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THE PHOTOPEROXIDATION OF UNSATURATED ORGANIC MOLECULES
XXV: MODIFICATION OF THE CAGE DISPLACEMENT MODEL FOR MIXED SOLVENT QUENCHING OF $O_2(^1\Delta_g)$ †

B. STEVENS

Department of Chemistry, University of South Florida, Tampa, FL 33620 (U.S.A.)

M. A. J. RODGERS

Center for Fast Kinetics Research, University of Texas at Austin, Austin, TX 78712 (U.S.A.)

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Summary

The lifetime τ_Δ of $O_2(^1\Delta_g)$ has been measured directly in binary mixtures of methylene chloride with various alkanes and alcohols as cosolvents. The dependence of τ_Δ on solvent composition is not satisfactorily reproduced by the solvent cage displacement model but is better described by equations developed from a modification of this model in which the solvent cage of the small oxygen molecule is treated as a collection of atomic groups (*e.g.* CH_3, CH_2, OH) rather than complete molecules. This provides some kinetic insight into the group additivity parameter for $O_2(^1\Delta_g)$ quenching by pure solvents.

1. Introduction

Time-resolved measurements of the $O_2(^1\Delta_g)$ emission intensity at 1.27 μm, following δ function excitation of a suitable sensitizer, have provided direct access to $O_2(^1\Delta_g)$ relaxation times τ_Δ in solution [1 - 5] which range from about 4 μs (H_2O) [4] to about 20 ms in Freon-113 [5]. One of us has recently proposed [6] a group additivity relationship, based on the number and contribution of different atomic groupings (*e.g.* CH_3, CH_2, CD_3, OH) in the solvent molecule, to account for the solvent dependence of τ_Δ. This originates with the Stern–Volmer relationship

$$\frac{1}{\tau_\Delta} = k_0 + k_\Delta[S] \tag{1}$$

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between τ_Δ, the (negligible) radiative decay constant k_0, the concentration [S] of pure solvent in moles per liter and a second-order quenching rate constant k_Δ expressed as

$$k_\Delta = \sum_j N_j \Delta_j \tag{2}$$

Here N_j is the number of atomic group j in the solvent molecule, with quenching additivity number Δ_j. Δ_{CH_3}, Δ_{CH_2} and Δ_{OH} are obtained from the slopes and intercepts of linear plots of k_Δ against the number of carbon atoms in normal alkane and alcohol solvents; other Δ_j are deduced by difference from these values and τ_Δ for other solvents containing these groups and the group j. Thus for 1,4-dioxane with $\Delta_{CH_2} = 813$ M^{-1} s^{-1} and $N_{CH_2} = 4$, $k_\Delta = 3250$ M^{-1} s^{-1} or, since [S] = 11.7 M, the estimated value of τ_Δ is 26.3 μs, close to the experimental value of $\tau_\Delta = 26.7$ μs and implying that $\Delta_{COC} = 0$.

Hurst and Schuster [7] have independently adopted a similar approach based on the additive contribution of solvent bonds (e.g. C—H, C—D, O—H) to $O_2(^1\Delta_g)$ quenching which is less satisfactory for secondary and tertiary alkanes and alcohols since the additive parameter for CH_3 is less than three times that for the CH group. In either case the kinetic significance of group additivity parameters is not immediately apparent except as a component of the rate constant k_Δ, which in bimolecular rate theory reflects an encounter quenching probability and a rate constant describing the diffusive encounter of luminescent and quenching species.

Since the diffusive approach of these species along reaction-mediated (or quenching-mediated) concentration gradients is an unrealistic quenching prerequisite in pure quenching solvents, a cage displacement model has been developed [5] to describe weak quenching of excited species in binary mixtures of quenching solvents A and B over the whole composition range. Here it is assumed that the excited molecule is produced in a cage of C solvent molecules i of mole fraction X_i and encounter quenching probability α_i, such that its cage survival probability P_s is given by

$$P_s = 1 - CX_A\alpha_A - CX_B\alpha_B \tag{3}$$

If its average residence time in the solvent cage is ν^{-1}, the probability that the potentially luminescent species remains excited after time t is

$$P_E(t) = P_s{}^{\nu t} \exp(-k_0 t)$$

$$= \exp\left(-\frac{t}{\tau}\right) \tag{4}$$

where τ is its observed relaxation time. Equations (3) and (4) rearrange, with $\alpha_i \ll 1$, to

