Quenching of excited carbonyl triplets by benzene derivatives*

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RESUMEN: Se ha medido la velocidad de desactivación de tripletes carbonílicos (biacetilo, bencilo, benzofenona y 4-metil-2-pentanona) por una serie de derivados del benceno. Los resultados pueden ser interpretados por un mecanismo de transferencia de carga. Los compuestos con hidrógenos lábiles (i.e. cumeno) muestran una mayor reactividad. La abstracción de hidrógeno ocurre desde el complejo de transferencia de carga.

La desactivación del triplete de la 4-metil-2-pentanona fue medida entre − 5 y 70°C. Las energías de activación obtenidas variaron entre 8.1 kcal (para el cumeno) y 10 kcal (para el benceno).

SUMMARY: The quenching of 4-methyl-2-pentanone, biacetyl, benzil and benzophenone triplets by several benzenes derivatives have been measured. The results obtained are compatible with a charge transfer mechanism in which the aromatic compound leads charge to the excited carbonyl. When the aromatic compounds has labile hydrogen atoms, the intramolecular hydrogen abstraction leads to a faster rate constant. This process takes place, at least for 4-methyl-2-pentanone, from the excited complex.

Quenching of 4-methyl-2-pentanone triplets are measured as a function of temperature (−5 to 70°C). The activation energies obtained range from 10 kcal (benzene as quencher) to 8.1 kcal (for cumene).

INTRODUCTION

Benzene and benzene derivatives are well known quenchers of excited carbonyl compounds. Quenching rate constants for the desactivation process and/or the lifetime of the carbonyl compounds when an aromatic hydrocarbon (usually benzene) is employed as solvent have been reported for acetone[1, 2, 3], aliphatic ketones[4, 5], α-tri-fluoroceto-phenones[6, 7, 8], benzophenone[3, 9, 10, 11] and acetophenone and benzaldehyde[8, 10]. Most of the results obtained have been interpreted in terms of a charge transfer mechanism with the aromatic ring acting as an electron donor towards the excited triplet[9, 12]. Nevertheless, when the aromatic compound has labile hydrogen atoms, contribution to the quenching rate by a hydrogen transfer process can not be disregarded[7, 8]. In spite of the bulk of data obtained in systems employing excited carbonyls and aromatic molecules, only in a work the measurements have been carried out at different temperatures[10]. In this work, the activation energies and the preexponential A factors varied in a rather erratic way. In particular it was observed that quenching of triplet benzaldehyde by benzene, in spite of a moderate quenching rate constant of 2×10^7 M^{-1} s^{-1} at 25°C, the activation energy obtained was negative. From the above considerations, and given the importance that as solvents have the aromatic hydrocarbons, the present work was carried out with three aims:

i)   To extend the presently available data regarding the quenching of carbonyl triplets by aromatics to other carbonyl compounds,

ii) To measure the rate for several alkyl benzenes with different degrees of α substitution in order to evaluate the contribution of the intramolecular hydrogen abstraction, and

iii) To obtain the Arrhenius parameters for several processes that occur through the formation of charge transfer complexes in order to evaluate if low, and even negative, energies of activation are a general feature of these processes.

EXPERIMENTAL

The experimental method employed when 4-methyl-2-pentanone was employed as donor was similar to that described previously[13]. The temperature was varied from -5 to 70°C. Quenching experiments employing benzophenone, biacetyl and benzil as donors were carried out by measuring the phosphorescence yield as a function of the added hydrocarbon concentration. The measurements were carried out at room temperature ($20 \pm 2°C$) in a 204-S Perkin Elmer Spectrofluorimeter.

RESULTS

The results obtained are summarized in Table 1 and 2. Values of k_Q at room temperature were obtained from the slopes of the Stern-Volmer plots and the known lifetimes of the sensitizers under the conditions employed[13,14]. The change in k_Q with temperature was determined by measuring at each temperature, the effect of the quencher considered and

that of cis-1, 3-pentadiene. From the relative values of the slopes of the Stern-Volmer plots, and taking for the quenching by the diene $k_Q = 5 \times 10^{10} \exp(-1.3/RT)$[15], values of k_Q for the quencher considered at each temperature can be obtained. By plotting these values as a function of the inverse temperature, the values of E_a and log A given in Table 1 were obtained.

