QUENCHING OF CHEMIEXCITED ACETONE PHOSPHORESCENCE BY ARYL ALKYL KETONES.
A SEARCH FOR ELECTRONIC EFFECTS

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ABSTRACT.—Thermolysis of acetonitrile solutions of tetramethyl-1,2-dioxetane provides a convenient source of chemically excited acetone phosphorescence. We have investigated the quenching of the latter by a series of aryl alkyl ketones possessing lower triplet energies than acetone. Quenching constants for phenyl alkyl ketones are considerably lower than diffusion control (kq = 10^8 - 10^9 M^-1 sec^-1), whereas those for quenchers with high electron affinity are close to diffusion control (kq = 10^10 M^-1 sec^-1). The difference is explained by assuming that π (acceptor) n (acetone) or π* (acetone) → π* (acceptor) interaction dominates as the first step of the quenching process.

Introduction

Triplet energy transfer normally operates by the exchange mechanism, which requires orbital overlap of donor and acceptor molecules. Since overlap is an inverse exponential function of distance, rapid exchange requires actual collisions between donor and acceptor, with a rate constant kE on the order of 10^-6-10^-13 sec^-1 describing exothermic energy transfer between an encounter pair of molecules.

The necessity for orbital overlap also suggests the possibility of steric and electronic effects. The search for such effects in solution photochemistry is complicated by the overall process usually becoming diffusion-controlled when energy transfer is exothermic, since kE then is faster than the rate at which the excited donor escapes its solvent cage proximity to acceptor. As pointed out previously, if energy transfer is totally diffusion-controlled, significant changes in kE could be obscured. However, there now is considerable evidence that even exothermic triplet energy transfer is only partially diffusion-controlled in nonvicious solvents. Since they do not overlap significantly, experiments designed to explore possible steric effects on energy transfer have produced mixed results, possibly because of varying degrees of diffusion control in the absence of steric hindrance.

There has been very little attention paid to the importance of electronic factors in energy transfer. Dexter's original formulation of the exchange process included a factor correcting for overlap and orbital symmetry; Ullman has reported the only example where orbital symmetries may be important. If one considers energy transfer involving an n, π* triplet as donor and/or acceptor, n, π, n*, π*, and n = π overlaps are all possible. It can then be asked which type of overlap—is any—is most favorable for energy transfer.

It is already known that thermoneutral triplet energy transfer between aliphatic ketones, which involves only n, π* triplets, is rather slow, kE = 10^8 M^-1 sec^-1. On the other hand, various indirect and recent direct evidence suggests that thermoneutral energy transfer between phenyl ketones is relatively fast, kE = 10^10 M^-1 sec^-1.

Since butyronaphthones and valerophenones have energetically proximate n, π* and n, π* triplets whose relative spacing is solvent and substituent dependent, we decided to measure rates of energy transfer to them from a common n, π* triplet, acetone. We overcome the experimental difficulty of selectively exciting the acetone in the presence of better absorbers by chemiluminescence via the thermal decomposition of tetramethyl-dioxetane, TMD 11.

Results and discussion

The experimental data for quenching of triplet acetone by valerophenones, butyronaphthones and some other compounds are presented in the Table. The experimentally observed rate constant (kE) is derived from the quenching of acetone phosphorescence. kE is the composite of a rate constant for electronic energy transfer (kE) and a rate constant for direct bimolecular conversion to the ground states of both partners (kE):

kE = kE + kE.

In solution the upper limit of kE is given by the rate constant of diffusion (kD). There is qualitative evidence that in our experiments quenching is predominantly due to energy transfer. The phenones underwent sensitized 11 type II elimination to yield the corresponding acetophenones, a known triplet reaction; the naphthone emitted sensitized phosphorescence. It is difficult to establish quantitative values due to experimental problems (low product concentration, energy transfer of the excited phenone to dioxetane etc.). These qualitative observations of sensitized triplet decay indicate that energy transfer accounts for at least some of the triplet acetone quenching.
Table. — Observed rate constants $k_4$ for the quenching of acetone phosphorescence by various quenchers at 56°C in CH$_3$CN.

