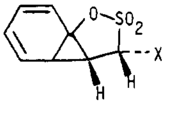
the process. The methylsulfene-8-methyl-8-azaheptafulvene cycloadduct underwent only partial rearrangement at room temperature, with the isolated product being identified as a 3:1 mixture of the (*Z*)-ω-styrenesulfonamide and *trans*-γ-sultam. All other γ-sultams rearranged completely to give excellent to quantitative yields of (*Z*)-ω-styrenesulfonamides.

In contrast to the γ-sultones, the γ-sultams are relatively thermally stable. The γ-sultones, when refluxed in dioxane for 1 h, lost sulfur dioxide and rearranged to give 2-hydroxystilbenes and styrenes.[1] Attempted thermolysis of several of these γ-sultams (both cis and trans isomers) failed, even when more vigorous conditions were used (145 °C in dimethylformamide for 20 h).

Further studies of this cycloaddition reaction and the interesting rearrangement of the resulting γ-sultams are underway and will be reported at a later date.

References and Notes

(1) W. E. Truce and C. M. Lin, *J. Am. Chem. Soc.*, **95**, 4426 (1973). There is a typographical error in formulas IVa and IVb in that publication; the correct respective formulas are



and the corresponding trans structure.
(2) N. L. Bauld and Y. S. Rim, *J. Am. Chem. Soc.*, **89**, 6763 (1967).
(3) The chemical shifts of H_a and H_b in the cis isomers generally appear further downfield than in the trans isomers.
(4) The structural assignments for the sulfonamides were supported unambiguously by their NMR, IR, and mass spectra. Recently the phenylsulfene–tropone cycloadduct has been similarly rearranged to give *trans*-1,2-diphenylethenesulfonic acid (unpublished results from this laboratory).
(5) W. von E. Doering and D. B. Denney, *J. Am. Chem. Soc.*, **77**, 4619 (1955).

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Time Independent Diffusion Controlled Reaction Rate Constants

Sir:

In this communication we report the observation of second-order reactions in the solid state that are diffusion controlled with a constant rate constant at all times; in other words reactions which follow accurately the following equation.

$$1/c - 1/c_0 = kt^{1/2} \qquad (1)$$

Based on the so-called Smoluchowski[1] boundary condition Waite[2] some time ago derived the following equation

$$\frac{1}{c} - \frac{1}{c_0} = \kappa\left[1 + \frac{2r_0}{(\pi D t)^{1/2}}\right]t \qquad (2)$$

for the second-order rate of a diffusion controlled reaction between like species where c is the concentration at time t, c_0 the initial concentration at zero time, κ is a constant equal to $4\pi r_0 D$, D is the sum of the diffusion coefficients of the individual reacting species, and r_0 is the free-radical separation distance within which they react and outside of which the potential of an unreacted radical is independent of position (Smoluchowski boundary condition). The radius r_0 may be considered to be the radius of the reaction cage. As shown before by us[3] eq 2 can be converted to a linear form

$$\left(\frac{1}{c} - \frac{1}{c_0}\right)\frac{1}{t^{1/2}} = \kappa t^{1/2} + \frac{2r_0\kappa}{(\pi D)^{1/2}} \qquad (3)$$

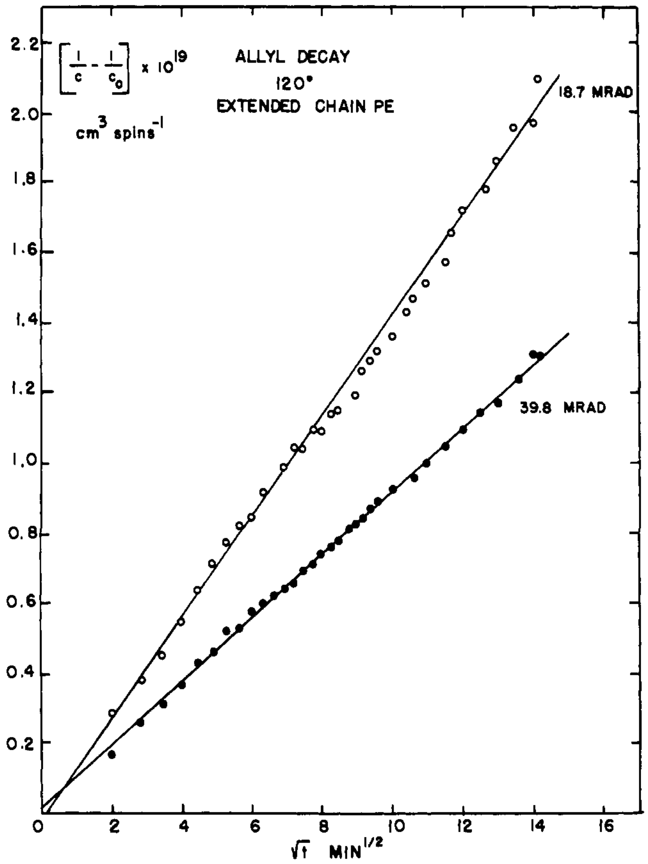

Figure 1. Chain allyl free-radical decay in vacuo at 120 °C in extended chain polyethylene irradiated to doses of 18.7 Mrad (open circles) and of 39.8 Mrad (solid circles) at 77 K. Solid lines represent a least-squares fit of eq 1 to the data.

so that by plotting the left-hand side of eq 3 as a function of $t^{1/2}$ it can be readily seen whether a linear relation is obtained and more importantly whether $(1/c - 1/c_0)/t^{1/2}$ extrapolates to a finite intercept at time t equal to zero in which case the reaction is diffusion controlled. An ordinary second-order reaction would give a zero intercept.

