THE RELAXATION OF $O_2(^1\Delta_g)$ IN CONDENSED SYSTEMS[†]

MICHAEL A. J. RODGERS

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

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Prior to the use of pulsed lasers for measuring absolute rate constants for the solvent-induced deactivation of the lowest singlet state of molecular oxygen, it became evident that there were significant solvent effects on the rates of photo-oxidation reactions [1 - 3]. Later experiments in which pulsed lasers were employed [4 - 6] to generate $O_2(^1\Delta_g)$ via photosensitizer triplet states indicated that these solvent effects were attributable to marked influences of environment on the lifetime τ_Δ of $O_2(^1\Delta_g)$ in the solvent medium. Using oxidizable solutes as monitors for singlet oxygen, these studies proved difficult, tedious and, in some instances, inaccurate. Very recently it has become possible to observe the 1.27 μm luminescence arising from the forbidden $^1\Delta_g \leftarrow {}^3\Sigma_g$ transition in both continuous [7] and time-resolved [8 - 12] photoexcitation experiments. This latter allows a rapid, convenient, precise and direct method for τ_Δ determination. These experimental improvements have now made it possible to examine systematically the influences on τ_Δ of making small structural changes on solvent molecules.

In this laboratory the variation in τ_Δ with the number N_{CH_2} of methylene groups in *n*-alkanes and *n*-alcohols has been studied [13]. Although the trends of τ_Δ with N_{CH_2} showed no useful pattern, using the relationship

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

where [S] is the molarity of the solvent, led to a linear relationship between k_Δ and N_{CH_2}. For the *n*-alkanes and *n*-alcohols, two linear plots of the same slope but with different intercepts were obtained. This led to the concept that deactivation of $O_2(^1\Delta_g)$ by solvent molecules was governed by the molecular composition of the solvent in an additive manner, and the values of the additivity parameter Δ_x (M^{-1} s^{-1}) for several atomic groupings were extracted (Table 1). All Δ_x values except those for CH_3, CH_2 and OH are from single-point determinations.

Following directly from this additivity concept, it therefore becomes possible to calculate τ_Δ for other solvents and to make comparisons with the

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128

TABLE 1

Additivity parameters for atomic groupings

Residue	Δ_x $(M^{-1} s^{-1})$
CH_3	550
CD_3	15
CH_2	813
CH^a	90
OH	2290
OD	165
C=O	100
C≡N	65

[a] For an aliphatic CH.

experimental determinations. This has been done and in most cases (non-aromatic) the agreement is extremely close [13].

In contemporaneous studies, Hurst and Schuster [14] and Krasnovsky et al. [15] evaluated τ_Δ values for a series of halogenated benzenes (and benzenes-d_6) and for a homologous series of fatty acids respectively. These experiments followed the same pattern as detailed above for the n-alkanes and n-alcohols but the Δ_x values extracted differed from those in Table 1. In particular, these groups were unable to distinguish additivity differences between CH_3, CH_2 and CH and are therefore less successful in predicting τ_Δ values, especially in highly branched solvents.

As an alternative method to using eqn. (1) for k_Δ and thence Δ_x evaluation, a procedure using dilute binary liquid mixtures was used. In an ideal mixture of liquids A and B

$$\frac{1}{\tau_\Delta} = k_A X_A + k_B X_B \tag{2}$$

where k_i is the decay rate of $O_2(^1\Delta_g)$ in a liquid of mole fraction X_i equal to unity. At low concentrations of B in a solvent such as CH_2Cl_2 or CS_2 wherein singlet oxygen has a relatively long lifetime, eqn. (2) becomes

$$\frac{1}{\tau_\Delta} = k' + k_B[B] \tag{3}$$

and k_B in eqn. (3) should be identical with k_Δ for liquid B. Measurements of τ_Δ in dilute $(X < 0.1)$ solutions of several n-alkanes in CS_2 showed linear behavior with alkane concentration. However, k_B values were not identical with the k_Δ parameters for these liquids and, although a plot of k_B versus N_{CH_2} was linear, it did not yield Δ_{CH_2} and Δ_{CH_2} values that were useful in computing τ_Δ parameters for pure liquids. It appears therefore that liquid mixtures, even dilute ones, are quantitatively different from pure liquids in their ability to quench $O_2(^1\Delta_g)$. An understanding of this phenomenon will enhance our comprehension of the nature of liquids and liquid mixtures.

Acknowledgments

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