EVIDENCE AGAINST REVERSIBLE TRIPLET ENERGY TRANSFER BETWEEN ACETOPHENONE AND NORBORNENE

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(Received June 13, 1977)

Summary

Kinetic absorption and emission spectroscopy has been used to monitor the decay of triplet acetophenone produced in benzene by both pulse radiolysis and pulse laser photolysis techniques. The dependence of this decay on the concentrations of norbornene and acetophenone shows that, in contrast to a previous claim, triplet energy transfer between acetophenone and norbornene is not reversible. These data, together with quantum yield measurements, indicate that in this system ground state acetophenone quenches triplet acetophenone and either triplet norbornene or a ketone triplet–olefin exciplex by processes which do not involve energy transfer.

Introduction

The mechanism by which simple olefins quench aromatic ketone triplets has been the subject of much discussion and experiment and it is now recognised that charge-transfer interaction may play an important role in the quenching act [1]. An important factor in the understanding of the overall energy profile of the process is the possibility of back transfer of triplet energy from olefin to ketone. The only reported evidence for such a process concerns the acetophenone–norbornene system which has played an important role in this field owing principally to work by Arnold [2, 3] and Schroeter [4]. The latter has shown that, as expected, the ratio ϕ_O/ϕ_D of oxetane to norbornene dimer formation is inversely proportional to the concentration of norbornene (N). However, it was also shown that this ratio increases with the concentration of acetophenone (A) and this result was presented as direct evidence for reversible triplet energy transfer between A and N. We report here evidence which shows that this cannot be the case.

Experimental

Kinetic absorption spectrometry of acetophenone triplet at 500 nm was carried out using the pulse radiolysis facility [5] of the Christie Hospital and Holt Radium Institute, Manchester, which incorporates a 10 MeV linear electron accelerator. Kinetic emission spectrometry of acetophenone phosphorescence was carried out using a Lamda Physik 1 MW pulsed nitrogen laser of pulse width 2.5 ns and wavelength 337 nm. Benzene solutions were de-aerated by prolonged bubbling with argon.

Quantum yields of oxetane and dimer formation were determined using benzophenone–benzhydrol actinometry in benzene. Reaction and actinometer solutions were irradiated on a merry go round in sealed Pyrex tubes which had been degassed ten times by the freeze–thaw method. The incident light consisted of an envelope centred at 313 nm obtained by filtering the light of a 550 W Hanovia medium pressure mercury arc with a solution of potassium chromate (0.002 M) in 1% aqueous potassium carbonate. Reaction solutions were analysed by GLC using dibenzyl ketone as standard on an Apiezon L column (3 ft, 12%, 190 °C, 10 lb in^{-2}). Actinometer solutions were also analysed by GLC using 2-naphthaldehyde as standard on an OV-225 column (3 ft, 3%, 125 °C, 10 lb in^{-2}).

Acetophenone was distilled immediately before use. Norbornene was purified by passage of an ether solution (approximately 50%) down a column of alumina followed by fractionation of the resulting mixture from sodium. It was used immediately. Benzene was purified by concentrated sulphuric acid, aqueous bicarbonate and water treatment, followed by distillation from phosphorus pentoxide.

Results and discussion

The following summarize Schroeter's reactions scheme:

$$^3A^* \xrightarrow{k_{dA}} A \tag{1}$$

$$^3A^* + A \xrightarrow{k_{sq}} A + A \tag{2}$$

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

$$A + {}^3N^* \xrightarrow{k_{-et}} {}^3A^* + N \tag{4}$$

$$^3A + N \xrightarrow{k_O} \text{oxetane} \tag{5}$$

$$^3A^* + N \xrightarrow{k_{ct}} [{}^3A^* \cdots\cdots N] \tag{6}$$

$$^3N^* + N \xrightarrow{k_D} \text{dimer} \tag{7}$$

$$^3N^* \xrightarrow{k_{dN}} N \tag{8}$$

Our inclusion of eqn. (6) recognizes the fact that charge-transfer complexation may be important in this system. The inclusion of steps (5) and (6) as separate processes may be artificial since the biradical prescursor of the oxetane may arise via the charge-transfer complex [1]. This does not affect our kinetic arguments.

