

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 chemiexcited 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 ($k_q = 10^8 - 10^9 \text{ M}^{-1} \cdot \text{sec}^{-1}$), whereas those for quenchers with high electronaffinity are close to diffusion control ($k_q = 10^{10} \text{ M}^{-1} \cdot \text{sec}^{-1}$). The difference is explained by assuming that π (acceptor) n (acetone) or π^* (acetone) $\rightarrow \pi^*$ (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 molecules¹. Since overlap is an inverse exponential function of distance, rapid exchange requires actual collisions between donor and acceptor, with a rate constant k_{ET} on the order of $10^{10} - 10^{11} \text{ sec}^{-1}$ describing exothermic energy transfer between an encounter pair of molecules^{2,3}.

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 k_{ET} then is faster than the rate at which the excited donor escapes its solvent cage proximity to acceptor. As pointed out previously², if energy transfer is totally diffusion-controlled, significant changes in k_{ET} could be obscured. However, there now is considerable evidence that even exothermic triplet energy transfer is only partially diffusion-controlled in nonviscous solvents³⁻⁵. Experiments designed to explore possible steric effects on energy transfer have produced mixed results^{2,6}, 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 process⁷ included a factor correcting for overlap and orbital symmetry; Ullman has reported the only example where orbital symmetries may be important⁸. If one considers energy transfer involving an n, π^* triplet as donor and/or acceptor, $\pi-\pi$, $n-\pi$, and $n-n$ orbital overlaps are all possible. It can then be asked which type of overlap—if 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, $k_q = 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ^{5,6}. On the other hand, various

indirect⁹ and recent direct¹⁰ evidence suggests that thermoneutral energy transfer between phenyl ketones is relatively fast, $k_q \sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

Since butyrophenones and valerophenones have energetically proximate n, π^* and π, π^* triplets whose relative spacing is solvent and substituent dependent¹¹, we decided to measure rates of energy transfer to them from a common n, π^* triplet, acetone. We overcame the experimental difficulty of selectively exciting the acetone in the presence of better absorbers by chemiexcitation via the thermal decomposition of tetramethyldioxetane, TMD¹².

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 (k_q) is derived from the quenching of acetone phosphorescence. k_q is the composite of a rate constant for electronic energy transfer (k_{ET}) and a rate constant for direct bimolecular conversion to the ground states of both partners (k_{π}):

$$k_q = k_{ET} + k_{\pi}$$

In solution the upper limit of k_q is given by the rate constant of diffusion (k_{diff}). There is qualitative evidence that in our experiments quenching is predominantly due to energy transfer: The phenones underwent sensitized¹² type II elimination to yield the corresponding acetophenones, a known triplet reaction¹³; 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.

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Table. — Observed rate constants k_q for the quenching of acetone phosphorescence by various quenchers at 56°C in CH₃CN.

Quencher	I. P. ^c (eV)	k_q^a (l. mol ⁻¹ . sec ⁻¹)	E_T^b (kcal. mol ⁻¹)	Configuration of T_1
1	8.31 $\pi^{f,g}$	6×10^9	58	$\pi-\pi^*^h$
	9.00 π			
	9.21 n_o			
2	9.57 n_o^d	1.8×10^9	65	$\pi-\pi^*^h$
3	9.80 π_S	1.3×10^9	69	$\pi-\pi^*^i$
	10.22 π_A			
	8.6 $\pi^{f,g}$			
4	9.1 n_o	1×10^9	71	$\pi-\pi^*^{k,l}$
	9.44 π			
	9.3			
5	9.3	8×10^8	72	$n-\pi^*^k$
	9.55			
	9.3 n_o, π^d			
6	9.3 n_o^d	8×10^8	72	$n-\pi^*^k$
	9.46 π_S			
	9.5 π_A			
7	9.02 π_S	7×10^8	72	$\pi-\pi^*^l$
	9.32 π_o			
	9.50 π_A			
8	9.02 n_o	6.5×10^8	72	$n-\pi^*^m$
		9.46 π	5×10^8	70
9	9.02 n_o	4×10^8	71	$n-\pi^*^n$
		9.46 π	3×10^8	
10	9.02 n_o	4×10^8	71	$n-\pi^*^n$
		9.46 π	3×10^8	
11	11.15 ^f	1.1×10^{10}	63	$\pi-\pi^*^p$
		11.15 ^f	1.1×10^{10}	~72
12	11.15 ^f	1.1×10^{10}	63	$\pi-\pi^*^p$
		11.15 ^f	1.1×10^{10}	~72
13	9.55 $n_o^{(+)}$	$> 5 \times 10^9$ ^p	57	$n-\pi^*^q$
14	7.58 ^f	1×10^9 ^q	40	$\pi-\pi^*^r$
15	8.84	1×10^9 ^q	40	$\pi-\pi^*^r$

