34% yield;[2] the latter is inaccessible using $Na^+Mn(CO)_5^-$ in THF.[11,12]

(11) M. D. Curtis, *Inorg. Chem.*, 11, 802 (1972).

(12) This work was supported by the National Science Foundation, the Alfred P. Sloan Foundation, and the Materials Science Center of Cornell University. We thank the Climax Molybdenum Co., a Division of American Metal Climax, Inc., for gifts of chemicals.

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Triplet State of Ketones in Solutions. Quenching Rate Studies of Thioxanthenone Triplets by Flash Absorption[1]

Sir:

The quenching of the triplet $\pi\pi^*$ state of aromatic ketones by the ground-state ketones (self-quenching) has been of interest in studies of triplet sensitization of photochemical reactions, especially because of the possible intervention of a triplet exciplex in the quenching process.[2,3] Chapman and Wampfler[2] first reported the interesting observation that triplet thioxanthenone underwent a self-quenching process. A self-quenching rate constant (k_{sq}) of 6×10^{10} M^{-1} sec^{-1} in $(CH_3)_3COH$ was obtained, based on thioxanthenone sensitization studies of 4,4-dimethyl-2-cyclohexenone and assuming that triplet energy transfer was diffusion controlled. Recently, the k_{sq} for thioxanthenone was redetermined by DeBoer and Schlessinger[3] (using *trans*-stilbene as a triplet quencher) and was found to be $(2.3 \pm 0.5) \times 10^9$ M^{-1} sec^{-1} in benzene. The latter authors pointed out that energy transfer from triplet thioxanthenone (E_T = 65 kcal mol^{-1}) to the enone (E_T = 70 kcal mol^{-1}) should be considerably less than diffusion controlled. Based on known triplet energy transfer data,[4] the k_q for processes which are endothermic by 5 kcal mol^{-1} can be predicted to be two or three orders of magnitude less than those of the diffusion controlled or to be $\sim 1 \times 10^7$ M^{-1} sec^{-1} in this case. Taking this lower value for enone quenching of triplet thioxanthenone, and the data of Chapman and Wampfler,[2] a k_{sq} $\sim 2 \times 10^8$ M^{-1} sec^{-1} in $(CH_3)_3COH$ can be calculated. This recalculated value for k_{sq} is ten times lower than the recently reported value in benzene[3] and could imply a large solvent effect, a genuine inconsistency, or some other factor such as differences in purity of the thioxanthenone.

A transient absorption at λ_{max} 625 ± 5 nm was observed when a degassed solution of 5×10^{-4} M thioxanthenone[5] in acetonitrile (620 ± 5 nm in $(CH_3)_3COH$) was flash photolyzed.[6] Monitoring at 600 nm, the transient lifetime was observed to decrease as the concentration of thioxanthenone was increased from 1×10^{-4} to 5×10^{-3} M in acetonitrile. From a plot of k_{obsd} $(= 1/\tau)$ against concentration of thioxanthenone, we obtained τ = 73 μsec from the intercept and $k_{sq} = (2.3 \pm 0.1) \times 10^7$ M^{-1} sec^{-1} from the slope. The lifetime is in good agreement with the lifetime of triplet thioxanthenone of 77 μsec reported earlier by Herkstroeter and Hammond.[4b] To obtain further data on the transient, we measured the k_q in acetonitrile for several quenchers with different triplet energies (Table I). In confirmation with Hammond's assignment of the transient to the triplet excited state of thioxanthenone we observed diffusion-controlled quenching for quenchers with E_T lower than that of thioxanthenone (E_T 65 kcal mol^{-1} [7]) and found a sharp break in rate constants as the triplet energy of the quencher exceeded that of thioxanthenone.

Table I. Rate Constant for Quenching of Triplet Thioxanthenone

Quencher	E_T, kcal mol^{-1}	Solvent	k_q, M^{-1} sec^{-1}
Thioxanthenone[a]	65[f]	Acetonitrile	$(2.3 \pm 0.1) \times 10^7$
		Benzene	$(1.8 \pm 0.1) \times 10^6$
		$(CH_3)_3COH$	$(8.4 \pm 0.5) \times 10^6$
Thioxanthenone[b]		Acetonitrile	$(4.9 \pm 0.1) \times 10^7$
Thioxanthenone		$(CH_3)_3COH$	1.4×10^8 [c]
Thioxanthenone		Benzene	$(2.3 \pm 0.5) \times 10^9$ [d]
4,4-Dimethyl-2-cyclohexenone	70[g]	Acetonitrile	$(2.5 \pm 0.1) \times 10^7$
		$(CH_3)_3COH$	$(8.6 \pm 0.7) \times 10^6$
Dibenzothiophene		Acetonitrile	7.8×10^5
Fluorene	68[h]	Acetonitrile	$(2.2 \pm 0.1) \times 10^8$
Naphthalene	61[h]	Acetonitrile	$(1.3 \pm 0.1) \times 10^{10}$
trans-1,3-Pentadiene	59[i]	Acetonitrile	$(8.2 \pm 0.5) \times 10^9$ [e]
		$(CH_3)_3COH$	$(1.2 \pm 0.1) \times 10^9$ [e]
trans-Stilbene	50[j]	Acetonitrile	$(2.6 \pm 0.1) \times 10^{10}$

