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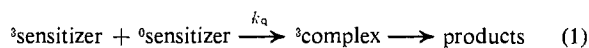
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### Rate of the Self-Quenching Reaction for Thioxanthone Triplets

Sir:

The choice of a sensitizer for a photochemical reaction can often be of critical importance. It has been pointed out that the absorption spectrum, the intersystem crossing ratio, and the triplet energy all need to be considered in the choice of a sensitizer for a given reaction.<sup>1</sup> To these may be added the consideration of the self-quenching reaction (eq 1), which has recently been reported for Michler's ketone,<sup>2</sup> thioxanthone,<sup>3</sup> and various alkoxy-substituted acetophenones.<sup>3</sup>



The rates for the self-quenching reactions reported in the literature are given in Table I. They range from 9

Table I

Sensitizer	$k_q$ (eq 1), l./mol sec
<i>p</i> -Methoxyacetophenone <sup>a</sup>	$9 \times 10^7$
<i>m</i> -Methoxyacetophenone <sup>a</sup>	$8 \times 10^8$
Michler's ketone <sup>b</sup>	$1 \times 10^9$
3,4-Methylenedioxyacetophenone <sup>a</sup>	$4 \times 10^9$
Thioxanthone <sup>a</sup>	$6 \times 10^{10}$

<sup>a</sup> Reference 3. <sup>b</sup> Reference 2.

$\times 10^7$  l./mol sec) for *p*-methoxyacetophenone to  $6 \times 10^{10}$  l./mol sec) for thioxanthone. The latter value is larger than that for a diffusion-controlled reaction and would imply a long-range mechanism for the self-quenching reaction rather than complex formation as shown in eq 1. The existence of such a long-range quenching mechanism would have serious theoretical consequences as well as the practical one of rendering thioxanthone unfit as a sensitizer for many photochemical reactions. We have therefore examined the photochemistry of thioxanthone and would like to report data that confirm the existence of the self-quenching reaction for thioxanthone, but establish its rate as  $2.3 \pm 0.5 \times 10^9$  l./mol sec) rather than the reported  $6 \times 10^{10}$  l./mol sec).

As we reported in an earlier communication,<sup>4</sup> no quenching is observed in the isomerization of 0.1 *M* solutions of *trans*-stilbene in degassed benzene with a thioxanthone concentration of up to 0.05 *M*. The same

(1) C. D. DeBoer, N. J. Turro, and G. S. Hammond, *Org. Syn.*, **47**, 64 (1967).

(2) T. H. Koch and A. H. Jones, *J. Amer. Chem. Soc.*, **92**, 7503 (1970).

(3) O. L. Chapman and G. Wampfler, *ibid.*, **91**, 5390 (1969).

(4) A. G. Schultz, C. D. DeBoer, W. G. Herkstroeter, and R. H. Schlessinger, *ibid.*, **92**, 6088 (1970).

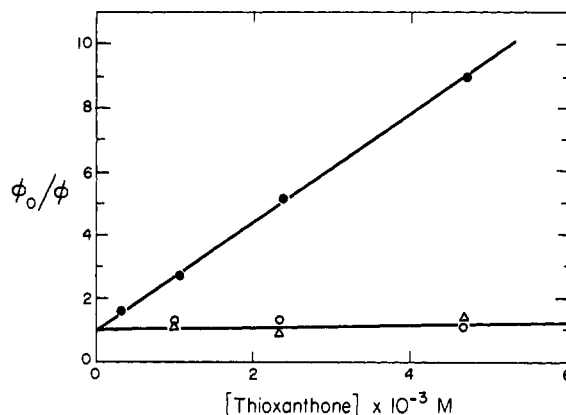
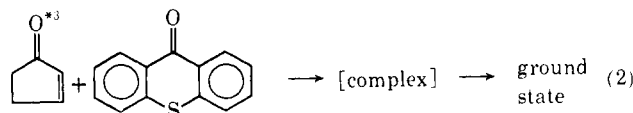


Figure 1. Quenching of cyclopentenone dimerization by thioxanthone: irradiation at ●, 365 nm; ○, 313 nm; and △, 335 nm.

