Evidence for Triplet Exciplex Formation in the Reaction of Amines with 1-Phenyl-2-acetoxy-2-methyl-propanone-1

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1-Phenyl-2-acetoxy-2-methylpropanone-1 has been irradiated with 25ns flashes of 347 nm light in benzene or cyclohexane solution. Absorption measurements yielded the following: at the end of the flash the triplet-triplet spectrum was observed (triplet decay rate constant: $k_T = (3.0 \pm 0.2)\ 10^5\ s^{-1}$). In the presence of aliphatic amines (e.g. triethanol amine) radicals were formed much more slowly than triplets disappeared, as clearly indicated by spectral changes at wave lengths between 330 and 380 nm. The radical precursor thus evidenced is presumed to be an exciplex. Rate constants: $k_{T+\text{amine}}$: $(1.2 \pm 0.2)\ 10^9$ l/mol s; k_{exciplex}: $(9 \pm 1)\ 10^6\ s^{-1}$.

Many ketones undergo rapid photochemical reactions with various amines, and it is generally assumed that in these reactions exciplexes of electronically excited ketones in their triplet states and amines in their ground states are formed, which eventually dissociate into pairs of free radicals or radical ions [1–4]:

$$K + h\nu \rightarrow {}^1K^* \rightarrow {}^3K^*, \tag{1}$$

$${}^3K^* + A \rightleftarrows \underset{\text{Exciplex}}{[{}^3K^*-A]}, \tag{2}$$

$$[{}^3K^*-A] \begin{cases} \rightarrow R_1^{\cdot} + R_2^{\cdot}, & (3a) \\ \rightarrow K^{\cdot -} + A^{\cdot +}. & (3b) \end{cases}$$

K: ketone; A: amine; $R_1^{\cdot}$ and $R_2^{\cdot}$: free radicals; $K^{\cdot -}$ and $A^{\cdot +}$: radical anions and radical cations, respectively.

Most work of the past devoted to the detection of exciplexes dealed with complexes formed by singlet-excited molecules. In that work, which has been reviewed in a series of articles several years ago [5], prominence was given to the interaction of singlet-excited hydrocarbons with amines [6–12]. Evidence for the formation of exciplexes was obtained in various cases from characteristic fluorescence and/or optical absorption spectra.

Contrary to the situation encountered with singlet exciplexes little is known about triplet exciplexes. With respect to the reaction of triplet excited ketones with amines, half-wave reduction and oxidation potentials of carbonyl compounds and amines, respectively, have been used to estimate the location of triplet charge transfer states [13]. Spectroscopic evidence, obtained from optical absorption and emission measurements, has been reported for the formation of exciplexes of triplet-excited benzophenone with aromatic amines in rigid solutions at 77 K [14].

The present authors' interest in the photoreduction of aromatic ketones by amines derives from the fact that ketone/amine systems are suitable for initiating the photochemical polymerization of many unsaturated compounds. Continuing an investigation on the kinetics and mechanism of photoinitiation processes [15], ketone/amine systems were also studied [16]. Of prominent importance for the understanding of the photochemistry of these systems appears to be the question whether or not triplet exciplexes are actually formed.

Therefore, we have tried to find out whether by absorption measurements in conjunction with flash photolysis exciplexes can be identified and information about their lifetimes can be obtained.

This paper reports results which are quite conclusive with respect to the formation of exciplexes in the reaction of triplet excited 1-phenyl-2-acetoxy-2-methyl-propanone-1 (PAMP)

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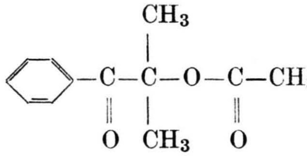


with di-[2-hydroxyethyl]-methyl amine (DEMA) and tri-[2-hydroxyethyl]-amine (TEA).

Together with other hydroxy alkylphenones and O-substituted derivatives of hydroxyalkylphenones, PAMP has been the object of a recent investigation [16]. During that study the triplet-triplet absorption spectrum of PAMP shown in Fig. 1 (spectrum (a)) was recorded upon irradiating dilute cyclohexane or benzene solutions of this compound with 25 ns flashes of 347 nm light. The triplet lifetime was determined as 2.3 μs by measuring the rate of phosphorescence decay after the flash.

In subsequent work, being reported here, the following results have been obtained:

Upon addition of DEMA or TEA to PAMP solutions the triplet lifetime was drastically reduced, as indicated by the increased rate of decay of the T–T absorption spectrum. By measuring the rate of triplet decay at $\lambda > 400$ nm (where reaction products absorb only weakly) as a function of the amine concentration, the following rate constants were obtained: $k_{\mathrm{T+DEMA}} = 1.0 \times 10^9$ l/mol s and $k_{\mathrm{T+TEA}} = 1.4 \times 10^9$ l/mol s. The rate constants determined in benzene and cyclohexane were equal within the error limit of $\pm 15\%$.

