

Mechanisms of Photochemical Reactions in Solution. XLI.¹

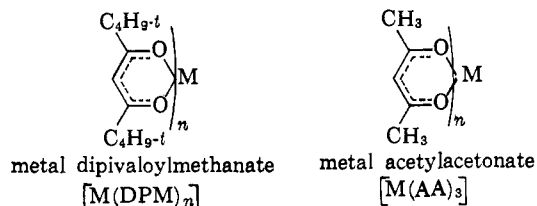
Comparison of Rates of Fast Triplet Quenching Reactions

Albert J. Fry, Robert S. H. Liu, and George S. Hammond

Contribution No. 3119 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California. Received April 11, 1966

Abstract: Quenching of representative triplets by ferrocene and various metal chelate compounds has been compared with quenching by conjugated dienes. The rates of quenching by dienes fall off as expected as the available excitation energy of the sensitizer triplets decreases. However, the organometallic compounds quench low-energy triplets almost as readily as those having high excitation energies. The reactivity of chelate compounds varies as the nature of the central metal atom is changed and appears to be sensitive to the extent to which the unsaturated systems of the ligands are shielded by attached alkyl groups.

Organometallic compounds derived from transition elements are well known to be efficient quenchers for triplet states of a number of molecules commonly used as photosensitizers.^{2,3} Bell and Linschitz³ measured rates close to the expected diffusion-controlled limit for quenching of 1-naphthaldehyde and benzophenone triplets by tris(dipivaloylmethanato)iron(III) [Fe(DPM)₃] and tris(acetylacetonato)iron(III) [Fe(AA)₃]. However, comparison of quenching of benzophenone triplets by a number of acetylacetonates and dipivaloylmethanates, using a competitive kinetic method, showed that the former were consistently more reactive,⁴ suggesting that steric hindrance might be a significant factor in determining quenching reactivity. The unsaturated parts of the ligands are obviously well-sheltered in dipivaloylmethanates. Other recent work has shown that quenching rates in purely organic systems can be decreased by bulky groups located close to the site of excitation in a donor.¹



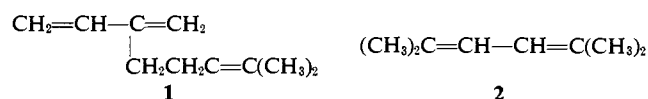
In order to gather more relevant information we have measured rate constants for quenching of a number of triplets, having varying excitation energies, by flash spectrophotometry. Several metal chelates were used as quenchers. For purposes of comparison, and because the data were needed for another purpose, a parallel study was carried out using conjugated dienes as quenchers.

Results and Discussion

The measured quenching constants are summarized in Table I. Measurements could not be made with all combinations that would have been desirable either because of interference with the spectrophotometric monitoring of triplet-triplet absorption by competitive

absorption by the quencher or because of the photo-decomposition of some sensitizers.

The largest values of the quenching constants are nearly identical to the largest values obtained in other, extensive series of flash kinetic measurements.⁵ Quenching constants for the dienes are a sensitive function of the excitation energies of the sensitizers, as would have been predicted from our studies of sensitized photodimerization reactions.⁶ The vertical excitation energies for the S₀ → T₁ transitions of *s-trans* forms of the dienes are at about 60 kcal/mole and the vertical transitions of the *s-cis* forms are placed at about 53 kcal/mole. Since the *s-cis* form is believed to be only a minor constituent in samples of isoprene at ambient temperatures, quenching by isoprene should become markedly inefficient as the excitation energy available in the sensitizer is lowered toward 60 kcal/mole. This is clearly the case. On the other hand, 1,3-cyclohexadiene which is constrained to the *s-cis* configuration should remain a good quencher until the 53 kcal level is approached. The three data available agree with this expectation. The rates of quenching by myrcene, **1**, and 1,1,4,4-tetramethylbutadiene, **2**, show intermediate fall-off patterns. Perhaps myrcene contains larger amounts of the *s-cis* forms than does isoprene and it is possible that the vertical transition energies of both forms of **2** are lower than those of the corresponding forms of 1,3-butadiene.



It is very interesting to note that with the two dienes with which measurements were made, there is still easily measurable quenching activity toward anthracene. The excitation energy of anthracene is lower by 10 kcal/mole than is required to effect vertical excitation of even the *s-cis* forms of the dienes. The result was expected because low-energy sensitizers do effect the sensitized dimerization of isoprene and butadiene.⁶ By arguments identical with those advanced in discussion of quenching of low-energy sensitizers by the stilbenes and 1,2-diphenylpropenes⁴ we adduce that the dienes find an excitation path to twisted triplet states.

(1) Part XL: W. G. Herkstroeter, L. B. Jones, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4777 (1966).

(2) W. M. Moore, G. S. Hammond, and R. P. Foss, *ibid.*, **83**, 2789 (1961).

(3) J. A. Bell and H. Linschitz, *ibid.*, **85**, 528 (1963).

(4) G. S. Hammond and R. P. Foss, *J. Phys. Chem.*, **68**, 3739 (1964).