result has now been obtained in the isomerization of 0.1 *M* dimethyl fumarate, the dimerization of 0.1 *M* indene, and the dimerization of 0.1 *M* methyl indene-2-carboxylate, when sensitized by 0.001–0.1 *M* thioxanthone. On the other hand, Chapman<sup>3</sup> reports strong quenching in the thioxanthone-sensitized rearrangement of 0.1 *M* 4,4-dimethylcyclohexenone in *tert*-butyl alcohol, and we now report a similar strong quenching by thioxanthone on the dimerization of 1.22 *M* 2-cyclopentenone. At first glance it might appear that the enone triplet state and the thioxanthone ground state are involved in the quenching reaction (eq 2) since the



quenching is observed only with enones. However, reaction 2 is ruled out by a wavelength experiment. When benzene solutions of 1.22 *M* cyclopentenone and  $5 \times 10^{-3}$  *M* thioxanthone are irradiated at 365 nm (absorption by thioxanthone), strong quenching is observed. When 313- or 335-nm radiation is used (absorption by cyclopentenone), no quenching is seen. This experiment clearly shows that the quenching reaction involves the thioxanthone triplet and the thioxanthone ground state (eq 1). These results are plotted in Figure 1. We believe that the reason quenching by thioxanthone ( $E_t = 65$  kcal/mol)<sup>5</sup> has been observed with enones but not with stilbene (0.1 *M*,  $E_t = 50$  kcal/mol),<sup>6</sup> indene (0.1 *M*,  $E_t = 59$  kcal/mol),<sup>7</sup> or dimethyl fumarate (0.1 *M*,  $E_t = 61$  kcal/mol)<sup>6</sup> is that energy transfer from thioxanthone to these low-energy acceptors is diffusion controlled, but is considerably less than diffusion controlled to the enone systems. Our observations are in agreement with de Mayo's estimate for the triplet energy of the enone chromophore ( $E_t = 70$  kcal/mol)<sup>8</sup> and with his observation that energy transfer from benzophenone ( $E_t = 68.5$  kcal/mol)<sup>5</sup> to cyclopentenone is much slower than diffusion con-

(5) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 298.

(6) G. S. Hammond, J. Saltiel, A. A. Lamolo, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and J. C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

(7) R. C. Heckman, *J. Mol. Spectrosc.*, **2**, 27 (1958).

(8) P. de Mayo, *Accounts Chem. Res.*, **4**, 41 (1971).

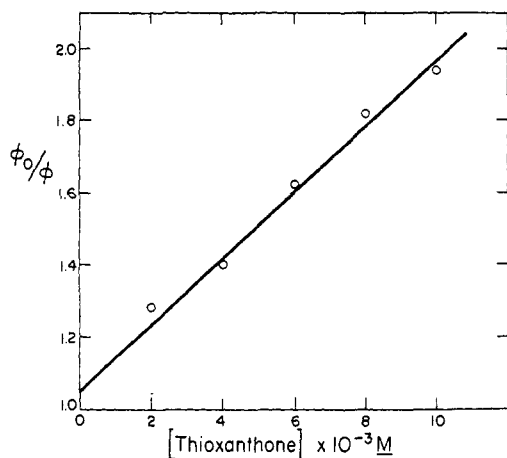
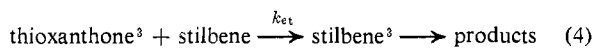
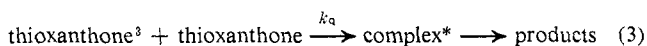


Figure 2. Quenching of  $5 \times 10^{-3} M$  stilbene isomerization by thioxanthone.

trolled.<sup>9</sup> Our results further imply that the rate of the thioxanthone self-quenching reaction (eq 3) is also less than diffusion controlled.

In order to establish the actual rate of the self-quenching reaction for thioxanthone, the following experiments were carried out. Solutions of  $5 \times 10^{-3} M$  *trans*-stilbene in degassed benzene with various concentrations of thioxanthone were irradiated at 365 nm. Quenching was observed, as shown in Figure 2. From the known rate of energy transfer from thioxanthone triplets to stilbene,<sup>10</sup> the rate of the self-quenching reaction can be calculated to be  $2.3 \pm 0.5 \times 10^9 l./(\text{mol sec})$ .



$$\phi_0/\phi = 1 + k_a[\text{thioxanthone}]/k_{et}[\text{stilbene}] \quad (5)$$

We conclude (1) that thioxanthone is a practical triplet-state sensitizer provided that energy transfer is much faster than  $2 \times 10^9 \times [\text{thioxanthone}] \text{ sec}^{-1}$  and (2) that the triplet states of simple enones such as cyclopentenone and cyclohexenone are higher than that of thioxanthone (65 kcal/mol).

