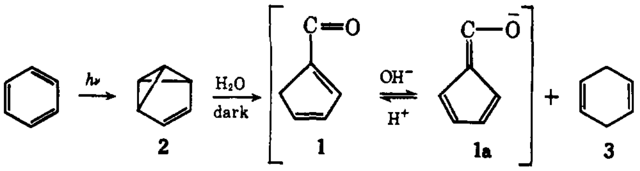
Photooxidation of Aqueous Benzene. II. Role of Benzvalene in the Formation of Cyclopentadienecarboxaldehyde[1,2]

Sir:

The formation of an acidic aldehyde upon irradiation of aerated aqueous benzene at 253.7 nm has been reported previously,[3,4] and the intermediacy of an oxygen adduct with benzvalene[3] or another labile isomer of benzene[4] has been postulated. In the preceding communication[2] we have identified this aldehyde as 1,3-cyclopentadiene-1-carboxaldehyde (**1**) or its anion **1a**. We now wish to report that formation of the photoaldehyde does not require O_2, but only aqueous benzvalene (**2**). In water free from O_2, one molecule of benzvalene is oxidized to the aldehyde while a second is reduced to 1,4-cyclohexadiene (**3**).



In the presence of O_2, two molecules of benzvalene are likewise required to produce one molecule of the aldehyde: 1,4-cyclohexadiene is not formed in this case, but a peroxide is. In both cases, the reactions following the photoisomerization of benzene[5] are purely thermal and appear to be radical chain processes. Aldehyde formation occurs equally well in the presence or absence of O_2 and exhibits the same dependence on acidity from pH 4 to 12.

Our conclusions are derived both from photochemical studies and from dark experiments with benzene solutions of benzvalene.[6] In a particularly enlightening series of experiments, the solutions of preformed benzvalene were distilled *in vacuo* (10^{-4} Torr) into a 1000-fold volume of thoroughly degassed water at pH 10. The carboxaldehyde was formed within minutes in good yield, as determined by the uv absorption[2,3] of the anion in the still-evacuated vessel. Since the aldehydic oxygen must have been acquired from water, a search was made for a complementary reduction product. No H_2 was found above the solution, but benzene recovered by evacuation and analyzed by gc was found to contain 1,4-cyclohexadiene in an amount comparable to that of the aldehyde. The origin of the cyclohexadiene was established by isotopic labeling: cyclohexadiene formed from the benzvalene solution mixed (after preparation) with benzene-d_6 (0.3 mol fraction) contained no deuterium; that formed from benzvalene-d_6 in benzene-d_6 was exclusively $C_6H_2D_6$. These results demonstrate that the cyclohexadiene is formed by addition of two H atoms from water to a molecule of benzvalene. In contrast to the rapid formation of aldehyde in these experiments, it was formed only very slowly in the presence of 10^{-4} *M* 3-mercaptopropionic acid. The fact that benzvalene could be recovered from such solutions 30 min after its introduction indicates that the mercaptan inhibits attack on benzvalene, presumably by interrupting a radical-chain process. The dark reaction in the presence of oxygen was studied only at pH 2 and 6. At pH 2, no aldehyde was found but bicyclo[3.1.0]hex-3-en-2-ol, the known[7] photohydration product of benzvalene, was formed in good yield. At pH 6, the yield of aldehyde was comparable to that in the evacuated pH-10 system; no cyclohexadiene was found in the recovered benzene, but the aqueous solution responded to a test for peroxide.[8] Mercaptopropionic acid (10^{-4} *M*) completely suppressed aldehyde formation; in this case benzvalene could not be recovered, presumably because of its conversion to bicyclohexenol.

In the photochemical experiments, benzene-saturated aqueous solutions of various pH were irradiated at 253.7 nm while sweeping with benzene-saturated O_2 or N_2. Aldehyde formation was observed (spectrophotometrically[2,3]) over the pH range[9] 3–12, but the rate of reaction became progressively slower. At pH 13 the aldehyde was not formed; recovered benzene contained *ca.* 4% benzvalene. At pH 12, the anion absorption appeared only slowly during irradiation and continued to grow for several hours thereafter; the presence of benzvalene in benzene recovered during this period precludes rapid, irreversible formation of a benzvalene-O_2 adduct. At pH 10 the reaction was complete within a few minutes after irradiation, $\Phi = 0.07$. The quantum yield was unchanged, with either O_2 or N_2 sweep, from pH 10 to 6. As the pH was lowered further, the quantum yield decreased, presumably because hydration of benzvalene became competitive with aldehyde formation. Under these competitive conditions, the quantum yield of aldehyde decreased as the intensity of the incident radiation (and hence the steady-state concentration of benzvalene) decreased. At a given pH both Φ and its intensity dependence were the same in N_2-swept and O_2-swept solutions. At pH 5, with intensities of 10^{17} and 10^{16} quanta $\text{min}^{-1}\,\text{cm}^{-2}$, quantum yields were 0.052 and 0.016, respectively; corresponding values at pH 4 were 0.032 and 0.005. The direction of the intensity effect and its magnitude indicate that aldehyde formation is almost one order higher in benzvalene than the hydration reaction, both in the presence and absence of O_2.