The term $2r_0/(\pi D t)^{1/2}$ inside the brackets of eq 2 will usually be negligible with respect to unity because in most liquid systems D will be of the order 10^{-6} cm^2/s and $r_0 \sim 10^{-7}$ cm, but, if the reaction occurs in times of the order of micro- or nanoseconds, then $2r_0/(\pi D t)^{1/2}$ will no longer be negligible and the reaction becomes diffusion controlled. However, if the diffusion constant is orders of magnitude smaller than 10^{-6} cm^2/s as in reactions occurring in the solid state, there is the possibility that the term $2r_0/(\pi D t)^{1/2}$ of eq 2 may be much greater than unity at all times up to 100 min, for example. For unity being only 10% of $2r_0/(\pi D t)^{1/2}$ at t equal to 100 min or 6×10^3 s, it is necessary that r_0 be as large as 4×10^{-7} cm and D as small as 3.4×10^{-19} cm^2/s. If unity can be neglected in eq 2, then we obtain eq 1 in which

$$k = [2r_0\kappa/(\pi D)^{1/2}] = 8r_0^2(\pi D)^{1/2} \qquad (4)$$

We call such situations reactions with "time independent diffusion controlled reaction rate constants".

As an example of the applicability of eq 1 to a solid-state reaction, we have plotted in Figure 1 data for the decay of the allyl free radical at 120 °C in samples of extended chain (98% crystalline) polyethylene irradiated in vacuo to 18.7 and 39.8 Mrad, respectively, at 77 K and then heated to 120 °C in vacuo to observe the allyl radical recombination reaction. Over the time period illustrated ~20% of the allyl radicals decayed. Equation 1 is accurately followed with intercepts at zero time determined by the least-squares method equal to −0.019 and

0.020×10^{-19} cm^3 spins^{-1}, respectively. These intercepts are probably equal to zero within the experimental uncertainty of the data. The solid lines represent values calculated from the slope and intercept determined by the least-squares method. The slopes were 0.143×10^{-19} and 0.0899×10^{-19} cm^3 spin^{-1} min$^{-1/2}$ for the 18.7- and 39.8-Mrad experiments. Assuming r_0 is 4×10^{-7} in both cases, diffusion coefficients of the individual species ($\frac{1}{2}D$) are calculated to be 3.31×10^{-19} and 1.31×10^{-19} cm^2/s which are of the same order of magnitude of $\frac{1}{2}D$ equal to 1.7×10^{-19} cm^2/s as given above for the required value of $1/2D$ to make the term in eq 2 $2r_0/(\pi Dt)^{1/2}$ at t equal to 100 min ten times greater than unity.

It is interesting to note at the higher dose where there would be expected to be more cross links produced by the irradiation and, therefore, less chain mobility that the allyl radical diffusion coefficient is only about half as great as at the lower dose.

Details of the experimental work[4] and further application of eq 1 to other systems will be given in the full paper. The relationship of this treatment to the kinetics of decay involving two simultaneous second-order reactions observed by us[5] and others will also be clarified.

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(1) M. W. Smoluchowski, *Z. Phys. Chem.*, **92**, 192 (1917).
(2) T. R. Waite, *Phys. Rev.*, **107**, 463 (1957).
(3) W. Y. Wen, D. R. Johnson, and M. Dole, *J. Phys. Chem.*, **78**, 1798 (1974).
(4) Gordon Patel, V. M. Patel, C. S. Hsu, N. Gvozdic, and M. Dole, unpublished work.
(5) M. Dole, C. S. Hsu, V. M. Patel, and G. N. Patel, *J. Phys. Chem.*, **79**, 2473 (1975).

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Photosensitized Oxygenation of Alkenes and Sulfides via a Non-Singlet-Oxygen Mechanism

Sir:

A number of electron-rich compounds react with singlet oxygen in a different way from less electron-rich compounds. Enamines[1] and vinyl ethers[2] produce dioxetanes, phenols[3] give hydroperoxydienones, and sulfides[4] react to give sulfoxides or quench singlet oxygen, depending on the conditions. There are indications that several of these reactions may go by way of electron transfer from the electron-rich molecule (D) to singlet oxygen.[1a] Because of its excitation energy, singlet oxygen should have an $E_{1/2}$ 1 V higher than ground-state oxygen ($E_{1/2} = -0.57$ V).[5] The resulting ion pair could react either to give product (DO_2) or to quench singlet oxygen.

