

PHOTOCHEMISTRY OF DISULFIDES. II. RATES OF REACTION OF  
( $n, \pi^*$ ) TRIPLET KETONES WITH BENZYL DISULFIDE.

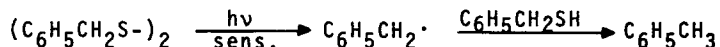
H. Gruen, H. N. Schott, G. W. Byers, H. G. Giles, and J. A. Kampmeier\*

Department of Chemistry, University of Rochester, Rochester, New York 14627

(Received in USA 10 May 1972; received in UK for publication 14 August 1972)

The previous paper<sup>1</sup> describes the quantitative evaluation of the role of C-S cleavage in the  $n, \pi^*$  ketone photosensitized decomposition of several disulfides. The present paper makes use of C-S cleavage as a probe for the details of the interaction of sensitizers with benzyl disulfide. The results are not in accord with a simple triplet-triplet energy transfer mechanism and seem best rationalized by a charge-transfer interaction between sensitizer and disulfide.

The photosensitized C-S cleavage of benzyl disulfide in benzene containing 0.1 M benzyl mercaptan as a radical scavenger was studied in detail. The quantum



yield for toluene formation,  $\phi_{RH}$ , was monitored as a function of disulfide concentration for three different ( $n, \pi^*$ ) triplet ketone sensitizers. The steady-state analysis of the most economical kinetic scheme for a competition between decay and reaction of ketone triplet with disulfide yields  $\phi_{RH} = \frac{1}{\phi_{ST}} \left(1 + \frac{k_d}{k_t [RSSR]}\right)^{-1} F$  where  $k_d$  is the rate constant for decay of ketone triplet in the presence of 0.1 M mercaptan,  $k_t$  is the rate constant for reaction of ketone triplet with disulfide and F is the fraction of excited disulfides which yield toluene.  $\phi_{ST}$  is the quantum yield for formation of ketone triplet from the singlet and is unity for the ketones studied.<sup>2,3</sup> Plots of  $1/\phi_{RH}$  vs.  $1/[RSSR]$  are linear; the intercepts ( $1/F$ ) agree with the limiting quantum yields reported in the previous paper.<sup>1</sup>

The rate constant for reaction of sensitizer with disulfide,  $k_t$ , is obtained

by studying  $\phi_{RH}$  in the presence of a diffusion controlled ( $k_q$ ) ketone triplet quencher (trans-stilbene).<sup>4</sup> The simplest kinetic scheme and steady state assumption for this competition between disulfide and stilbene for triplet<sup>5</sup> gives  $\frac{1}{\phi_{RH}} = \frac{1}{\phi_{ST}} \cdot \frac{1}{F} \left( 1 + \frac{k_d + k_q[\text{stilbene}]}{k_t[\text{RSSR}]} \right)$ . Plots of  $1/\phi_{RH}$  vs. [stilbene] are linear.<sup>6</sup> Values of  $k_t$  are calculated from the known values of  $1/F$ , [RSSR], the least square slopes, and the published values of  $k_q$  in benzene;<sup>7</sup> the results are presented below. Using *cis*-piperylene as the quencher gives comparable results. In addition, the same rate constants ( $\pm 5\%$ ) are obtained from plots of  $1/\phi_{RH}$  vs.  $1/[\text{RSSR}]$  with [stilbene] constant at a concentration (0.1 M) such that  $k_q[\text{stilbene}] \gg k_d$ .

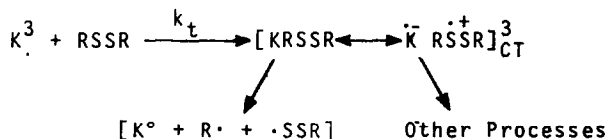
Rates of Reaction of Benzyl Disulfide With ( $n, \pi^*$ ) Triplet Ketones<sup>a</sup>

Sensitizer	$k_t, M^{-1} \text{ sec}^{-1}$	$E_3$ (kcal/mole)	$-E_{1/2}$ (V) <sup>b</sup>
PhCOCH <sub>3</sub>	$3.4 \pm .30 \times 10^8$ (4 DF)	74 <sup>c</sup>	1.49 <sup>d</sup>
Ph <sub>2</sub> CO	$1.5 \pm .05 \times 10^8$ (2 DF)	68.5 <sup>c</sup>	1.22 <sup>d</sup>
2-Methyl-anthraquinone (2-MAQ)	$18 \pm .08 \times 10^8$ (2 DF)	63 <sup>e</sup>	0.33 <sup>d, f</sup>

(a) In purified, deoxygenated benzene  $\sim 0.1$  M in benzyl mercaptan at room temperature; [RSSR] = 0.1 - 0.2 M. Precision stated as standard deviation of the mean; D. F. = degrees of freedom. (b) Reduction potential in dimethylformamide-tetramethylammonium iodide vs. the mercury pool. (c) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", John Wiley and Sons, Inc., New York, 1966, p. 298. (d) P. H. Given, M. E. Peover and J. Schoen, *J. Chem. Soc.*, 2674 (1958). (e) W. C. Nealy and H. H. Dearman, *J. Chem. Phys.*, 44, 1302 (1966). (f) V. E. Ditsent, *Zhur. Obsch. Khim.*, 29, 1370 (1959).