Upon continued irradiation at pH 10, with N_2 as the sweep gas, a limiting concentration (5×10^{-4} *M*) of aldehyde was reached. In neutral water with O_2 the limiting concentration was the same, but with N_2 it was only a tenth as great. Continued growth of 1,4-cyclohexadiene in the latter case shows this to be a photostationary state. The higher steady-state concentration in the presence of O_2 is plausibly attributed to inhibition of the photodestruction of aldehyde. Clearly oxygen can also play a role in the formation of the aldehyde; since cyclohexadiene is eliminated and peroxide is formed in its presence, it would appear that

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] Paper I: L. Kaplan, L. A. Wendling, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, **93**, 3819 (1971).

[3] E. Farenhorst, *Tetrahedron Lett.*, 4835 (1968).

[4] M. Luria and G. Stein, *Chem. Commun.*, 1650 (1970).

[5] K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *J. Amer. Chem. Soc.*, **89**, 1031 (1967).

[6] Benzene, recovered after irradiation in hexadecane,[5] contained *ca.* 1% benzvalene and no significant amounts (nmr,[5] gc) of other products.

[7] E. Farenhorst and A. F. Bickel, *Tetrahedron Lett.*, 5911 (1966).

[8] C. J. Hochanadel, *J. Phys. Chem.*, **56**, 587 (1952).

[9] 0.001 *N* H_2SO_4; acetate buffers; H_2O; borate buffers; 0.01 *N* NaOH. The use of phosphate buffers for pH 5–8 gave anomalous results.

O_2 rather than benzvalene is reduced. The correspondence of quantum yields, intensity effects, and rates for aldehyde formation to those in the absence of O_2, however, suggests that two molecules of benzvalene are consumed in both cases. It appears that oxygen intercepts a precursor of the cyclohexadiene without diminishing the effectiveness of the chain-carrying process.

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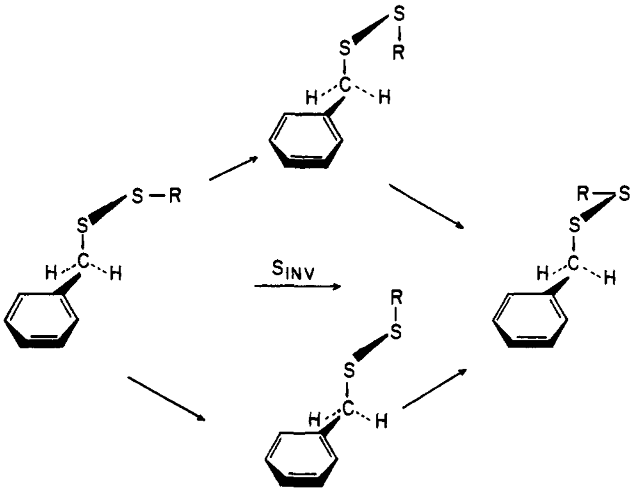
Barriers to Rotation about the Sulfur–Sulfur Bond in Acyclic Disulfides[1]

Sir:

Although the presence of a barrier to rotation about the S–S bond of a disulfide was established over 20 years ago, empirical estimates of its size have varied between 2 and 16 kcal/mol.[2] In addition, barriers to rotation in H_2S_2 have recently been calculated[3] to be 9.3 and 6.0 kcal/mol for the cis and trans transition states, each of which is produced by a 90° rotation about the S–S bond from the ground-state conformation[2a] (see Scheme I). These values agree well with the qualitative conclusions arrived at from a study of the rotational spectra of H_2S_2 and D_2S_2.[4] Of the existing data on this rotational process, the most interesting result is provided by Kessler and Rundel[2e] who found a barrier of 15.7 kcal/mol in bis(4-methyl-2,6-di-*tert*-butylphenyl)disulfide. This figure represents a minimal value for the S–S barrier since rotation about both the C–S and S–S bonds must be restricted for separation of the meta proton signals to be observed by nmr. Less hindered diaryl disulfides show hindrance to rotation about the C–S bonds only.[2e]

Scheme I



We wish to report a study of the low-temperature nmr spectra of a series of eight acyclic disulfides from which the barriers to rotation about the S–S bond can be *directly* and *unambiguously* determined. Assessment of the influence of structure on the height of the barrier in this series provides strong evidence that the cis transition state, previously assumed to be less stable,[2b,4,5] is actually of lower energy than the trans transition state.

