Chemistry of Singlet Oxygen. XVI. Long Lifetime of Singlet Oxygen in Carbon Disulfide[1]

Sir:

Two recent studies concluded that neither the rate of reaction of singlet oxygen with substances (k_A) nor its decay rate (k_d) vary much in organic solvents.[2,3] Both of these studies were limited by the fact that only the ratio of k_d to another rate, either k_A[2,3] or the calculated diffusion-controlled rate of singlet oxygen quenching by β-carotene (k_Q),[3] could be determined. By the latter technique, k_d in benzene–methanol (4:1) was calculated to be 10^5 sec^{-1},[3,4] a value which has recently been confirmed by direct measurement.[5]

Highly anomalous effects on β (k_d/k_A) in CS_2 have been reported for self-sensitized oxygenations of anthracene derivatives; decreases in β of a factor of 12–60 on going from aromatic solvents to CS_2 were found.[6] We now report that these effects are real and not caused by possible effects of CS_2 on any processes in anthracene, and that the effect of CS_2 is to increase the lifetime of singlet oxygen by an order of magnitude compared to benzene or methanol.

Sensitized photoxygenation of anthracene was carried out in various solvents; consumption of anthracene was monitored by loss of uv absorption at 387 nm. Self-sensitization was prevented by filtering the exciting light through anthracene solutions, when sensitizer was dinaphthalenethiophene (DNT), or through $K_2Cr_2O_7$ solutions, when sensitizer was tetraphenylporphine (TPP). In addition, quenching of 2-methyl-2-pentene (2M2P) photoxygenation by β-carotene and by DABCO (diazabicyclo[2.2.2]octane) in various solvents was measured by previously reported techniques.[4,7] Results are shown in Table I.

Table I. Values of β (k_d/k_A) or β^Q (k_d/k_Q)

Solvent	Anthracene[a] $\beta \times 10^3$, M	2M2P $\beta \times 10^2$, M	β-Carotene $\beta^Q \times 10^7$, M	DABCO[b] $\beta^Q \times 10^4$, M
C_6H_6	47	10[c]	33[f]	9.6
CH_3OH		16[c]	61[g]	65
CS_2	2.6	2.2[d,e]	1.5[d]	1.70
$\beta(C_6H_6)$/ $\beta(CS_2)$	18	4.6	22	5.7
$\beta(CH_3OH)$/ $\beta(CS_2)$		7.3	40	38

[a] DNT sensitized. [b] Zinc TPP sensitized. [c] Reference 2. [d] TPP sensitized. [e] Average of four independent determinations, range ±0.004; value in ref 2 is in error. [f] C_6H_6–CH_3OH, 4:1 (ref 4). [g] Reference 3.

The values of β for anthracene in CS_2 and benzene, 2.6 and 47 $\times 10^{-3}$ M, are the same within experimental error as those reported previously (2.0–3.6 and 45 $\times 10^{-3}$ M)[6] for self-sensitized oxygenation; thus, the complicated behavior, including fluorescence quenching and λ_{max} changes which anthracene (as a sensitizer) undergoes in CS_2,[6] do not cause the increase in reactivity in CS_2; in any case, β is independent of sensitizer.[7]

It is obvious that all the ratios of decay rate to reaction or quenching rate are much smaller in CS_2 than C_6H_6 or CH_3OH. The only reasonable explanation for these changes is that the major cause is a decrease in k_d by an order of magnitude in CS_2, since k_A and k_Q for the four substrates probably involve several different mechanisms and need not all behave in a precisely parallel fashion in going from C_6H_6 or CH_3OH to CS_2. In particular, k_Q for β-carotene, which is already diffusion controlled in benzene,[4,5] cannot increase by the factor of 20 in CS_2 which would be required if k_d were constant.

This conclusion is confirmed by the results of Merkel and Kearns, who find an increase of k_d in CS_2 by factors of 8 and 28 in C_6H_6 and CH_3OH, respectively.[8] These values agree well with the changes in β in Table I, if allowance is made for probable small changes in k_A and k_Q in the various solvents. These results are sufficient to account for the anomalous effects of CS_2 on self-sensitized oxidation of anthracenes[6] and the reported effects of CS_2 on other photooxidation rates.[9]

A further solvent anomaly on the self-sensitized oxidation rates of anthracene is that addition of a few per cent of other solvents to CS_2 causes large changes in β.[6] Table II shows that this effect is also found in the sensitized oxygenation, and is even more bizarre than originally thought; β for anthracene goes through an enormous increase on addition of only 3.5% C_6H_6 to CS_2; a broad maximum occurs at about 25% C_6H_6.

Table II. Effect of Mixtures of CS_2 and C_6H_6 on β and λ_{max} for Anthracene

Mol % C_6H_6	$\beta \times 10^3$, M	Anthracene λ_{max}, nm
0	2.5[a]	387
3.5	27[a]	386
7	52[a]	386
25	94[b]	385
50	77[b]	383
100	46[a]	379

[a] DNT sensitized. [b] TPP sensitized.