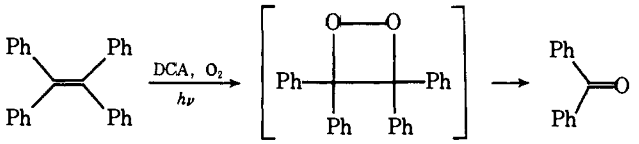
$$\begin{tikzcd}[row sep=tiny]
 & & DO_2 \\
D + {}^1O_2 \arrow[r] & D^{\cdot +} + O_2^{\cdot -} \arrow[ur] \arrow[dr] & \\
 & & D + {}^3O_2
\end{tikzcd}$$

We now report that 9,10-dicyanoanthracene (DCA) sensitizes the photooxygenation of certain substrates in oxygen-saturated CH_3CN solution. The reactions do not seem to involve singlet oxygen, and we propose the following mechanism involving a donor radical cation and DCA radical anion which subsequently reduces O_2 to superoxide. The ultimate products are similar to those of electron-rich substrates with $^1O_2$. Our rationale for this mechanism was the use by Shigemitsu and Arnold[6] of electron-deficient sensitizers to add alcoholic solvents to electron-rich olefins, and by Evans and Farid et al. and Roth and Manion[7] to dimerize alkenes. With $E_{1/2}(R/R^-)$ for DCA of -0.82 V[8] and -0.57 V for oxygen,[5] the electron transfer from $DCA^{-}\cdot$ to O_2 should be exothermic ($\Delta G° = -5$ kcal/mol). Our preliminary evidence is described below.

$$\begin{tikzcd}
DCA \arrow[r, "h\nu"] & {}^1DCA^* \arrow[r, "D"] & {[DCA^{\cdot -} + D^{\cdot +}]} \arrow[d, "{}^3O_2"] & \\
 & & DCA + O_2^{\cdot -} + D^{\cdot +} \arrow[r] & DO_2
\end{tikzcd}$$

DCA Fluorescence Quenching. Diffusion-controlled rate constants were found for the quenching of DCA fluorescence in nitrogen-saturated CH_3CN and C_6H_6 by 1,3-cyclohexadiene, 1,4-dimethyl-1,3-cyclohexadiene, 1,4-dimethoxy-1,4-cyclohexadiene, diphenyl sulfide, tetraphenylethylene, and *trans*-stilbene.[9] Near-diffusion-controlled rate constants have also been obtained by Ware, Holmes, and Arnold[10] for the quenching of DCA fluorescence in the same solvents by substituted 1,1-diphenylethylenes. From the reduction potential and singlet excitation energy (2.89 eV, 66.6 kcal/mol)[11] of DCA, an electron-transfer mechanism[12] should be possible for substrates with oxidation potentials less than ~2.0 V. All of the substrates mentioned above comply with this requirement: e.g., *trans*-stilbene, $E_{1/2}(R^+/R) = +1.51$ V;[13] diphenyl sulfide, +1.45 V; and tetraphenylethylene, +1.33 V.[14]

Tetraphenylethylene (1) and *trans*-Stilbene (2). Irradiation[15,16] of **1** in CH_3CN containing DCA (10^{-4} M) gave 2 equiv of benzophenone (**3**, 57%), triphenylmethanol (14%), benzopinazolone (8%), tetraphenyloxirane (1.5%), an unidentified product (~1%), and small amounts of benzoic acid and benzaldehyde. All products were identified by comparison with authentic samples. The presence of water (0.3%) results in an increased yield of **3** at the expense of the other products. Addition of small amounts of CCl_4 greatly speeds up the reaction without changing the product distribution appreciably. This result is similar to that obtained by Bartlett and Landis.[17] No products were formed (0.5% of **3** would have been detected) if oxygen or DCA was absent, and addition of 7.7×10^{-5} M of the singlet oxygen quencher bis(2,3-dithiolato-2-butene)nickel(II)[18] ($k_q = 2.8 \times 10^{10}$ M^{-1} s^{-1}) did not quench the formation of **3**.[19] Reaction was slower in CH_2Cl_2 and acetone and no products were detected in benzene, diethyl ether, cyclohexane, *p*-dioxane, CCl_4, or ethyl acetate. More importantly, no products were formed in an oxygen-saturated CH_3CN solution of **1** containing the singlet oxygen sensitizers, rose bengal or methylene blue, irradiated at $\lambda > 500$ nm.[20] Thus, it appears that the DCA photooxygenation of **1** does not involve singlet oxygen, but involves an initial reaction of substrate with *singlet* excited DCA to give a polar intermediate, as in the electron-transfer mechanism above. The initial product is presumably 3,3,4,4-tetraphenyl-1,2-dioxetane; under the reaction conditions, this dioxetane would be expected to decompose to **3** by direct photolysis at the wavelength used.



1 **3**

This possibility and the mode of formation of the intriguing by-products are currently under investigation. Some of the products may be formed by a mechanism analogous to that