The disulfides studied have the general structure $C_6H_5CH_2SSR$. Because of the asymmetry of a disulfide in its ground-state conformation, the methylene protons of the benzyl group are diastereotopic and may possess a nonequivalence of chemical shift when rotation about the S–S bond is slow on the nmr time scale. Scheme I shows a three-dimensional representation of the two enantiomeric forms of an alkyl benzyl disulfide and the possible pathways for their interconversion (racemization). At low temperature the 90- or 100-MHz nmr absorption of the benzylic protons appears as an AB quartet.[6,7] As the temperature is raised the strong central lines broaden and move toward each other. From the temperature at which the two lines coalesce, T_c, the rate constant for interconversion of enantiomers has been calculated using the expression[6] $k = \pi/\sqrt{2}(\Delta\nu_{AB}^2 + 6J_{AB}^2)^{1/2}$. The rates determined by this method for the eight disulfides are presented in Table I in the form of free energies of activation. Problems of solubility and fortuitous shift equivalence required the use of several different solvents and mixed solvents for the series. As can be seen, the barriers measured for R = CCl_3 in four different solvents are constant within experimental error, which indicates the solvent effect on $\Delta G^{\ddagger}$ to be negligible. The effect of concentration on $\Delta G^{\ddagger}$ was also examined for the trichloromethyl derivative and found to be negligible in that the barrier remained at 9.4 kcal/mol for 0.03–0.4 *M* solutions of disulfide in vinyl chloride–toluene (3:1). In order to make reliable comparisons between the $\Delta G^{\ddagger}$'s in Table I, $\Delta G^{\ddagger}$ must be temperature independent, *i.e.*, $\Delta S^{\ddagger}$ must be near zero. We have therefore measured the rotation rates over the range of temperatures amenable to a complete line-shape (CLS) method of analysis[6] for three of the disulfides. The values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in these cases also appear in Table I. The values of $\Delta S^{\ddagger}$ show a variation of 5 eu, which is within the limits of accuracy of the CLS method. This range of $\Delta S^{\ddagger}$ appears sufficiently small to allow a meaningful comparison of the $\Delta G^{\ddagger}$'s in Table I.

Examination of the barriers to rotation throughout the series reveals the presence of two structural effects on barrier height. With the exception of R = CCl_3 and CF_3 all compounds show an increase in $\Delta G^{\ddagger}$ as the size of R increases.[8] The additional enhancement

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[1] This work was presented at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., Mar 28–April 2, 1971, Abstract ORGN-082.

[2] (a) O. Foss, *Advan. Inorg. Chem. Radiochem.*, **2**, 237 (1960); (b) D. W. Scott, H. L. Fink, M. E. Gross, G. B. Guthrie, and H. M. Huffman, *J. Amer. Chem. Soc.*, 72, 2424 (1950); (c) D. W. Scott, H. L. Fink, J. P. McCullough, M. E. Gross, R. E. Pennington, and G. Waddington, *ibid.*, **74**, 2478 (1952); (d) G. Claeson, G. Androes, and M. Calvin, *ibid.*, **83**, 4357 (1961); (e) H. Kessler and W. Rundel, *Chem. Ber.*, 101, 3350 (1968).

[3] A. Veillard and J. Demuynck, *Chem. Phys. Lett.*, **4**, 476 (1970).

[4] G. Winnewisser, M. Winnewisser, and W. Gordy, *J. Chem. Phys.*, **49**, 3465 (1968).

[5] J. A. Barltrop, P. M. Hayes, and M. Calvin, *J. Amer. Chem. Soc.*, **76**, 4348 (1954).

[6] For a review of the measurement of rate processes by nmr, see G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).

[7] The nature of this spectral pattern at low temperature is consistent only with a "freezing out" of the S–S rotational process. Retardation of rotation about the C–S bond would be expected to produce an AB pattern for the gauche rotamer and a singlet for the trans rotamer. The exclusive presence of this gauche rotamer is extremely unlikely.