^a k_q , quenching constants calculated from Stern-Volmer-plots with $\tau_{ph} = 7.5 \mu\text{sec}$ in CH₃CN at 56°C. ^b E_T , energy of the lowest triplet state. ^c I. P., vertical ionization potentials from PES-Data. ^d From T. Koenig, R. Wielessek, L. L. Miller, and Y. H. So, *J. Amer. Chem. Soc.*, **99**, 7061 (1977). ^e L. G. Christophorous, *Atomic and Molecular Radiation Physics*, J. B. Birks, and S. P. McGlynn, Eds., Wiley Interscience, 1971. ^f From C. N. R. Rao, P. K. Basu, and M. S. Hegde, *Appl. Spectrosc. Rev.*, **15**, 1 (1979). ^g I. P. values of the corresponding acetyl-compounds. ^h From J. N. Pitts, H. W. Johnson, and T. Kuwana, *J. Phys. Chem.*, **60**, 2456 (1962). ⁱ P. J. Wagner, and E. Siebert, unpublished results. ^k Ref. ¹¹. ^l N. C. Yang *et al.*, *J. Amer. Chem. Soc.*, **89**, 5466 (1967). ^m P. J. Wagner, M. Thomas, and E. Harris, *J. Amer. Chem. Soc.*, **98**, 7675 (1976). ⁿ P. J. Wagner *et al.*, *J. Amer. Chem. Soc.*, **92**, 5269 (1970). ^p From T. Takemura, H. Baba, and M. Fujita, *Bull. Chem. Soc. Jpn.*, **46**, 2625 (1973); k_q was determined at lower temperature. ^q From N. J. Turro *et al.*, *J. Amer. Chem. Soc.*, **96**, 1627 (1973) measured under slightly different conditions.

Perusal of the Table reveals three main effects:

- k_q for phenyl alkyl ketones is consistently smaller than k_{diff} ($\approx 2 \times 10^{10}$) and than k_q for olefins and butyronaphthone.
- k_q values for alkyl phenones having n , π^* lowest triplets, are rather similar to those having $\pi-\pi^*$ lowest triplets¹⁵.
- α -alkyl substitution lowers k_q to a minor degree¹⁴.

Although the triplet energies of all quenchers listed in the Table are lower than that of acetone, the measured k_q values of phenyl alkyl ketones are considerably lower than maximum measured values near $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ of other quenchers like *t*-dicyano-ethylene, maleic anhydride (see also ref. ⁴), naphthalene 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 triplet excited acetone and triplet energy acceptors:

- $n-n$ -interaction, with electron transfer of an n -electron of the acceptor into the half filled n -orbital of the donor.
- $n-\pi$ -interaction with electron transfer of a π -electron of the acceptor into the half filled n -orbital of the donor.
- $\pi^*-\pi^*$ -interaction with electron transfer of the π^* -electron of the donor into the empty π^* -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 energetics of the orbitals