TABLE 1

Rate constants and Arrhenius parameters for the quenching of
4-methyl-2-pentanone triplets by substitutes benzenes[a].

Quencher	(k_Q) 20°C x 10^{-6}	E_a	log A
benzene	1.1	9.1	12.8
toluene	3.6	9.1	13.3
ethylbenzene	5.3	8.2	12.8
isoproylbenzene	4.1	7.4	12.1
tert-butylbenzene	2.7	7.9	12.3
cyclohexene	4.3	9.0	13.3

a) n-hexane as solvent.

TABLE 2

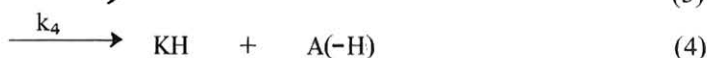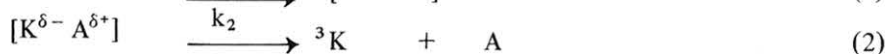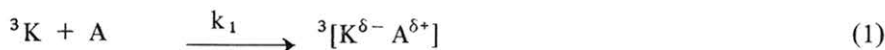Quenching of carbonyl excited triplets by substitutes benzenes[a]

Quencher	Donor			
	IP	Biacetyl	Benzil	Benzophenone
toluene	8.8	0.2	0.01	50
p-chlorotoluene	8.69	0.1	0.04	23
tert-butylbenzene	8.68	6.0	0.22	34
p-xylene	8.4	3.8	0.34	310
p-methylanisole	8.1	3.9	0.63	2450
isopropylbenzene		16.0	1.10	370

a) Rate constants given in $10^4 M^{-1} s^{-1}$. Benzene as solvent.

DISCUSSION

For a quenching process involving a charge transfer complex with partial charge transference from the acceptor to the excited triplet the quenching rate constant increases when the Ionization Potential of the quencher decreases. This type of dependence is shown by all the data given in Table 1 and 2. Furthermore, Figure 1 shows that as expected[9], there

exist a nearly linear relationship between log k_Q and the quencher IP. Nevertheless, it is relevant to consider that for all the systems considered in the present work the cumene quenches the donors at a faster rate than that expected from its ionization potential. This can be explained by a contribution of the hydrogen transfer to the quenching process. This photoreduction can take place from the charge transfer complex or by a parallel and completely independent reaction path[7,8]. In order to decide between this two possibilities it is useful to compare the behaviour of the $n-\pi^*$ excited triplet to that of the tert-butoxy radical, that is a good model for simple hydrogen abstractions. The relative rates (cumene/cyclohexane) are ~ 10 for the excited 4-methyl-2-pentanone (from this work and ref. 4), ~ 1.6 for benzophenone triplets[16] and ~ 0.38 for tert-butoxy radicals at $40°C$[17]. The difference between both set of values would favour a hydrogen transfer contribution from the exciplex and not as a completely unrelated process. Furthermore, the values for ethylbenzene and cumene relative to toluene are 1.47 and 1.13 for 4-methyl-2-pentanone and 4.5 and 3.8 for tert-butoxy radicals[18]. The small selectivity shown by 4-methyl-2-pentanone triplets is also compatible with a hydrogen abstraction process that take place from the excited complex. The mechanism to be considered then for the aliphatic ketones (and probably also for the other carbonyl compounds) can be represented, as in the quenching by amines, by the following set of reactions

$$^3K + A \xrightarrow{k_1} {}^3[K^{\delta-} A^{\delta+}] \tag{1}$$

$$[K^{\delta-} A^{\delta+}] \xrightarrow{k_2} {}^3K + A \tag{2}$$

$$\xrightarrow{k_3} K + A \tag{3}$$

$$\xrightarrow{k_4} KH + A(-H) \tag{4}$$

This mechanism leads to

$$k_Q = k_1 \frac{k_3 + k_4}{k_2 + k_3 + k_4} \tag{5}$$

The value of k_Q would depend then upon the lability of the hydrogen atoms and the "selectivity" would depend not only of the relative values of k_4 but also upon the relative values of k_4 and $(k_2 + k_3)$.

