

Short Communication

Quenching of 2-pentanone singlets by aliphatic amines

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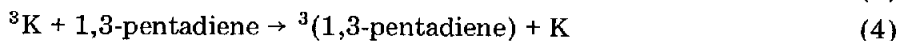
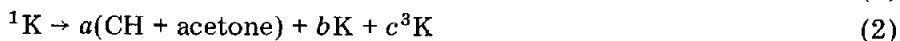
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The quenching of excited carbonyl compounds by amines has been widely investigated [1], but most studies have been carried out on the quenching of the triplet state of aromatic ketones. Aliphatic ketones have been much less studied [2], and the only reported data on singlet quenching have been obtained with biacetyl as donor [3]. In the present work, we report data on the quenching of the singlet state of 2-pentanone by several aliphatic amines.

The experimental conditions were similar to those previously described [4]. Photolyses were carried out in a "merry-go-round" apparatus, at room temperature and employing n-hexane as solvent. Since the light source was a medium pressure mercury lamp and the reaction tubes used were made of Pyrex, most of the absorbed radiation was in the 3130 Å region. The amines do not modify the absorption of the 2-pentanone solutions at this wavelength. Furthermore, the absorption spectrum of the solution remains unchanged during the photolysis.

The amines (Fluka) were employed after trap-to-trap distillation. No further purification was attempted since, owing to the short lifetime of 2-pentanone singlets, small amounts of impurities cannot affect the results.

The quenching of the singlet state by the amines was followed by measuring the change in acetone quantum yield. A double quenching technique with 1,3-pentadiene as selective triplet quencher was employed [5]. All runs were then carried out in the presence of 0.3 mol/l of 1,3-pentadiene. Under these conditions the 1,3-pentadiene quenches practically all 2-pentanone triplets without significant singlet quenching [6]. The change in type II product with amine concentration can then be related to the quenching of the singlet state. The results obtained were found to be independent of the reaction time and 2-pentanone concentration employed, and can be interpreted in terms of the following set of reactions:



where reaction (2) involves all the reactions of the excited singlet state in the absence of amine. From this mechanism, equation (5) can be derived:

$$\Phi_A^\circ / \Phi_A = 1 + k_3 \tau_S \quad (\text{amine}) \quad (5)$$

where Φ_A° = acetone quantum yield in the absence of amine, and τ_S = singlet state lifetime.

In order to obtain equation (5) it was assumed that k_2 and a are not solvent dependent. This assumption is supported by the data obtained in other mixed solvents [7].

The data obtained with triethylamine (TEA) as quencher are shown in Fig. 1, plotted according to equation (5). From the slope of this plot we obtain the result: $k_3 \tau_S = 4 M^{-1}$.

Since the singlet lifetime is 1.8×10^{-9} s [8], we find for TEA that: $k_3 = 2.2 \times 10^9$.

For reaction (6):



a value of $k_6 = 3.2 \times 10^8 M^{-1} s^{-1}$ has been obtained under similar experimental conditions [9]. The increased reactivity of the singlet state can be related to its higher energy. If we assume that the rate of quenching is determined by the free energy of formation of the charge transfer complex, we can expect a linear relationship between $\log k_Q$ and $(\Delta E_0 - E_{(A^+/A)})$ for a given quencher (ΔE_0 is the energy of the excited state and $E_{(A^+/A)}$ is the reduction potential of the ketone) [10]. For TEA, the slope of the plot is nearly -0.25 kcal/mol and predicts $k_3/k_6 \approx 10$, in fairly good agreement with the value reported here.

For the other amines studied (diethyl amine, dimethyl amine and isopropyl amine (IPA)) the values of $k_3 \tau_S$ were indistinguishable from the one obtained with TEA, even though the ionization potential (IP) of the amines changes from 7.5 (TEA) to 8.7 (IPA). This result is rather surprising since the quenching of acetone triplets in acetonitrile is strongly dependent on the IP of the amine (the quenching rate constant is $1.9 \times 10^6 M^{-1} s^{-1}$ for *t*-butyl amine and $2.9 \times 10^8 M^{-1} s^{-1}$ for TEA) [2]. Furthermore, the data previously reported for the quenching of biacetyl singlets indicate that primary amines are much less efficient quenchers than secondary and tertiary amines (k_Q goes from less than 10^7 for IPA to $2.4 \times 10^9 M^{-1} s^{-1}$ for TEA) [3]. Actually, the source of these discrepancies is not clear but we can conclude that, at least in solvents of low dielectric constant and with highly reactive singlets, the IP is no longer a significant parameter. Similar results have lately been reported for the quenching of the triplet state of benzophenone. The value of the quenching rate constant was found to stay virtually constant with changing ionization potential for aromatic and aliphatic amines in perfluoromethylcyclohexane in spite of the fact that the results obtained in benzene and acetonitrile were strongly dependent on the IP [11].

In order to determine whether reaction (3) involves reactive quenching, we follow the decrease in 2-pentanone concentration when it is photolyzed

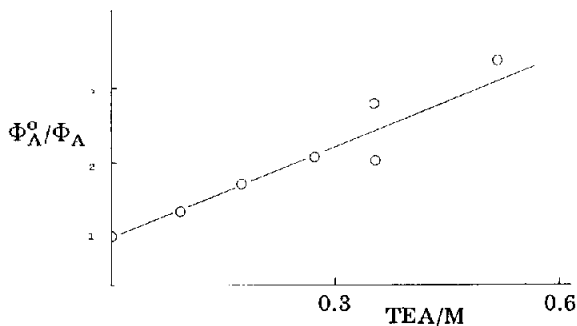


Fig. 1. Effect of added TEA on the acetone quantum yield. Solvent: n-hexane; 2-pentanone concentration: 0.1 M; 1,3-pentadiene concentration: 0.3 M; temperature: 25 °C.

in the presence of TEA. At the highest amine concentration, we find that the quantum yield of ketone consumption is nearly 0.2. This result, although only of qualitative value owing to the high conversion needed to evaluate the parent ketone consumption (nearly 20%), seems to indicate that a significant proportion of reaction (3) involves reactive quenching.

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