Kinetics of the decay of the acetophenone triplet

We have carried out experiments designed to diagnose reversible energy transfer in two possible situations.

Firstly, if rapid equilibration between $^3A^*$ and $^3N^*$ were to occur, *i.e.* if the forward and reverse rates of transfer were fast relative to the rate of the processes which drain the equilibrium, the initial concentration of ketone triplets produced after an energy pulse should decrease linearly with norbornene concentration, or a fast followed by a slow exponential decay should be observed. This is not the case. Pulse radiolysis of benzene solutions of acetophenone (5×10^{-2} mol l^{-1}) converts a small fraction of the ketone into triplet states within 1 μs of the end of the 20 ns exciting pulse. In the absence of N the ketone triplet, which was monitored by kinetic absorption spectrophotometry, decays with a half-life of 3 μs. On addition of N (up to 10^{-2} mol l^{-1}) the single exponential decay of triplet acetophenone is enhanced but no change in the initial absorbance is observed.

Secondly, if back transfer (eqn. (4)) is a slow but significant process the differential equation describing the decay of $^3A^*$ under time resolved conditions contains a term involving $[^3N^*]$. However, in the absence of such transfer the following standard integrated relationship should hold, where $k_q = k_{et} + k_o + k_{ct'}$ is the overall quenching rate constant:

$$-\ln [^3A^*] = (k_{dA} + k_q [N] + k_{sq}[A]) t + \text{constant} \qquad (9)$$

We have monitored the decay of the phosphorescence of acetophenone triplet produced in benzene by a 1 MW pulsed nitrogen laser and, at all concentrations of A and N employed, excellent agreement with eqn. (9) was observed. Standard first order plots gave gradients $K' = k_{dA} + k_q [N] + k_{sq} [A]$. Plots of K' *versus* [N] at various fixed [A] (Fig. 1) and of K' *versus* [A] at various fixed [N] gave sets of parallel lines of slopes $k_q = 1.5 \times 10^8$ l mol^{-1} s^{-1} and $k_{sq} = 4.8 \times 10^6$ l mol^{-1} s^{-1} respectively*. In the latter case the intercept for [N] = 0 gave k_{dA} for $^3A^*$ in benzene as 2.4×10^5 s^{-1}. The intercepts in Fig. 1 should equal $k_{dA} + k_{sq}$ [A] and the calculated values (▲) show that this is the case. Thus, even under conditions where [A]:[N] > 100, which strongly favour back transfer (eqn. (4)) over forward transfer (eqn. (3)), no deviation from kinetics that conform with eqn. (9) was observed.

It has been shown by Porter [6] and Sandros [7] that for a reversible energy transfer system one should observe a variation in the experimentally determined exponential decay of the donor triplet, *i.e.* in K', with donor (A)

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*An identical value for k_q was obtained by pulse radiolysis using 0.05 M acetophenone solutions.
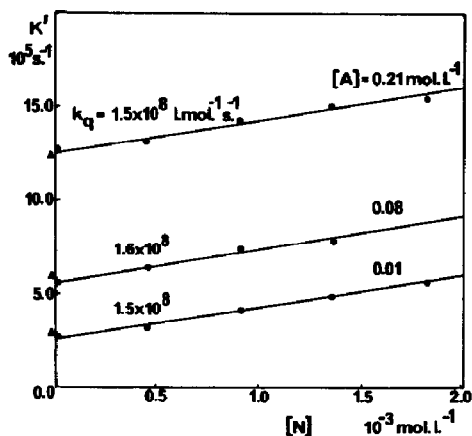
Fig. 1. Dependence of the measured rate constant for quenching of acetophenone triplet by norbornene (N) on the concentration of acetophenone (A).