$$\frac{1}{\tau} = k_0 + \nu C(X_A\alpha_A + X_B\alpha_B) \tag{5}$$

and the generally non-linear dependence of $1/\tau$ on X_B has been attributed [5] to a solvent composition dependence of displacement frequency ν described by

$$\frac{1}{\nu} = \frac{X_A}{\nu_A} + \frac{X_B}{\nu_B} \tag{6}$$

with C constant. Since eqn. (5) reduces to

$$\frac{1}{\tau_i} = k_0 + \nu_i C \alpha_i \tag{7}$$

for pure solvent i, and the corresponding displacement frequency ν_i may be expressed [5, 8] in terms of viscosity η_i and molar volume V_i by $\nu_i \eta_i V_i = RT$, eqns. (5) and (6) rearrange to

$$\frac{1}{\tau} = \frac{1}{\tau_A} + \frac{\eta_B V_B X_B}{\eta_B V_B X_B + \eta_A V_A X_A} \left(\frac{1}{\tau_B} - \frac{1}{\tau_A} \right) \tag{8}$$

which satisfactorily describes the dependence of $O_2(^1\Delta_g)$ relaxation time τ_Δ on composition of the CS_2–Freon-113 solvent system [5].

To describe the weak quenching of aromatic hydrocarbon fluorescence by bromobenzene (or o-dichlorobenzene) (B) in non-quenching cosolvents (A), eqn. (8) has been modified [9] to accommodate preferential fluor solvation by A (or B); in this case the mole fractions Y_A and Y_B of each component in the solvent cage are related to mole fractions X_A and X_B in the bulk solvent by [10]

$$\frac{Y_A}{X_A} = \frac{Y_B}{X_B} \exp(\gamma_A)$$

and eqn. (8) is rearranged to the form

$$\frac{1/\tau_B - 1/\tau}{1/\tau - 1/\tau_A} = \frac{\eta_A V_A X_A}{\eta_B V_B X_B} \exp(\gamma_A) \tag{9}$$

which permits evaluation of the index γ_A of preferential solute solvation by solvent A in the presence of B.

In this contribution an investigation is reported of the dependence of τ_Δ on composition of several mixed solvent systems, conducted with a view to (a) assessing the various factors contributing to the non-linear dependence of τ_Δ^{-1} on solvent composition X and (b) examining the kinetic significance of the group quenching additivity parameter Δ_j of eqn. (2).

2. Experimental details

The instrumental procedure for obtaining lifetimes of $O_2(^1\Delta_g)$ by monitoring its luminescence decay at 1.27 μm has been described previously [6]. Mixed solvent systems were prepared by combining measured volumes

of solvent B, solvent A (CH_2Cl_2 or CS_2) and of solutions of the sensitizer in solvent A, to ensure constant sensitizer concentration. The mixed solutions were thoroughly shaken before use. Tetraphenylporphine (Aldrich) was used as the sensitizer throughout at a concentration of 35 μM to provide an optical density of 0.3 at the excitation wavelength (532 nm) with less than 3% sensitizer quenching of $O_2(^1\Delta_g)$ in CH_2Cl_2. Organic solvents of spectroscopic or reagent grade were used as supplied. All solutions were air saturated at the experimental temperature of 22 °C.

