Aliphatic Sulphides: Physical Quenchers and Photoreducing Agents

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WE have observed that aliphatic sulphides are physical quenchers for excited benzophenone whilst simultaneously acting as weak photoreducing agents.

Di-n-butyl sulphide was purified by g.l.c. Methyl phenyl sulphide and diphenyl sulphide contained less than 1% impurity (g.l.c.) Solutions of benzophenone and isoborneol, with and without added sulphide, were degassed and irradiated simultaneously with a G.E. medium-high pressure H-85w-A3 lamp under argon in Pyrex tubes. Quantum yields were determined by ferrioxalate actionmetry[1] at 334 nm. on a Bausch and Lomb 38–86–01 grating monochromator, Osram high-pressure SP-200w lamp. Reduction of benzophenone was followed by decrease in absorbance at 343 nm. Formation of camphor and consumption of sulphides were followed by g.l.c. Disappearance of benzophenone and formation of camphor, in a 2 : 1 molar ratio, showed zero-order kinetics to at least 50% reaction.

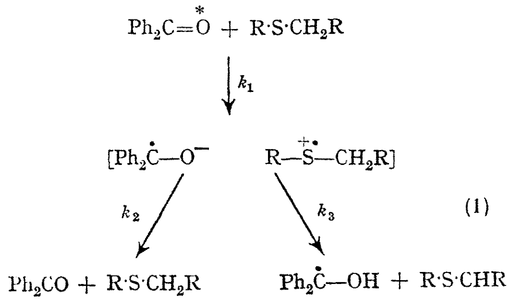
The quantum yield for photoreduction of 0·064 M-benzophenone by 0·17 M-isoborneol in benzene at 334 nm. was 1·38. Rates of photoreduction were determined at 0·05 to 2·0 M-isoborneol and converted to relative quantum yields. A plot of $1/\phi$ *vs.* $1/c$ leads to a limiting quantum yield of 1·84 and k_d/k_r = 0·058 M, the ratio of rate constants for deactivation of triplet to that for abstraction of hydrogen. The quantum yield for photoreduction of 0·062 M-benzophenone by 0·01—0·10 M-di-n-butyl sulphide was 0·05.

Rates, and relative quantum yields, for photoreduction of 0·06 M-benzophenone by 0·2 M-isoborneol in benzene were determined, alone and in the presence of varying concentrations (10^{-3} to 10^{-2} M) of (*a*) a known diffusion controlled quencher, naphthalene,[2] (*b*) di-n-butyl sulphide, and (*c*) methyl phenyl sulphide. Linear Stern–Volmer plots were obtained. With naphthalene, the ratio of rate constant for quenching to that for abstraction, k_q/k_r, is 570, and leads to $k_r = 1{\cdot}0 \times 10^7$ M^{-1} sec.$^{-1}$, based[3] on $k_q = 6{\cdot}0 \times 10^9$ M^{-1} sec.$^{-1}$. With di-n-butyl sulphide, k_q/k_r = 66, and $k_q = 6{\cdot}6 \times 10^8$ M^{-1} sec.$^{-1}$, *ca.* 0·1 that of naphthalene. With methyl phenyl sulphide k_q/k_r = 7·5 and $k_q = 7{\cdot}5 \times 10^7$ M^{-1} sec.$^{-1}$.

The quantum yield for photoreduction of 0·067 M-benzophenone by 0·21 M-isoborneol in benzene was decreased from 1·58 to 0·46 by the presence of 0·0084 M-di-n-butyl sulphide, which was slowly consumed. In the presence of the sulphide, 0·055 M-benzophenone was reduced after irradiation for 90 min., a period sufficient to lead to the photoreduction of 0·189 M-benzophenone in the absence of sulphide. Of the ketone protected, a fraction, *ca.* 1/1·84, results from quenching of the excited ketone by the sulphide, the remainder from absence of the subsequent dark reaction of the ground-state ketone with the alcohol-derived radical.[4] In this period, 0·072 M excited ketone was quenched and 0·0031 M sulphide was consumed, and each molecule of sulphide prevented reaction of *ca.* 23 excited ketone species before it underwent reaction.

Analysis of a solution of 0·06 M-benzophenone and 0·2 M-isoborneol containing initially 0·0070 M methyl phenyl sulphide indicated consumption of 0·0020M-sulphide after irradiation for 40 min. The sulphide had reduced the rate of photoreduction from 0·091 to 0·067 M hr.$^{-1}$, indicating that four excited ketone species were quenched for each molecule of the sulphide consumed. The smaller value of this ratio than that for the dialkyl sulphide appears to result largely from the lower vlaue of k_q, the lower quenching effectiveness of the aryl alkyl sulphide. Diphenyl sulphide, showed very little, if any, quenching,[5] 0·0082M of this sulphide reducing the rate of photoreduction of 0·07M-benzophenone by 0·10 M-isoborneol to 0·94 times that in the absence of the sulphide.

We suggest a two-step mechanism for the effects of sulphides, similar to that proposed for the efficient photoreduction by amines:[6] (i) very efficient interaction of the excited ketone with the non-bonding electrons of sulphur, leading to a complex of the two species, and (ii) reaction of the complex in two ways, either completing the abstraction of hydrogen by ketone from thioether, or forming electronically non-excited ketone and thioether, completing a quenching process:


(1)

With the aliphatic sulphides, $k_2 \gg k_3$ and efficient quenching and minor consumption of sulphide, apparently by hydrogen abstraction, result. In the amine system, rates of the two reactions of the complex are comparable and efficient photoreduction, ϕ *ca.* 1, results.

That the phenyl sulphides are less effective quenchers than aliphatic sulphides indicates that they do not behave like phenylamines, in which nitrogen leads to increased electron density in the ring, more favourable interaction between excited species and the conjugated system, and to efficient quenching.[7] Quenching by a sulphide arises from interaction at the non-bonding electrons of sulphur; electron withdrawal by the phenyl group decreases effectiveness.

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[1] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, *A*, **618**, 235.

[2] A. Beckett and G. Porter, *Trans. Faraday Soc.*, 1963, **59**, 2038.

[3] P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, 1966, **88**, 1245.

[4] J. N. Pitts, jun., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *J. Amer. Chem. Soc.*, 1959, **81**, 6334.

[5] S. G. Cohen, S. Orman, and D. A. Laufer, *J. Amer. Chem. Soc.*, 1962, **84**, 3905.

[6] S. G. Cohen and J. I. Cohen, *J. Amer. Chem. Soc.*, 1967, **89**, 164; *J. Phys. Chem.*, 1968, **72**, 3782; S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, 1968, **90**, 165; S. G. Cohen and J. B. Guttenplan, *Tetrahedron Letters*, 1968, 5353.

[7] A. H. Weller and H. Leonhard, *Ber. Bunsengesellschaft Phys. Chem.*, 1963, **67**, 791.