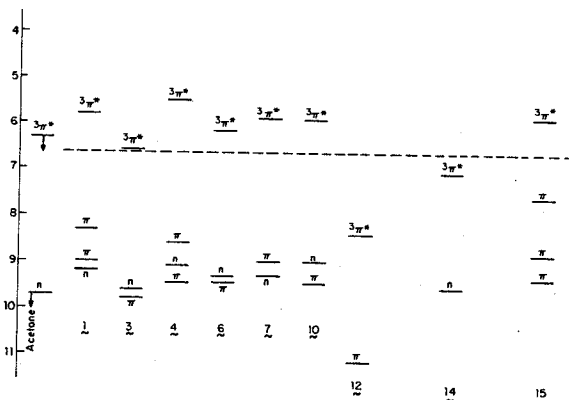
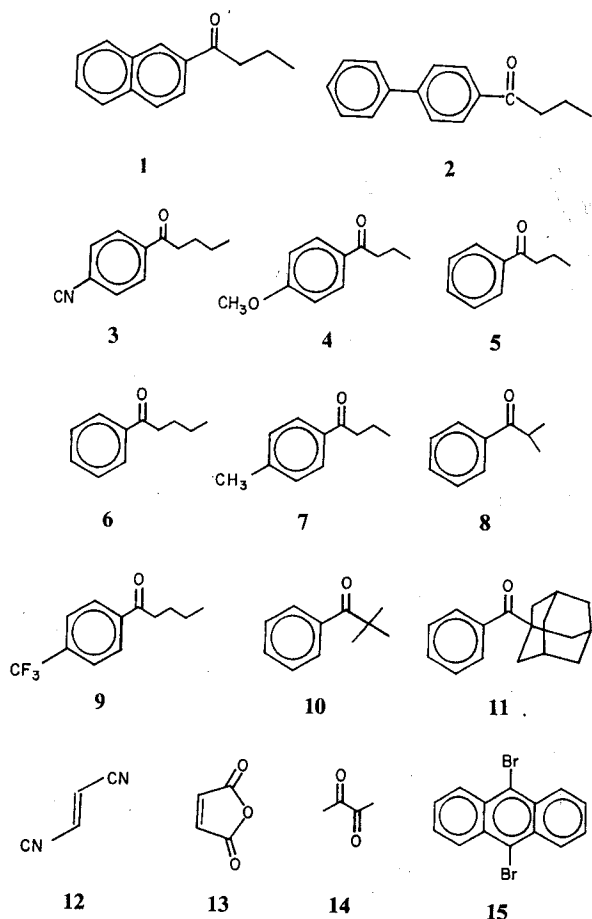


Figure 2. — Molecular orbital levels of various quenchers, n and π^* energies are vertical ionization potentials derived from PES data, π^* energies are obtained by adding triplet energies to the energy of the highest occupied molecular orbital (see text). n and π energies of 1 and 4 are the values for the corresponding acetyl compounds.

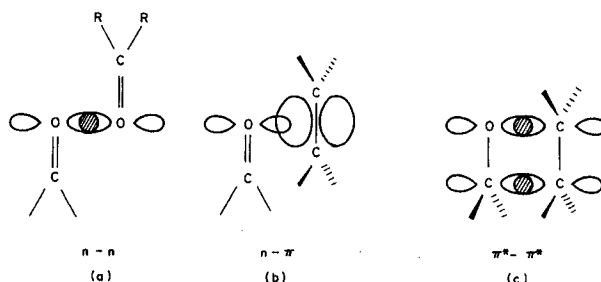


Figure 3. — Orbital overlap between ketone donor and olefin acceptor for: (a) in plane; (b) perpendicular, and (c) parallel encounter.

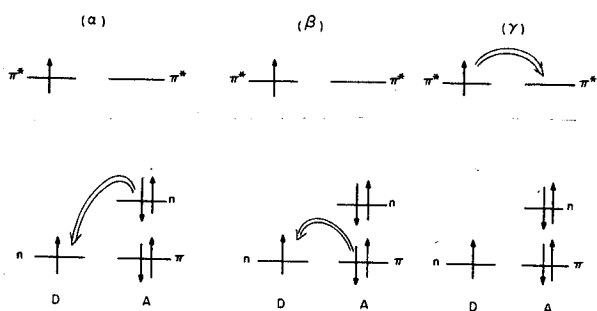


Figure 1. — Possible orbital interactions for n , π^* donors with acceptors possessing low lying n , π^* and π , π^* states.

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 π^* -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 π^* -electron into an empty π^* -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_q , whereas transfer of the second electron determines the efficiency of energy transfer (e.g. the ratio k_{ET}/k_{IT}).