3. Results and discussion

The observed dependence of τ_Δ on solvent composition X is displayed in Figs. 1 - 4. Neither eqn. (5) with νC constant nor eqn. (8) affords a satisfactory description of these data as illustrated in Fig. 4 for the CH_2Cl_2–$C_{11}H_{24}$ system. The application of eqn. (9) provides values of the adjustable parameter γ_A ranging from -0.6 for $CH_2Cl_2(A)$–n-C_5H_{12} to 2.3 for $CH_2Cl_2(A)$–n-$C_{16}H_{34}$, which would imply a considerable variation in oxygen
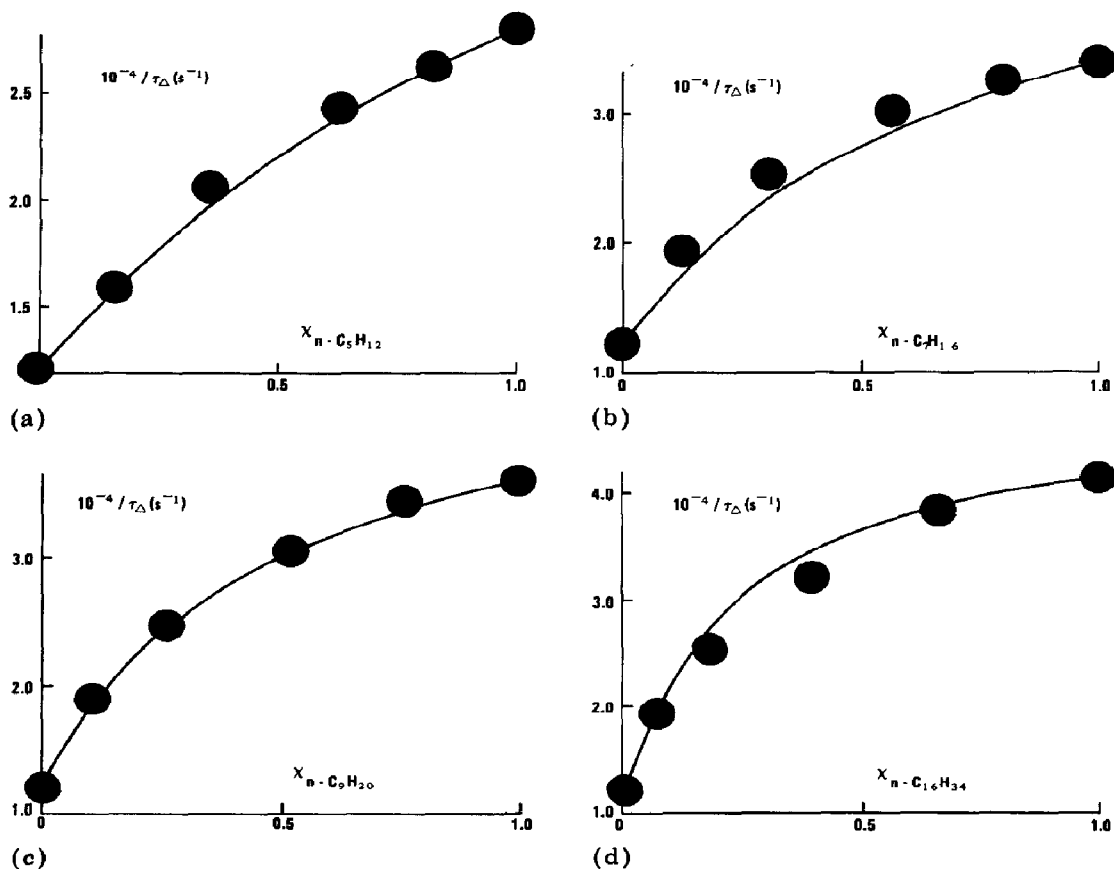
Fig. 1. Variation in $1/\tau_\Delta$ with mole fraction of (a) n-C_5H_{12}, (b) n-C_7H_{16}, (c) n-C_9H_{20} and (d) n-$C_{16}H_{34}$ in CH_2Cl_2 as cosolvent: ——, drawn in accordance with eqn. (12).
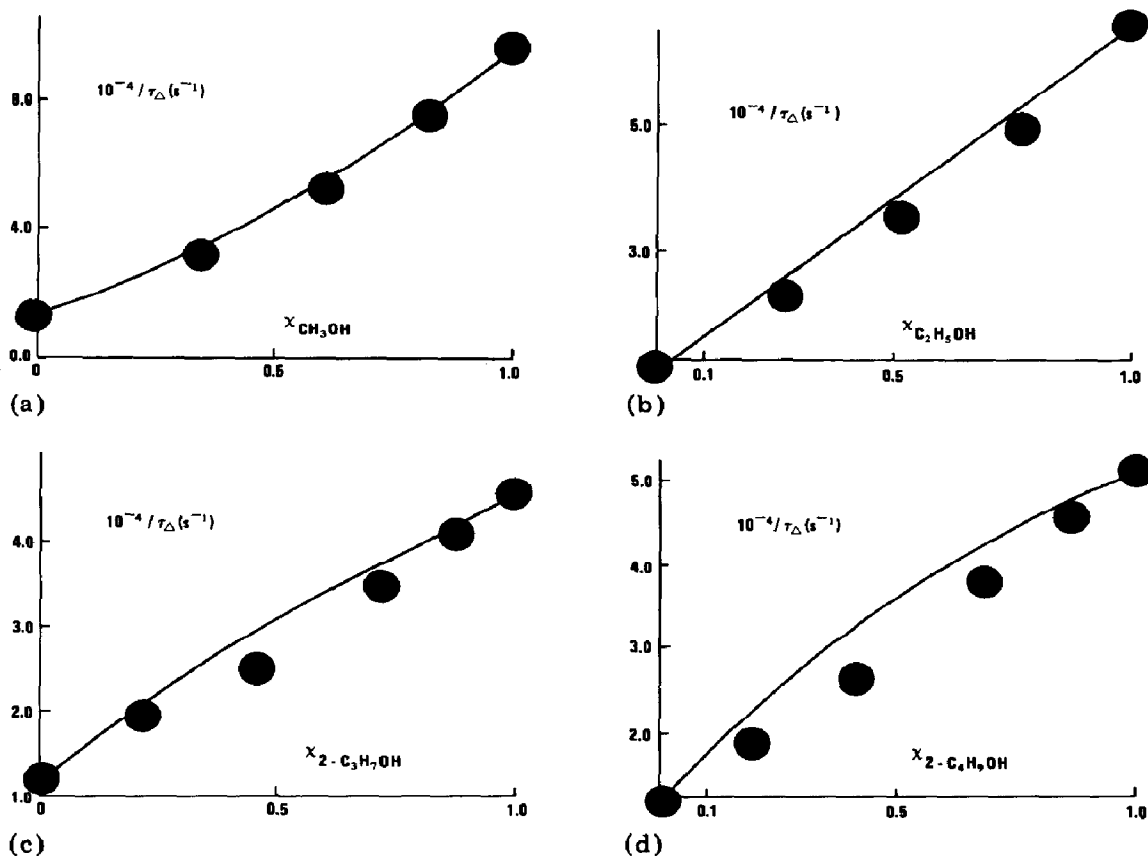
Fig. 2. Variation in $1/\tau_\Delta$ with mole fraction of (a) CH_3OH, (b) C_2H_5OH, (c) $2\text{-}C_3H_7OH$ and (d) $2\text{-}C_4H_9OH$ in CH_2Cl_2 as cosolvent: ———, drawn in accordance with eqn. (12).