**Acknowledgment.** The authors thank Mr. John Mead for valuable technical assistance.

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

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## A New, General Approach to Ligand Field Calculations. The Effective Perturbation Method

Sir:

Crystal or ligand field theory, introduced by Bethe<sup>1</sup> over 40 years ago, has played a central role in the

(1) H. A. Bethe, *Ann. Phys. (Leipzig)*, **3**, 133 (1929).

development of coordination chemistry. Even in its simplest form, involving the point charge model, electrostatic perturbation theory (EPT) has been remarkably successful in accounting for spectral, magnetic, and even some thermodynamic properties for transition metal complexes.<sup>2</sup> It is now generally realized that the physical models involved in EPT calculations are unrealistic. The semiquantitative or even qualitative agreement of experiment with *ab initio* point charge or point dipole calculations of this type is fortuitous.<sup>3</sup> When viewed as a phenomenological theory such objections vanish. For complexes of cubic symmetry ( $O_h$  or  $T_d$ ), a single parameter ( $\Delta$  or  $10Dq$ ) is involved and the success of EPT may be regarded as a manifestation of group theoretical principles. For point groups of inferior symmetry the situation is less satisfactory. In addition to the fourth power radial integral ( $r^4$ ) (subsumed in  $Dq$ ), one has a  $\langle r^2 \rangle$  term. While for a given form of the d orbital wave functions these radial integrals may be calculated,<sup>4</sup> their use presumes the validity of a fallacious model and they are better treated as phenomenological parameters. This latter procedure of course destroys any predictive ability of EPT. The power of EPT lies in its ability to retain the *many electron* character of the free ion wave functions in the weak field formulation. On the other hand, *one electron* molecular orbital (MO) theory, which provides a more or less realistic description of bonding in transition metal complexes, ignores interelectronic interactions, nor can it account successfully for properties dependent on orbital angular momentum. EPT with its more limited pure d orbital basis can handle such subtleties.

In outline, a weak field EPT calculation for a  $d^n$  configuration proceeds as follows. Matrix elements  $\langle m_l | V_{el} | m_l' \rangle$  of the electrostatic potential  $V_{el}$  between the complex one electron d orbital functions  $|m_l\rangle$  are computed on the basis of a model. Diagonalization of the resulting  $5 \times 5$  matrix yields the eigenfunctions and eigenvalues of the problem in the one electron d orbital basis as in eq 1 where  $C$  is the matrix of column eigen-

$$V_{el}C = CE \quad (1)$$

vectors and  $E$  is the diagonal matrix of the energies. Next, the *many electron* wave functions,  $|L, M_L, S, M_S\rangle$ , for the free ion states to be included in the calculation are expressed as Slater determinantal wave functions involving the d orbital basis. Matrix elements of the type  $\langle L, M_L | V_{el} | L', M_L' \rangle$  are easily evaluated in terms of the  $\langle m_l | V_{el} | m_l' \rangle$  matrix elements. For an adequate description of magnetic properties, matrix elements of the spin-orbit coupling perturbation  $\lambda L \cdot S$  must also be included. Diagonalization of the many electron matrix yields the desired energies and wave functions. The key feature of the above method is that the *many electron* properties depend ultimately upon the *one electron* matrix elements  $\langle m_l | V_{el} | m_l' \rangle$  of  $V_{el}$ .

(2) Among the standard texts on the subject are H. L. Schläfer and G. Gliemann, "Ligand Field Theory," Wiley-Interscience, New York, N. Y., 1969; C. J. Ballhausen, "Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962; J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, Cambridge, U. K., 1961.

(3) See, for instance, R. E. Watson and A. J. Freeman, *Phys. Rev.*, **134**, A1526 (1964); S. Sugano and R. G. Shulman, *ibid.*, **130**, 517 (1963); W. H. Kleiner, *J. Chem. Phys.*, **20**, 1784 (1952); P. O'D. O'Fenhardt, *J. Amer. Chem. Soc.*, **91**, 5699 (1969), and references therein.

(4) (a) C. J. Ballhausen and E. M. Ancmon, *Mat. Fys. Medd. Dansk. Vid. Selsk.*, **31**, 1 (1958); (b) F. E. Ilse and H. Hartmann, *Z. Phys. Chem.*, **197**, 239 (1951).