The data given in Table 1 show that the activation energies and the pre-exponential A factors are relatively high for all the systems considered. The experimentally determined activation energies, defined by

$$E_{exp} = -R \frac{d \ln k_Q}{d (1/T)}$$

and the pre-exponential A factor, defined by

$$\log A = \log k_Q + E_{exp}/RT$$

will be related to the Arrhenius parameters of k_1, k_2, k_3 and k_4 in a rather complex way (see Eqn. 5). A simple relationship will be obtained only in the limit where $k_2 \ll (k_3 + k_4)$. Nevertheless, in the present case and due to the low binding energy of the complex, the back dissociation is a fast process and cannot be disregarded[1]. It is then difficult to assign to
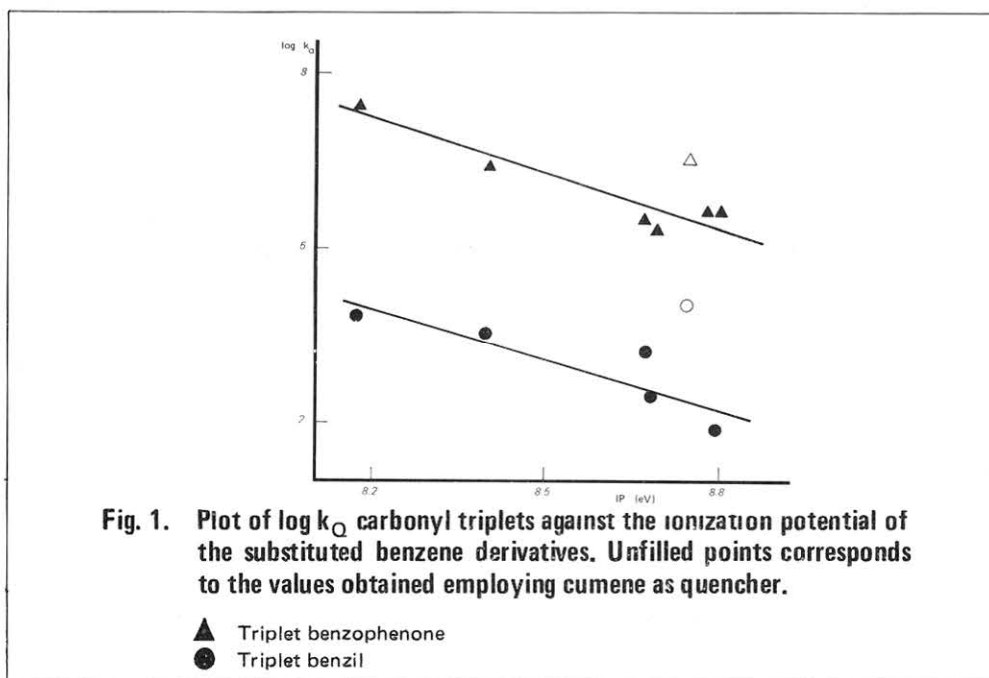
the values given in Table 1 a meaning in terms of the parameters of the individual steps. Nevertheless, it is relevant to point out that the values of E and A obtained in the present work are substantially different to those reported other systems where the quenching is also assumed to take place through the formation of charge transfer complexes[10,19]. Nevertheless, in all these studies aromatic carbonyls were employed as donors, and the plot of Fig. 2 would indicate that the complex behaviour could be significantly different when different types of carbonyls are employed. For example, the fact that the reactivity of 4-methyl-2-pentanone seems to be larger that expected from its $(E_T + E_{(A-/A)})$ value (see figure 2) would imply that $(k_3 + k_4) / k_2$ can be particularly large in these types of compounds. These differences could lead to significantly different "Arrhenius parameters" for the experimentally determined quenching rate constants.
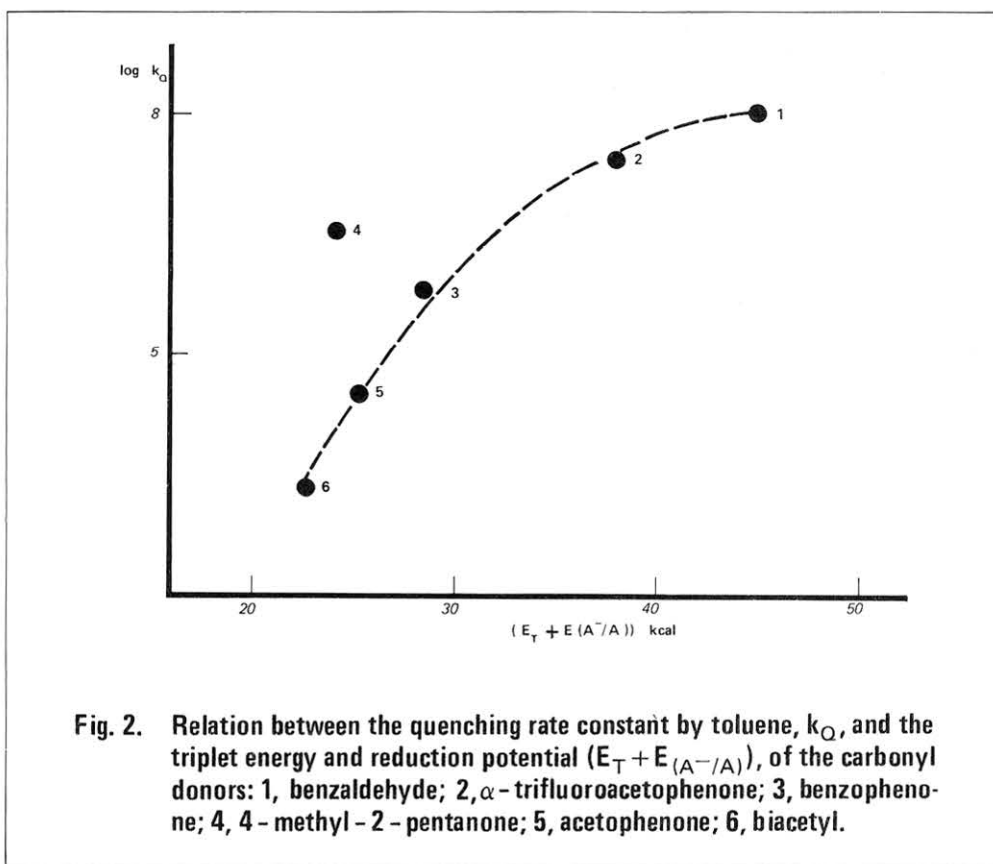
The data given in Table 1 and 2, as well as the plots of $\log k_Q$ v/s IP are rather similar for all the carbonyls considered in spite of the fact that the absolute rates differ by more than two orders of magnitude. This lack of relationship between "selectivity" and "reactivity" is a general feature of processes that take place through charge transfer complexes. A possible reason why these processes do not obey the Hammond's rule has been given elsewhere[20].