[a] Obtained from Baker Chemical Co. and purified according to ref 4. [b] Unpurified sample from Baker Chemical Co. We were unable to observe any transient from an unpurified sample from Aldrich Chemical Co. in the concentration range used with the Baker purified and unpurified samples. [c] Recalculated value using our measured k_q for the enone and the data of ref 2. [d] Reference 3. [e] S. K. Dogra, unpublished results. [f] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 298. [g] Reference 8. [h] Reference 7. [i] R. E. Kellogg and W. T. Simpson, *J. Amer. Chem. Soc.*, 87, 4230 (1965). [j] Reference 4b.

Quenching and self-quenching measurements were determined in $(CH_3)_3COH$, benzene, and acetonitrile (Table I). Included among the quenchers were 4,4-dimethyl-2-cyclohexenone, *trans*-1,3-pentadiene, and dibenzothiophene. Our value of $k_q = 8.6 \times 10^6$ M^{-1} sec^{-1} for quenching by the enone in $(CH_3)_3COH$ agrees with de Mayo's estimate of 70 kcal mol^{-1} for the triplet energy of the enone chromophone.[8] Taking our directly measured value for triplet quenching by 4,4-dimethyl-2-cyclohexenone in $(CH_3)_3COH$, we can recalculate a k_{sq} of 1.4×10^8 M^{-1} sec^{-1} for thioxanthenone from the results reported by Chapman.[2] This is over ten times higher than our measured k_{sq} of 8.4×10^6 M^{-1} sec^{-1} in the same solvent but is lower than the revised value of 2.3×10^9 M^{-1} sec^{-1} (in benzene) recently reported by DeBoer and Schlessinger.[3] Our directly measured value of k_{sq} in benzene

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(1) Issued as National Research Council of Canada Contribution No. 13327.

(2) O. L. Chapman and G. Wampfler, *J. Amer. Chem. Soc.*, 91, 5390 (1969).

(3) C. D. DeBoer and R. H. Schlessinger, *J. Amer. Chem. Soc.*, 94, 655 (1972).

(4) (a) K. Sandros and H. L. J. Backstrom, *Acta Chem. Scand.*, 16, 958 (1962); (b) W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, 88, 4769 (1966); (c) R. W. Yip, W. D. Riddell, and A. G. Szabo, *Can. J. Chem.*, 48, 987 (1970).

(5) Purified by recrystallization from ethanol three times and then sublimed twice, mp 209–210°.

(6) The degassing procedure and apparatus were as previously described: R. W. Yip, W. D. Riddell, and A. G. Szabo, *Can. J. Chem.*, 48, 987 (1970).

(7) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, 86, 4537 (1964).

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

does not agree with the higher value[3] reported in that solvent.

The most obvious explanation for the discrepancies in k_{sq} is to assume differences in purity of thioxanthenone (see Table I) used by the different groups of investigators. However, no information on the purity of the sample used was given in the previous reports so that it is difficult to judge whether this is the correct explanation. We have also considered the possibility of a diffusion-controlled singlet quenching mechanism. In terms of this mechanism, the thioxanthenone sensitized reactions of Chapman[2] and DeBoer[3] in which ϕ_0/ϕ[9] is plotted against (thioxanthenone) would yield a Stern–Volmer slope of $k_q{}^s\tau_s$, where $k_q{}^s$ is the diffusion-controlled singlet quenching rate constant and τ_s the excited singlet lifetime of thioxanthenone. The slopes obtained by these workers were 162 M^{-1} in $(CH_3)_3COH$[2] and ~100 M^{-1} in benzene.[3] Assuming a diffusion-controlled value of $k_q{}^s$ in benzene of 5×10^9 M^{-1} sec^{-1}, a singlet excited lifetime of 20 nsec would be required. Preliminary experiments on the fluorescence lifetime of thioxanthenone indicate that the lifetime is less than 2 nsec, therefore denying the singlet quenching mechanism.

The mechanism of the triplet self-quenching process cannot be elucidated at the present time. However, our low value for k_q by dibenzothiophene would appear to rule out the involvement of the sulfur atom which could presumably act as an electron donor in the formation of a charge-transfer complex.

