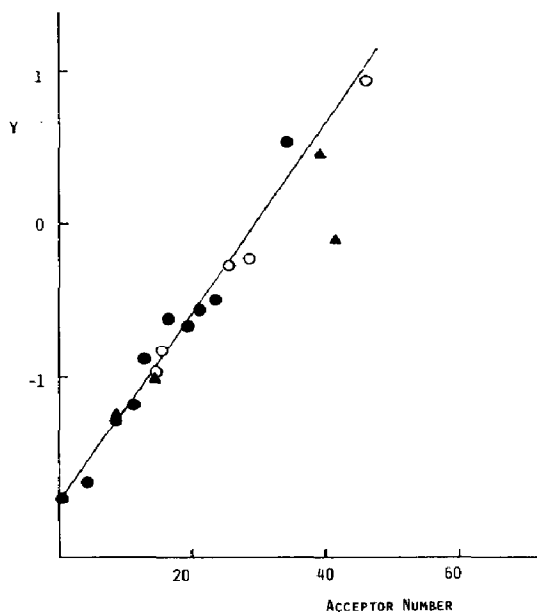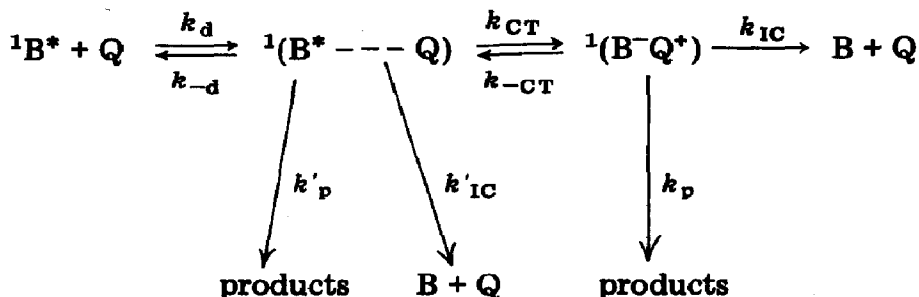The mechanism of quenching can be represented by the following scheme [14].

Fig. 2. A plot of $Y = \log\{k_Q/\eta(k_{\mathrm{diff}} - k_Q)\}$ against solvent acceptor number AN: ▲, compounds whose τ_s values have been measured; ●, compounds whose τ_s values have been estimated; ○, solvent mixtures. (Values of η, k_{diff} and AN were calculated assuming additivity.)

$$^1B^* + Q \underset{k_{-d}}{\overset{k_d}{\rightleftarrows}} {}^1(B^* \text{---} Q) \underset{k_{-CT}}{\overset{k_{CT}}{\rightleftarrows}} {}^1(B^-Q^+) \xrightarrow{k_{IC}} B + Q$$

$$k'_p \qquad k'_{IC} \qquad k_p$$

products   B + Q   products

The dependence of k_Q on the solvent acceptor number implies that the main role of the solvent is to stabilize the charge transfer complex through an interaction with the B^- moiety of the complex. Nevertheless, an alternative explanation can be put forward in which the role of the solvent precedes the formation of the CT complex. If the dipolar characteristics of the singlet are considered (i.e. $C^{\delta-}=O^{\delta+}$), then an increase in AN can increase the amount of positive character of the oxygen atom, increasing its reactivity towards the electron-rich double bond. The data obtained in the present work are insufficient to decide between these alternative explanations.

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