solubility in these hydrocarbon solvents. Moreover a description of the solvent cage around the small oxygen molecule in terms of relative numbers of much larger solvent molecules is not realistic. In the light of the applicability of the group additive effect on k_Δ to these solvents, the cage displacement model is modified to accommodate the smaller oxygen solute as follows.

(1) The "solvent cage" around $O_2(^1\Delta_g)$ is assumed to be made up of atomic groups j (e.g. CH_3, CH_2, OH) of which numbers $N_j{}^A$ and $N_j{}^B$ are present in solvent molecules A and B respectively.

(2) The group distribution throughout the solvent is assumed to be random such that the average number C_j of group j in the cage is determined by its mole fraction X_j, i.e.

$$C_j = CX_j = C(N_j{}^A X_A + N_j{}^B X_B)\Big/\sum_j (N_j{}^A X_A + N_j{}^B X_B)$$

(3) The average displacement frequency ν of $O_2(^1\Delta_g)$ from one "cage" to the next is assumed to be independent of solvent (cage) composition.

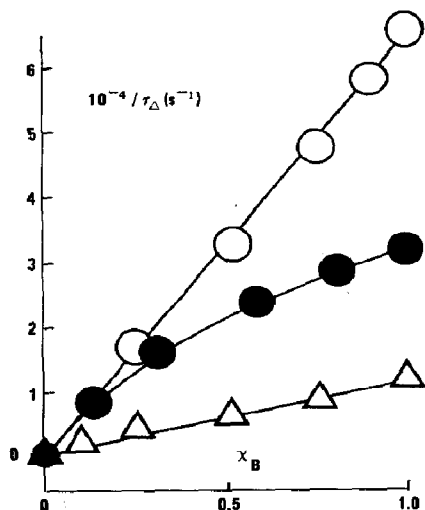If α_j is the encounter quenching efficiency of group j, eqn. (5) becomes