(5) W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966).

(6) R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *ibid.*, **87**, 3406 (1965).

Table I. Rate Constants for Quenching Triplets of Various Sensitizers^a ($k_q, M^{-1} \text{sec}^{-1} \times 10^{-9}$)

Quencher	Sensitizer (E_T) ^c							
	Triphenyl-ene (66.6)	Phenan-threne (62.2)	Naph-thalene (60.9)	2-Aceto-naphthone (59.3)	Benzil (53.7)	Fluorenone (53.3)	Benzan-throne (47.0)	Anthracene (42.6)
Fe(AA) ₃	<i>d</i>	3.3	1.8	1.9	2.7	1.2	1.0	0.7
Ferrocene	5.9		<i>d</i>	5.4	7.0	5.1	5.7	4.4
Cu(AA) ₂	1.3			1.9	1.7	1.0	2.3	0.6
Cr(AA) ₃	3.8			1.1	0.4	1.1	1.3	1.3
Ni(DPM) ₂					0.3			
Cu(DPM) ₂				0.5				0.3
Isoprene	6.4	0.49		0.28		0.002		
Tetramethylbutadiene	4.6	3.6		1.4	0.43			0.07
Myrcene	2.6	1.3		0.25				0.01
1,3-Cyclohexadiene	1.3	2.3			0.30			

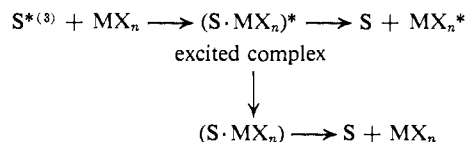
^a Benzene solution. ^b Precision of the rate constants is $\pm 50\%$. ^c E_T is the excitation energy of the triplet state of the sensitizer. ^d Experiments attempted but unsuccessful because of overlap of absorption by the sensitizer triplet and by the quencher.

The pattern of results with the organometallic compounds contrasts strongly with that observed with the dienes. In all cases there is very little variation in the rates at which a given compound quenches all of the sensitizers. The low rate of quenching of benzil by Cr(AA)₃ is regarded with some suspicion since benzil has frequently given trouble in sensitized reactions because of its tendency to undergo unwanted side reactions. Excluding that datum, none of the quenchers shows a variation of more than a factor of five with sensitizers having excitation energies covering the range from 43 to 67 kcal/mole. This remarkable behavior compels one of two conclusions. Either all of the metallic compounds have very low-lying states to which they can be promoted by energy transfer or with these compounds quenching does not involve energy transfer. The latter possibility has been suggested frequently.^{3,7} If a metallic quencher and a triplet are brought in contact, even very weak electronic interactions may allow spin-orbit coupling arising mostly from the central metal atom, to effect rapid intersystem crossing of the complex as a whole so that it may relax and dissociate as two ground-state molecules. We still cannot provide a strong argument for choice between the two possibilities.

One conclusion seems very clear. The variation in reactivity of the organometallic compounds is not associated with variations in excitation energies. Furthermore, there is no obvious correlation of the results with the spin statistical factors discussed by Porter and Wright.⁷ Note, for example, that Fe(AA)₃, which almost surely has a spin of $5/2$, is a better quencher than the other chelates which have lower spins. If all combinations of complexes were formed between a triplet and the iron chelate and in relative amounts simply depending on their statistical weights, only one-third of the complexes should be capable of decaying directly to the ground states of the two molecules.⁸

(7) G. Porter and M. P. Wright, *J. Chim. Phys.*, **55**, 705 (1958).

The superiority of ferrocene as a quencher and the fact that acetylacetonates are more reactive than dipivaloylmethanates suggests that stereochemical factors are important. All of the results reported here indicate that metal chelates are far more reactive than solvated transition metal ions.⁷ We conclude that close contact between the triplet and the unsaturated ligands attached to the metal facilitates quenching. With ferrocene, in which the unsaturated parts of the molecule are completely exposed, the quenching rate is as high as any that we have observed.⁵ This suggests that the critical interactions involve some kind of coupling of the π systems of the triplet and quencher. Since we have not yet found any evidence for formation of excited states of the chelates, the data are equally compatible with the following two mechanisms.



Experimental Section

Metal chelates were obtained from Dr. Chin-Hua Wu and were either sublimed or recrystallized before use. Ferrocene was obtained from Mr. Joseph Dannenberg. Sensitizers were purified by either zone refining or chromatography on alumina followed by recrystallization. Dienes were purified by preparative vapor chromatography. The procedures described previously⁵ were used for preparation of the samples and study of the triplet decay rates.

Acknowledgment. This work was supported by a grant from the Atomic Energy Commission. We are also indebted to Dr. W. G. Herkstroeter for helpful discussion and advice.

(8) One may be surprised that the spin statistical factor does not appear, regardless of the quenching mechanism assumed. The failure of the factor to appear may indicate that spin transitions among the various complex states may be rapid in comparison with the time that two molecules spend as nearest neighbors in solution.