<table>
<thead>
<tr>
<th>Quencher</th>
<th>I. P. ( (eV) )</th>
<th>$k_4$ ( \text{(1.mol}^{-1}.\text{sec}^{-1}) )</th>
<th>$E_T$ ( \text{(kal.mol}^{-1}) )</th>
<th>Configuration of $T_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.31 ( \pi^- )</td>
<td>( 6 \times 10^9 )</td>
<td>58</td>
<td>( \pi-\pi^- )</td>
</tr>
<tr>
<td>2</td>
<td>9.00 ( \pi )</td>
<td>( 6 \times 10^9 )</td>
<td>65</td>
<td>( \pi-\pi^- )</td>
</tr>
<tr>
<td>3</td>
<td>9.21 ( \pi )</td>
<td>( 1.8 \times 10^9 )</td>
<td>69</td>
<td>( \pi-\pi^- )</td>
</tr>
<tr>
<td>4</td>
<td>9.57 ( \pi )</td>
<td>( 1.3 \times 10^9 )</td>
<td>71</td>
<td>( \pi-\pi^- )</td>
</tr>
<tr>
<td>5</td>
<td>6.6 ( \alpha )</td>
<td>( 1 \times 10^9 )</td>
<td>( \pi-\pi^- )</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>9.1 ( \pi )</td>
<td>( 8 \times 10^8 )</td>
<td>72</td>
<td>( \pi-\pi^- )</td>
</tr>
<tr>
<td>7</td>
<td>9.44 ( \pi )</td>
<td>( 8 \times 10^9 )</td>
<td>72</td>
<td>( \pi-\pi^- )</td>
</tr>
<tr>
<td>8</td>
<td>9.3 ( \pi )</td>
<td>( 9 \times 10^8 )</td>
<td>72</td>
<td>( \pi-\pi^- )</td>
</tr>
<tr>
<td>9</td>
<td>9.58 ( \pi )</td>
<td>( 7 \times 10^8 )</td>
<td>72</td>
<td>( \pi-\pi^- )</td>
</tr>
<tr>
<td>10</td>
<td>11.15 ( \pi )</td>
<td>( 1 \times 10^{10} )</td>
<td>63</td>
<td>( \pi-\pi^- )</td>
</tr>
<tr>
<td>11</td>
<td>11.10 ( \pi )</td>
<td>( 1 \times 10^{10} )</td>
<td>( \pi-\pi^- )</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>9.55 ( \pi )</td>
<td>( 5 \times 10^9 )</td>
<td>57</td>
<td>( \pi-\pi^- )</td>
</tr>
<tr>
<td>13</td>
<td>9.3 ( \pi )</td>
<td>( 1 \times 10^9 )</td>
<td>40</td>
<td>( \pi-\pi^- )</td>
</tr>
</tbody>
</table>


Perusal of the Table reveals three main effects:

a) $k_4$ for phenyl alkyl ketones is consistently smaller than $k_{av}$ (\( \approx 2 \times 10^{15} \)) and than $k_4$ for olefins and butyronaphthone.

b) $k_4$ values for alkyl phenones having $\pi-\pi^*$ lowest triplets, are rather similar to those having $\pi-\pi^*$ lowest triplets.

c) $\pi$-alkyl substitution lowers $k_4$ to a minor degree.

Although the triplet energies of all quenchers listed in the Table are lower than that of acetone, the measured $k_4$ values of phenyl alkyl ketones are considerably lower than maximum measured values near $10^{15} \text{M}^{-1} \text{sec}^{-1}$ of other quenchers like t-dicyano-ethylene, maleic anhydride (see also ref. 9), naphthale and biacetyl. To evaluate the reason for these discrepancies between rate constants for "good" and "poor" quenchers one has to look at the electron exchange quenching mechanism in more detail (fig. 1).

There are in principal three limiting possibilities for primary orbital interactions between excited acetone and triplet energy acceptors:

a) $\pi-\pi^*$-interaction, with electron transfer of an $\pi$-electron of the acceptor into the half filled $\pi$-orbital of the donor.

b) $\pi-\alpha^*$-interaction with electron transfer of a $\alpha^*$-electron of the acceptor into the half filled $\alpha^*$-orbital of the donor.

c) $\pi-\pi^*$-interaction with electron transfer of the $\pi^*$-electron of the donor into the empty $\pi^*$-orbital of the acceptor.

We analyze our results by assuming that quenching of acetone triplets by aryl alkyl ketones occurs via a series of steps involving electron transfers, since it seems to us that, whatever the nature of the detailed mechanism of quenching, charge transfer interactions are likely to be dominant. Given this hypothesis, which of the three possibilities really occurs is determined in first order by the relative energies of the orbitals.
involved, and, if the electron transfer step is exothermic, in second order by orbital interactions and steric factors.