Fig. 3. Variation in $1/\tau_\Delta$ with mole fraction of hexane ($\bullet$), CH_2Cl_2 ($\triangle$) and methanol ($\bigcirc$) with CS_2 as cosolvent: ———, drawn in accordance with eqn. (12).
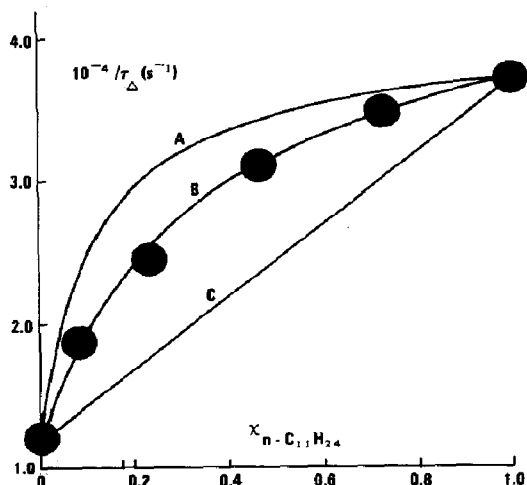
Fig. 4. Variation in $1/\tau_\Delta$ with mole fraction of n-$C_{11}H_{24}$ in CH_2Cl_2 as cosolvent: $\bullet$, experimental points; curves A, B, C, drawn according to eqns. (8), (12) and (5) respectively.

$$\frac{1}{\tau_\Delta} = k_0 + \nu\sum_j C_j\alpha_j$$

$$= k_0 + \nu C\sum_j\alpha_j(N_j^A X_A + N_j^B X_B)\bigg/\sum_j(N_j^A X^A + N_j^B X_B) \tag{10}$$

This reduces to

$$\frac{1}{\tau_i} = k_0 + \nu C\sum_j\alpha_j N_j^i\bigg/\sum_j N_j^i \tag{11}$$

for pure solvent i, and the elimination of $\nu C\Sigma_j\alpha_j N_j^i$ from eqns. (10) and (11) provides

$$\frac{1}{\tau_\Delta} = \frac{1}{\tau_A} + X_B\left\{X_B + \left(\sum_j N_j^A\bigg/\sum_j N_j^B\right)X_A\right\}^{-1}\left(\frac{1}{\tau_B} - \frac{1}{\tau_A}\right) \tag{12}$$

used to draw the curves in Figs. 1 - 3 and Fig. 4, curve B, with $\Sigma_j N_j^i$ equal to the number of atoms other than hydrogen in a molecule of solvent i. As shown in Fig. 4, eqn. (12) is clearly superior to eqns. (5) and (8) for the systems examined but is not very satisfactory for the secondary alcohols; this is probably a consequence of the least justifiable assumption of a random distribution of atomic groupings which are primarily correlated by the structure of solvent molecules from which they originate.

4. Conclusions

For the limited number of systems examined here, it is apparent that the group solvation model provides an improved description of $\tau_\Delta^{-1}(X)$ for the small $O_2(^1\Delta_g)$ molecule. As distinct from the treatment of large aromatic solutes [9] it is unnecessary to invoke preferential group solvation of $O_2(^1\Delta_g)$, and the implicit absence of solvent complexation with $O_2(^1\Delta_g)$ is consistent with the assumption that its displacement frequency ν is independent of solvent cage composition. It is noted, however, that eqn. (8) provides a better description of the Freon-113–CS_2 system [5] with $\eta_A V_A/\eta_B V_B = 3.8$, than does eqn. (12) with

$$\sum_j N^A_j \Big/ \sum_j N^B_j = 2.7$$

A comparison of eqns. (1) and (2) with eqn. (8) provides the identity

$$\sum_j N_j \Delta_j = \frac{1}{\tau_\Delta[S]} = \frac{V}{\tau_\Delta}$$

$$= \nu C V \sum_j \alpha_j N_j \Big/ \sum_j N_j$$

or

$$\Delta_j = \nu C V \alpha_j \Big/ \sum_j N_j = \nu C \bar{v}_j \alpha_j$$

for a pure solvent where

$$\bar{v}_j = V \Big/ \sum_j N_j$$

is an average "molar volume" of the atomic groups. To the extent that $\bar{v}_j$ is constant for first row atoms, the quantity $\Sigma_j N_j^A/\Sigma_j N_j^B$ in eqn. (12) may be replaced by V_A/V_B which accounts for the linear dependence of $1/\tau_\Delta$ on volume fraction of solvent B exhibited by the acetone–benzene system [6].

Acknowledgments

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