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[9] ϕ represents the quantum yield of the sensitized reaction in the presence of sensitizer and ϕ_0 the limiting quantum yield as the concentration of the sensitizer approaches zero.

[10] Division of Chemistry.

[11] Division of Biological Sciences.

Additions and Corrections

Preparation and Fragmentation of the 3-Thiabicyclo-[3.1.0]hexane 3,3-Dioxide Ring System. A Synthesis of 1,4-Dienes [*J. Amer. Chem. Soc.*, **92,** 6918 (1970)]. By William L. Mock, Department of Chemistry, University of Illinois, Chicago, Illinois 60680.

In the analysis of the nmr spectrum of the title substance (Table I and the ensuing discussion) the assignments of protons H^A and H^B were reversed. The corrected assignments place the δ 0.65 resonance in the *endo* position and the δ 1.23 resonance in the *exo* position. Similarly, $J_{A,C}$ and $J_{B,C}$ were also reversed. We thank Professor Robert S. Cooke of the University of Oregon for drawing our attention to this error.

Relaxation Amplitudes for Systems of Two Coupled Equilibria [*J. Amer. Chem. Soc.*, **94,** 356 (1972)]. By Darwin Thusius, Laboratoire d'Enzymologie Physicochimique et Moleculaire, Groupe de Recherche du C.N.R.S. Associé à la Faculté des Sciences, 91 Orsay, France.

Under "limiting case" of Table I the second Γ factor should read: $A^0/(1 + B^0K)[1 + (B^0K)^{-1}]$.

Equations 30 and 31 should read

$$\Delta\phi_A = a_3\phi_{A_3} + c_A\phi_C - a_1\phi_{A_1} - a_2\phi_{A_2} \qquad (30)$$

$$\Delta\phi_B = b_3\phi_{B_3} + c_B\phi_C - b_1\phi_{B_1} - b_2\phi_{B_2} \qquad (31)$$

In the text above eq 37, $\alpha_1' = 2.3(\epsilon_D - \epsilon_{ED})l(\delta \ln K_A)$ and $\alpha_2' = 2.3(\epsilon_D - \epsilon_{ED})l(\delta \ln K_B)$, where l = optical path length.

In eq 59 the term $S/2$ should be placed between brackets.

The concentration variables in eq 61 are $\delta A_1/a_1$ and $\delta \bar{B}_1/b_1$.

In and above eq 66: ϕ_B and b_1 should read $\Delta\phi_B$ and b_{11}.

Electron Spectroscopy of Organic Ions. III. Alkyl- and Aryloxocarbenium Ions (Acyl Cations) [*J. Amer. Chem. Soc.*, **94,** 7191 (1972)]. By Gheorghe D. Mateescu, J. Louise Riemenschneider, James J. Svoboda, and George A. Olah,* Case Western Reserve University, Cleveland, Ohio 44106.

It has been mistakenly stated that the difference in C 1s electron binding energies of the two carbon atoms in acetonitrile is 3.0 eV. This value is <0.5 eV, as already shown by M. Barber and D. T. Clark [*Chem. Commun.*, 22 (1970)]. The 3.0 eV binding energy difference was meant to compare the difference of C 1s E_b's of CO^+ in CH_3CO^+ with CH_3CN.

Thermodynamics and Kinetics of Complex Formation between Cobalt(II), Nickel(II), and Copper(II) with Glycyl-L-leucine and L-Leucylglycine [*J. Amer. Chem. Soc.*, **94,** 8031 (1972)]. By Robert F. Pasternack,* Linda Gipp, and Helmut Sigel, Department of Chemistry, Ithaca College, Ithaca, New York 14850, and Institute of Inorganic Chemistry, University of Basel, CH-4000 Basel, Switzerland.

Equilibria 6 and 7 on page 8032 should read

$$Cu^{2+} + H_2L^+ \rightleftharpoons CuL^+ + 2H^+$$
$$K^{2H}{}_{(Cu+H_2L)} = [CuL][H]^2/[Cu][H_2L] \qquad (6)$$

$$Cu^{2+} + H_2L^+ \rightleftharpoons Cu(L\text{-}1H) + 3H^+$$
$$K^{3H}{}_{(Cu+H_2L)} = [Cu(L\text{-}1H)][H]^3/[Cu][H_2L] \qquad (7)$$

On page 8032, column 2 (including eq 8 and 9), and on page 8033, column 1, the expressions $K^{H}{}_{(Cu+HL)}$ and $K^{2H}{}_{(Cu+HL)}$ should be replaced by $K^{2H}{}_{(Cu+H_2L)}$ and $K^{3H}{}_{(Cu+H_2L)}$, respectively. All the numbers are correctly given.