For a given quencher it has been proposed[9] that the values of k_Q could be related to the triplet energy of the donor and to its reduction potential through

$$\log k_Q \; \alpha \; E_T \; + \; E_{(A^-/A)} \tag{6}$$

The conditions that must be fulfilled to apply this equation to systems that involves only partial charge transfer makes the validity of this equation only relative[21]. Nevertheless, when the data obtained in the present and previous works employing toluene as quencher are plotted according to Eqn. (6), (see figure 2) in fair correlationship is obtained, leading further support to the proposed mechanism. The lack of linear correlation can be partially due to the limitations of Eqn. (6) to the different solvents employed and to indeterminations in the $E_{(A^-/A)}$ values[22]. Furthermore, it has to be considered that Eqn. (6) refers to the thermodynamics of the exciplex formation and do not consider the possible differences in k_3 and k_4 values for different carbonyl compounds.

Fig. 1. Plot of log k_Q carbonyl triplets against the ionization potential of the substituted benzene derivatives. Unfilled points corresponds to the values obtained employing cumene as quencher.

▲ Triplet benzophenone
● Triplet benzil

Fig. 2. Relation between the quenching rate constant by toluene, k_Q, and the triplet energy and reduction potential ($E_T + E_{(A^-/A)}$), of the carbonyl donors: 1, benzaldehyde; 2, α-trifluoroacetophenone; 3, benzophenone; 4, 4-methyl-2-pentanone; 5, acetophenone; 6, biacetyl.

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