Upon monitoring the change of the optical absorption at various wavelengths it became obvious that the rate of formation of the spectrum of the ketyl radical was not correlated with the rate of decay of the triplet-triplet absorption. This is depicted in Fig. 2, where typical oscilloscope traces obtained upon irradiating benzene solutions of PAMP (3.3×10^{-3} mol/l) in the absence and presence of TEA are presented. Traces (a–1) and (b–1) show the decay of the T–T absorption at 450 nm and demonstrate that TEA reacts rapidly with triplet excited PAMP. Trace (a–2) depicts how in the presence of amine after the initial decay of the T–T absorption at 360 nm a new absorption is formed. It is clearly seen that the rate of triplet decay is much faster than the formation rate of the new absorption. Therefore, it can be concluded that the reaction of triplet excited PAMP with TEA does not result in the immediate formation of free radicals or radical ions but that an intermediate with a definite lifetime is formed, which is presumably identical with an exciplex. It has to be pointed out that quite similar results were obtained with benzene and cyclohexane solutions containing TEA

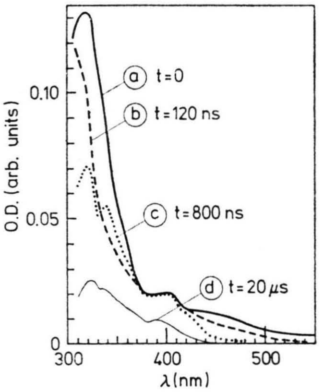


Fig. 1. Transient optical absorption spectra recorded at various times after irradiation of an Ar-saturated benzene solution containing PAMP (3.3×10^{-3} mol/l) and TEA (1×10^{-1} mol/l) with a 25 ns flash of 347 nm light. Absorbed dose per flash: 2.8×10^{-5} einstein/l.

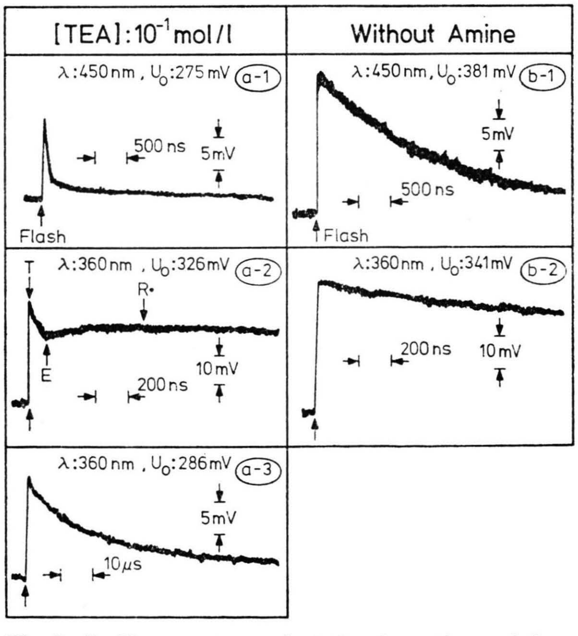
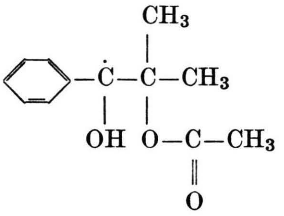


Fig. 2. Oscilloscope traces depicting formation and decay of the optical absorption at 360 nm and 450 nm obtained with an Ar-saturated benzene solution of PAMP (3.3×10^{-3} mol/l). Traces (a-1) to (a-3) were recorded in the presence of TEA, and traces (b-1) and (b-2) in the absence of amine. Absorbed dose per flash: 2.8×10^{-5} einstein/l. (Rate constants $k_{\mathrm{T+amine}}$ were determined at amine concentrations ranging from 10^{-5} to 10^{-3} mol/l).

or DEMA. From the 1st order increase of the radical absorption the rate constant of reaction (3a) was determined as $(9 \pm 1)\ 10^6\ s^{-1}$.

These results corroborate our former findings with PAMP solutions in neat DEMA [16]. In that case all triplets reacted with the amine already during the flash, allowing the observation of the exciplex absorption spectrum at the end of the flash. It appears that there is no significant difference in the shapes of the spectra of triplets and exciplexes although the extinction coefficients differ significantly at $\lambda < 380$ nm. A more remarkable difference exists, however, between the spectra of triplets and ketyl radicals of the structure:



as can be seen from a comparison of the spectra (a) and (d) in Figure 1.

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