The key point is that the observed rate constants,  $k_t$ , are not in accord with a "classical" triplet-triplet energy transfer mechanism of the type observed with biacetyl and trans-stilbene as acceptors.<sup>8</sup> According to this mechanism,  $k_t \approx k_{\text{diffusion}}$  when the energy transfer is exothermic by 3-4 kcal/mole. When the transfer is appreciably endothermic,  $k_t < k_{\text{diffusion}}$  and the observed rate constants fall off exponentially with decreasing excitation energy of the sensitizer.<sup>8</sup> The rate constants reported in the Table are less than the diffusion controlled limit, but do not show the expected dependence on the triplet energy

of the ketones. Most dramatically, 2-MAQ has the lowest triplet energy, but the highest rate constant for reaction with disulfide. The observed relationship of the rate constants suggests a mechanism in which both the excitation energies and the reduction potentials (see Table) of the ketones are pertinent to the rate determining step. Thus, the variation in excitation energy from acetophenone to benzophenone is apparently balanced by a concomitant change in the reduction potentials of the ketones; the low triplet energy of 2-MAQ is more than compensated by the ease of reduction of 2-MAQ. A charge-transfer interaction<sup>9</sup> between ( $n, \pi^*$ ) triplet ketone and disulfide seems, therefore, to be involved in the energy transfer mechanism.<sup>10</sup> A possible scheme is shown below. This scheme also accommodates the observation that the quantum yield for C-S cleavage of benzyl disulfide depends on the sensitizer.<sup>1</sup> Charge-transfer mechanisms may



also apply to the quenching of tryptophanyl and tyrosyl fluorescence by disulfides and to the photosensitized decompositions of cystine and cystyl containing peptides.<sup>11</sup>

**Acknowledgement.** This work was supported by a Public Health Service Grant, CA-06535, from the National Cancer Institute. We thank Professors J.C. Dalton and L.E. Friedrich for helpful discussions.

#### References

1. G.W. Byers, H. Gruen, H.G. Giles, H.N. Schott and J.A. Kampmeier, J. Amer. Chem. Soc., **94**, 1016 (1972).
2.  $\phi_{\text{ST}}$  for benzophenone and acetophenone, "Energy Transfer and Organic Photochemistry", Techniques of Organic Chemistry, Vol. XIV, A.A. Lamola and N.J. Turro, Eds., Interscience Publishers, John Wiley and Sons, Inc., New York, 1969, P. 500.
3.  $\phi_{\text{ST}}$  for 2-MAQ (2-methylanthraquinone) determined in this work by studying the quantum yield for the 2-MAQ sensitized isomerization of cis-piperylene (0.2 M), A.A. Lamola and G.S. Hammond, J. Chem. Phys., **43**, 2127 (1965). A recently reported  $\phi_{\text{ST}}$  for anthraquinone is  $0.97 \pm 0.04$ , G. Cauzzo, M. Casagrande and G. Baliozzo, Mol. Photochem., **3**, 59 (1971). In addition, there is no detectable fluorescence from 2-MAQ in benzene ( $\phi_f < 10^{-5}$ ) at room temperature.
4. W.G. Herkstroeter and G.S. Hammond, J. Amer. Chem. Soc., **88**, 4769 (1966)

5. Ketone singlets are not involved in the reactions of disulfides described in this paper. In brief, the linear kinetic plots indicate that only one excited state is being captured by the disulfide. The rate of intersystem crossing for these aryl ketones is  $\geq 10^{10} \text{ sec}^{-1}$ ; benzophenone and acetophenone, ref. 2, p. 198;  $k_{ST}$  for 2-MAQ estimated as  $> 10^{10} \text{ sec}^{-1}$  from the absorption spectrum and the observed quantum yield for fluorescence, J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", John Wiley and Sons, New York, 1967, p. 280. A comparable estimate is obtained for anthraquinone, S. A. Carlson and D. M. Hercules, J. Amer. Chem. Soc., **93**, 5611 (1971). Thus, even diffusion controlled ( $\sim 5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ ) bimolecular quenching of ketone singlets cannot compete effectively with intersystem crossing throughout the range of disulfide concentrations employed (0.4 - 0.01 M).
6. Controls show that neither stilbene singlet nor stilbene triplet sensitizes the decomposition of the disulfide. The concentrations of stilbene and disulfide were comparable ( $\sim 0.1 \text{ M}$ ) in the competitive experiments using 2-MAQ. *trans*-Stilbene, therefore, must be quenching ketone triplet and cannot also quench the excited disulfide at a rate competitive with product formation since this would lead to a dependence on  $[\text{stilbene}]^2$ .
7.  $k_q$  Taken as  $5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ ; W. D. Clark, A. D. Litt and C. Steel, ibid., **91**, 5413 (1969); G. Porter and M. R. Topp, Proc. Royal Soc., (London), **A**, **315**, 163 (1970).
8. Ref. 2, p. 44 f. Triplet energies of disulfides are not known. A maximum value for the triplet energy of benzyl disulfide is presumably that of the toluene triplet (83 kcal/mole), D. F. Evans, J. Chem. Soc., 2753 (1959).
9. D. Rehm and A. Weller, Israel J. of Chem., **8**, 259 (1970) and previous papers.
10. Charge-transfer mechanisms have been recently proposed for the reactions of excited ketones with sulfides, J. Guttenplan and S. G. Cohen, Chem. Commun., 247 (1969); R. S. Davidson and P. R. Steiner, ibid., 1115 (1971), and mercaptans, R. G. Zepp and P. J. Wagner, ibid., 167 (1972).
11. R. F. Steiner and E. P. Kirby, J. Phys. Chem., **73**, 4130 (1969); S. Arian, M. Benjamini, J. Feitelson and G. Stein, Photochem. Photobiol., 481 (1970); K. Dose, ibid., 437 (1967); L. I. Grossweiner and Y. Usui, ibid., 53 (1970); R. Cowgill, Biochim. Biophys. Acta, **207**, 556 (1970); note that, in principle, disulfides might function as either donors or acceptors as required by the nature of the sensitizer.