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 $n \leftarrow n$, $n \leftarrow \pi$ or $\pi^* \rightarrow \pi^*$ 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 unprobable and will not contribute significantly to the quenching of acetone by alkyl phenyl ketones.

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n - π overlap is best when donor and acceptor approach perpendicular (see Fig. 3b). Since the π -orbitals are more delocalized than the n -orbitals, the $n \leftarrow \pi$ interaction is more probable during an encounter of the two molecules. Therefore it seems justified to assume that quenching of acetone phosphorescence by alkyl aryl ketones (compounds 1-11) is initiated by $\pi \rightarrow n$ electron transfer. As the experimental quenching constants of 1-11 show (Table), this mode of interaction does not lead to diffusion controlled quenching.

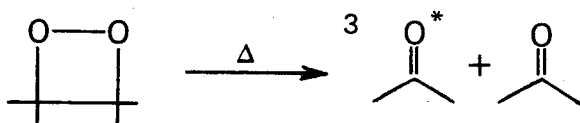
Compounds 12-14 however, do quench with high rate constants close to diffusion control, since here a $\pi^* \rightarrow \pi^*$ electron transfer initiates the quenching process. $\pi^* \rightarrow \pi^*$ -overlap is most efficient when donor and acceptor molecules approach in a parallel fashion (Fig. 3c). Comparison of the parallel and perpendicular encounter (Fig. 3c and 3b) explains the different quenching rate constants.

If the donor and acceptor ketones approach in a parallel way orbital overlap ($\pi^* \leftarrow \pi^*$) is maximized and steric hindrance minimized, whereas in the perpendicular approach orbital overlap is poorer because of the different nature of the n and π orbitals involved and because of the possible steric hindrance by bulky substituents.

This model²⁰ of different modes of orbital interaction between donor and quencher depending on the relative energetic levels of the orbitals involved explains even minor differences of the quenching constants in the Table and may not be limited to the examples discussed here. For example the quenching of ketone triplets by amines can be explained along the same lines.

Experimental

Triplet acetone can be formed selectively and efficiently by thermal cleavage of tetramethyldioxetane¹².



The phosphorescence intensity of triplet acetone was observed in a nitrogen purged acetonitrile solution with a standard commercial spectrofluorometer ($\lambda_{\text{max}}^{\text{phos}} = 430 \text{ nm}$) or by photon counting. Concentrations employed were $\sim 10^{-3} \text{ M}$ TMD for the former experiments and $\sim 10^{-5} \text{ M}$ TMD for the latter experiments. At about 56°C the emission intensity of an $2.4 \times 10^{-5} \text{ M}$ solution of dioxetane does 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 dioxetane concentrations no chain reaction due to sensitized decomposition occurs¹⁶. The butyrophenones and valerophenones themselves show no emission under the experimental conditions. Butyronaphthone exhibits emission at $\lambda_{\text{max}} \approx 560 \text{ nm}$, well separated from the acetone emission. For the other ketones formation of corresponding acetophenones was established by vcp analysis.

Stern-Volmer plots were linear in all cases. The lifetime of acetone was measured at 56°C by the single photon counting method using a $\sim 10^{-3} \text{ M}$ solution of acetone in acetonitrile. Acetone was excited with a N_2 -flushed arc lamp and the phosphorescence decay monitored at 430 nm . The lifetime was calculated to be $\tau(\text{CH}_3\text{CN}) = 7.5 \times 10^{-6} \text{ sec}$ in accord with earlier estimates¹⁷.

CHEMICALS

The following acceptors were commercial materials purified by either distillation, recrystallization or passing through alumina:

butyrophenone (Eastman), valerophenone (Eastman), isobutyrophenone (Aldrich), *p*-methyl-butyrophenone (Fluka), *p*-methoxybutyrophenone (K and K. Lab., Inc.), *trans*-dicyanoethylene, maleic anhydride (Aldrich).

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

Tetramethyl 1,2-dioxetane was prepared by Kopecky's method¹⁸.

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- Similar arguments were used to explain oxetane formation, see N. J. Turro "Modern Molecular Photochemistry", The Benjamin/Cummings Publishing Co., Inc., p. 432 and references therein.