J. Phys. Chem. A **2006,** *110,* 7749

COMMENTS

Comment on “Quenching Mechanism of Rose Bengal Triplet State Involved in Photosensitization of Oxygen in Ethylene Glycol”

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Received: February 8, 2006; In Final Form: April 21, 2006

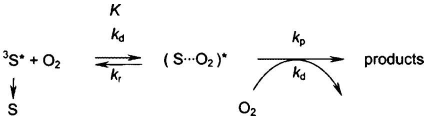
Shimizu et al. recently published results on the quenching of triplet excited rose bengal ($^3S^*$, RB) by O_2 in ethylene glycol.[1] The investigation comprises O_2 concentration-dependent time-resolved triplet−triplet (TT) absorption measurements at 20 °C and between 130 and 140 °C. They determined overall rate constants k_{obs} of triplet decay which, as commonly found, linearly depend on $[O_2]$ at 20 °C. However, at high temperatures, a stronger than linear increase of k_{obs} with $[O_2]$ was observed at low $[O_2]$ passing to a linear dependence only for larger $[O_2]$ values. These results led to the surprising conclusion that the quenching occurs principally by the interaction of a second O_2 molecule with the primarily formed exciplex $(^3S{\cdot}O_2)^*$ and only to a much lesser degree by the direct dissociation of $(^3S{\cdot}O_2)^*$. The proposed kinetics are illustrated by Scheme 1.

Here, k_0 is the rate constant of first-order decay of $^3S^*$ in the absence of O_2; k_d and k_r are the rate constants of $(^3S{\cdot}O_2)^*$ formation and $(^3S{\cdot}O_2)^*$ back-reaction to $^3S^*$ and O_2; $K = k_d/k_r$ is the corresponding equilibrium constant; and k_p is the rate constant of $(^3S{\cdot}O_2)^*$ dissociation to ground-state sensitizer S and O_2. Whereas these four steps have hitherto been sufficient to describe the overall triplet-state quenching by O_2, Shimizu et al. introduced as an additional quenching process the bimolecular reaction of the exciplex $(^3S{\cdot}O_2)^*$ with ground-state O_2 for which the same rate constant k_d was assumed as for the $(^3S{\cdot}O_2)^*$ formation reaction. On the basis of Scheme 1, they derived eq 1 for k_{obs}. Fits of eq 1 to the nonlinear oxygen concentration dependences of k_{obs} measured at high temperatures yielded experimental values for the rate constants and the equilibrium constant K. Evaluation of the temperature dependence of K resulted in the extraordinarily large negative reaction enthalpy $\Delta H = -150$ kJ mol^{-1} for $(^3S{\cdot}O_2)^*$ exciplex formation. Extrapolation of the high-temperature results yielded the large value of $K = 1.11 \times 10^{12}$ M^{-1} for 20 °C. It was pointed out that due to the large equilibrium constant even at the minimum oxygen concentration of 2.9×10^{-5} M almost all excited species are in the exciplex state $(^3S{\cdot}O_2)^*$, explaining the strictly linear dependence of k_{obs} on $[O_2]$ at 20 °C by the quenching of $(^3S{\cdot}O_2)^*$ by O_2.[1]

$$k_{obs} = \frac{k_0 + k_pK[O_2] + k_dK[O_2]^2}{1 + K[O_2]} \qquad (1)$$

These results could have important consequences for the singlet oxygen sensitization kinetics, which rest on the assumption of a bimolecular quenching process with an initially formed excited complex $(S{\cdot}O_2)^*$ dissociating to yield the products.[2] The bimolecular quenching mechanism relies on the linear dependence of the overall rate constants k_{obs} of excited-state decay on $[O_2]$.[3−7] But the results of Shimizu et al. apparently demonstrate that rate constants k_{obs} of triplet decay which depend linearly on $[O_2]$ could well be consistent with a mechanism where the interaction of a second O_2 molecule with $(^3S{\cdot}O_2)^*$ leads to sensitization.[1]

SCHEME 1



However, the evaluation of Shimizu et al. ends in physically unreasonable results:

(i) If almost all excited species of RB would be in oxygenated solution in the $(^3S{\cdot}O_2)^*$ exciplex state, then the transient absorption spectra should correspond to $(^3S{\cdot}O_2)^*$ and should differ from the TT absorption spectra of deoxygenated solutions of RB. It has been shown that the absorption spectra of exciplexes of several aromatic acceptor molecules (A) with the common electron donor (D) diethylaniline can be attributed to the combination of transitions from the $(A^-{\cdot}D^+)$ exciplex state to higher excited charge transfer states $(A^{-*}{\cdot}D^+)$ and $(A^-{\cdot}D^{+*})$, as well as to locally excited states $(A^*{\cdot}D)$ and $(A{\cdot}D^*)$.[8]

(ii) RB is a well-known triplet sensitizer of singlet oxygen.[7] Quantum yields of $O_2(^1\Delta_g)$ sensitization between 0.75 and 0.81 have been measured in H_2O, D_2O, CH_3OH, and C_3H_7OH.[9] The triplet-state energy of RB amounts to $E_T = 164$ kJ mol^{-1}.[10] Thus, the excitation energy of $(^3S{\cdot}O_2)^*$ is estimated with the value of ΔH to amount to only about 14 kJ mol^{-1}. Therefore, interaction of $(^3S{\cdot}O_2)^*$ with ground-state O_2 could never sensitize $O_2(^1\Delta_g)$ with an excitation energy of 95 kJ mol^{-1} in alcoholic solution. Thus, this evaluation must be wrong.

There are also deficits in the derivation of the formal quenching kinetics required to explain the nonlinear oxygen concentration dependence of k_{obs} measured in the high-temperature region. The reactions of O_2 with $^3S^*$ and with $(^3S{\cdot}O_2)^*$ are different and cannot have the same rate constant k_d. Designating the rate constant of the reaction of O_2 with $(^3S{\cdot}O_2)^*$ as k'_d leads to eq 2 for k_{obs} with $K' = k'_d/(k_r + k_p)$.

$$k_{obs} = \frac{k_0 + \{k_0 + k_pk_d/k'_d\}K'[O_2] + k_dK'[O_2]^2}{1 + K'[O_2]} \qquad (2)$$

References and Notes

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10.1021/jp060819k CCC: $33.50