Figure 2 lists the orbital energy levels of acetone and of some quenchers. The energy levels of the bonding orbitals are derived from vertical gas phase ionization potentials and those of the \( \pi^* \)-orbitals by addition of the triplet energies to the I.P.'s. We are quite aware that such a combination is not strictly correct and only of qualitative significance. Particularly the energy levels given for acetone are for the groundstate molecule, whereas we are referring to triplet excited acetone. Nevertheless the idea is nicely validated by the experimental values given in the Table and Figure 2. Generally it may be concluded that for compounds 1-11 and 15 electron transfer into the half filled \( n \)-orbital of acetone dominates the energy transfer, whereas for compounds 12-14 energy transfer is initiated by transfer of an acetone \( \pi^* \)-electron into an empty \( \pi^* \)-orbital.

When the first electron is transferred, the resulting ion pair will stick together until the second electron jumps back to the cation intermediate, leaving behind a neutral molecule either in its excited or in its ground state. Thus transfer of the first electron determines the quenching rate of acetone triplets \( k_{eq} \), whereas transfer of the second electron determines the efficiency of energy transfer (e.g. the ratio \( k_{eq} / k_{Te} \)).

Transfer of the second electron may be very fast resulting in a "concerted" energy transfer or quenching or in a relatively slow energy transfer or quenching via an "exciplex".

In this paper we are mainly concerned with the quenching rate, therefore we must consider the first electron jump.

Figure 3 visualizes the problems connected with electron transfer via the \( n - n \), \( n - \pi \) or \( \pi^* - \pi^* \) pathways in terms of orbital overlap and steric requirements.

In case of an electron transfer from a quencher \( n \)-orbital to an acetone \( n \)-orbital reasonable orbital overlap can only be achieved if the two molecules approach horizontally in one plane. Additionally the \( n \)-orbitals are localized at the oxygen, which represents only a very small part of the molecule. Thus we conclude that an encounter which allows \( n-n \)-overlap is very improbable and will not contribute significantly to the quenching of acetone by alkyl phenyl ketones.
The phosphorescence intensity of triplet acetone was observed in a nitrogen-purged acetonitrile solution with a standard commercial spectrophotometer (0.25 = 430 nm) or by photon counting. Concentrations employed were 10⁻² M TMD for the former experiments and 10⁻³ M TMD for the latter experiments. At about 50°C the emission intensity of an 2.4 x 10⁻² M solution of dicarbonylate did not change significantly for about 2 hours. This is long enough to measure the decrease of emission intensity as a function of different quencher concentrations. At low dicarbonylate concentrations no chain reaction due to sensitized decomposition occurs 16. The butyrophenones and valerophenones themselves show no emission under the experimental conditions. Butyrophenone exhibits emission at λ<sub>max</sub> = 560 nm, well separated from the acetone emission. For the other ketones formation of corresponding acetophenones was established by vpc analysis.

Stimulated emission spectra were identical in all cases. The lifetime of acetone was measured at 50°C by the single photon counting method using a 10⁻³ M solution of acetone in acetonitrile. Acetone was excited with a N₂-flashed arc lamp and the phosphorescence decay monitored at 430 nm. The lifetime was calculated to be τ(SCH(CN)) = 7.5 x 10⁻³ sec in accord with earlier estimates 17.

Chemicals

The following reagents were commercial materials purified by either distillation, recrystallization on passing through alumina:

- Butyrophenone (Eastman), valerophenone (Eastman), isobutyrophene (Aldrich), 2-p-methyl-butoxyphenone (Fluka), 2-phenyl-2-butoxyphenone (K. and K. Lab., Inc.), trans-dicyclohexylcyclopropene, maleic anhydride (Aldrich).

Pheny1-1-buty1 ketone and adamantyl phenyl ketone were obtained from H. C. Heine, Bayer A. G., West Germany; phenyl butyrophenone was prepared from biphenyl by Friedel-Crafts acylation and butyrophenone by acylation of naphthalene.

Tetramethyl-1,2-dioxetane was prepared by Kopecky's method 18.

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We also thank Dr. H. G. Heine, Bayer A. G., W. Germany, for samples of phenyl 1-buty1 ketone and adamantyl phenyl ketone.

References

15. Comparatively small steric effects have been noted before: for ref. 6 and G. Schuster, and N. J. Turro, Tetrahedron Lett., 2281 (1975).
16. Similar small differences have been reported for energy transfer between rare earth ions and ketones possessing differing lowest triplets (n, n* and n, n*); V. F. Marinov, and B. B. Sremskovic, Optics and Spectroscopy, 31, 316 (1971).
21. Similar arguments were used to explain oxetane formation, see N. J. Turro "Modern Molecular Photochemistry", The Benjamin/Cummins Publishing Co., Inc., p. 432 and references therein.

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