Although pronounced changes in λ_{max} of anthracene also occur, they do not seem to parallel the change in β, and are probably not related. In fact, the shift in λ is linear with mole per cent of C_6H_6. Like previous authors,[6] we are unable to account for the effect of small amounts of added solvents to CS_2; the effect of CS_2 on lifetime of singlet oxygen could be related to the

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fact that sulfides form adducts with $^1O_2$,[10] but further work will be required to establish this.

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A Linear Free Energy-Enthalpy-Entropy Relationship for the Ionization of Benzoic Acids

Sir:

It can be shown[1] that a linear relationship between the free energies of two reaction series can be expected only if each reaction series shows one of the following types of behavior: (a) $\Delta H°$ is constant throughout the series, (b) $\Delta S°$ is constant, or (c) $\Delta H°$ is linearly related to $\Delta S°$. Of the many linear free-energy relationships now known, the Hammett equation is undoubtedly the most widely used, yet, as many reviewers have noted (*e.g.*, ref 1-3), its defining reaction series, the ionization of benzoic acids, does not appear to belong to any one of these categories. This, as Shorter[2] has commented, makes the empirical success of the Hammett equation something of a mystery and it also, to some extent, reduces our confidence in the use of enthalpies and entropies as quantitative indexes of substituent effects on chemical reactivity.

Recently Larson and Hepler[4] have drawn attention to large discrepancies existing between sets of measurements of enthalpies of ionization of benzoic acids and also to the antiquity of some of the most frequently quoted measurements.

Table I. Thermodynamic Functions of Ionization of Benzoic Acids in Water at 25°

Acid	$\Delta G°_{25}$, cal mol^{-1}	$\Delta H°_{25}$, cal mol^{-1}	$\Delta S°_{25}$, cal deg^{-1} mol^{-1}	$\Delta C_p°_{25}$, cal deg^{-1} mol^{-1}
Benzoic	5732 (±2)[a]	−67 (±19)	−19.44 (±0.04)	−42 (±3)
m-Methoxybenzoic	5583 (±1)	22 (±12)	−18.65 (±0.04)	−23 (±2)
m-Toluic	5800 (±1)	−91 (±13)	−19.75 (±0.05)	−34 (±2)
m-Chlorobenzoic	5234 (±1)	178 (±17)	−16.95 (±0.06)	−38 (±3)
m-Bromobenzoic	5198 (±1)	197 (±17)	−16.77 (±0.06)	−45 (±3)
m-Nitrobenzoic	4720 (±2)	421 (±25)	−14.41 (±0.08)	−41 (±4)
p-Methoxybenzoic	6130 (±2)	258 (±26)	−19.69 (±0.09)	−45 (±4)
p-Toluic	5962 (±1)	−134 (±9)	−20.44 (±0.03)	−39 (±1)
p-Chlorobenzoic	5437 (±2)	100 (±26)	−17.90 (±0.09)	−44 (±4)
p-Bromobenzoic	5403 (±1)	107 (±28)	−17.76 (±0.09)	−35 (±2)
p-Iodobenzoic	5450 (±1)	78 (±15)	−18.01 (±0.04)	−32 (±2)
p-Nitrobenzoic	4671 (±1)	432 (±36)	−14.21 (±0.12)	−25 (±2)

[a] The number in parentheses is the standard error of the measurement at the 95% confidence level.

The thermodynamic enthalpies of ionization of meta- and para-substituted benzoic acids are extremely difficult to measure accurately. The acids are usually very insoluble in water, especially at temperatures below ambient, and the value of $\Delta H°_{25}$ is usually of the order of 100–400 cal mol^{-1}. These two factors combine to make accurate calorimetric measurements difficult. Furthermore, the very small $\Delta H°_{25}$ value means that the pK_a values show very little variation with temperature, making van't Hoff-type determinations of $\Delta H°_{25}$ also subject to large errors unless unusual precautions are taken.

After a thorough appraisal of the factors most likely to reduce accuracy in these systems we have now redetermined the enthalpies and entropies of ionization in water of benzoic acid and 11 meta- and para-substituted benzoic acids. For ten of these compounds we used an emf-spectrophotometric technique which has been shown to give reliable results for the heats and entropies of proton ionization of phenols[5] and anilinium ions[6] and for which good agreement has been observed between the results obtained and calorimetrically determined data. This method has the advantage that for acids of the benzoic acid charge type no extrapolation to zero ionic strength is required, thus removing one major source of uncertainty in the final results. For the two nitro-substituted acids we used a variation of an indicator spectrophotometric method described by Robinson and Bower.[7] This method required an extrapolation to zero ionic strength but this was carried out on a computer to minimize subjective influences on the final results, and the method was found to be highly reproducible. All of the acids were measured in several solutions of differing ionic strength and, wherever experimentally feasible, in more than one type of buffer solution.

In making these measurements great attention was paid to the accuracy and control of temperature and as wide a range of temperature as was experimentally possible (5–60°) was used. With such small variation in pK_a with temperature, different mathematical methods of determining $\Delta H°/\Delta S°$ from the pK_a–temperature data can give significantly different results.[8] We have used the full-multiple regression procedure of Clarke and Glew.[9]

Table I lists the values of the measured thermodynamic functions and their standard errors calculated

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