concentration, in particular when the donor triplet lifetime is similar to or longer than that of the acceptor and, of course, when back transfer competes with acceptor triplet decay. The first condition holds in our case since we have shown that the rate constant k_{dN} for natural decay of $^3N^*$ in benzene is 4.0×10^6 s^{-1} [8], which is much smaller than those for simple acyclic olefins [9] but is nevertheless 3 - 4 times larger than the value of 1.2×10^6 s^{-1} for $k_{dA} + k_{sq}$ [A] at our highest concentration of A[†]. The fact that no variation in K' other than the self-quenching effect is observed therefore shows that back transfer does not compete effectively with acceptor triplet decay. If we assume that we could not detect a 10% change of slope in Fig. 1 we can estimate that $k_{dN} \geqslant 10\, k_{-et}$ [A] which gives $k_{-et} \leqslant 2 \times 10^6$ l mol^{-1} s^{-1}. This maximum value would predict maximum changes in slope of ϕ_O/ϕ_D with [A] which are 2 - 3 times smaller than those observed by Schroeter [4]. In addition we have recently estimated [8] the vertical energy of the relaxed $^3N^*$ in benzene at room temperature to be 57.5 ± 1.5 kcal mol^{-1}. This is approximately 15.0 kcal mol^{-1} below the known triplet energy of $^3A^*$ in benzene at 25 °C [10], and strongly supports the present conclusions that back transfer of triplet energy from norbornene to acetophenone is insignificant.

Quantum yields

We have measured the absolute values of ϕ_O and ϕ_D over the concentration range of acetophenone employed by Schroeter and the results reproduced in Fig. 2 are in agreement with our conclusions. The line drawn for $1/\phi_O$ is that predicted for no reverse transfer, *i.e.* assuming $\phi_O = k_O$ [N] $/k_{dA} + k_q$ [N] $+ k_{sq}$ [A] and normalizing for k_O at [A] = 0.29 mol l^{-1}.

[†]The value of k_{dN} is independent of [N] at the concentrations used $((0 - 2) \times 10^{-3}$ mol l$^{-1})$ [8].
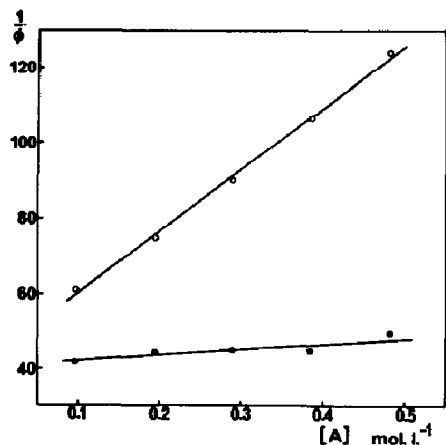
Fig. 2. Reciprocal dependence of the quantum yields for oxetane (•) and dimer (○) formation on the concentration of acetophenone (A).

Conclusions

The results described show that back transfer of triplet energy from norbornene to acetophenone is insignificant. The dependence of ϕ_O/ϕ_D on acetophenone concentration must therefore be a consequence of some other process. If one assumes, as have Arnold [2, 3] and Schroeter [4], that the free triplet of norbornene is a precursor of the dimer in this system, the inclusion of the reaction

$$A + {}^3N^* \longrightarrow A + N \tag{10}$$

will explain the experimental data. However, if (as may be the case), the principal mode of quenching involves charge-transfer interaction (eqn. (6)) the substitution of the steps

$$[{}^3A^* \cdots N] + A \longrightarrow A + A + N \tag{11}$$

$$[{}^3A^* \cdots N] + N \longrightarrow \text{dimer} + A \tag{12}$$

for eqns. (3), (4) and (7) would fit the present and previous data. The occurrence of step (12) more readily explains the anomalous exo–endo stereochemistry [3] of the dimer produced in this reaction since complexation of the ketone triplet at the exo face of the olefin would necessitate endo attack by the second olefin molecule. However, in such a situation the quantum yield data would require that the oxetane arise via the uncomplexed acetophenone triplet, *i.e.* eqn. (5). Further work on this system is in progress.

Acknowledgments

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