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Triplet–Triplet Annihilation of $Ru(bpy)_3{}^{2+}$ in Micelle Solutions

Sir:

Considerable attention has been paid in the past few years to photochemical and radiation-chemical reactions in micellar systems.[1-5] In the present work solutions of ruthenium tris-(2,2′-bipyridyl) [$Ru(bpy)_3{}^{2+}$] in negatively charged sodium dodecyl sulfate (SDS) micelles[6] are submitted to pulsed N_2 laser excitation. The purpose of the study is to show that the nonhomogeneous distribution of excited triplet states of molecules incorporated in micelles may be used for markedly enhancing the efficiency of triplet–triplet annihilation.

Experiments were first carried out exposing 10^{-4} M deaerated (SDS free) aqueous solutions of $Ru(bpy)_3{}^{2+}$ to the exciting (8 ns, 337.1 nm, 0.5 mJ) pulses in an N_2 laser photolysis system.[7] The solutions were found to exhibit transient absorbance changes identical with those previously reported by Bensasson et al.[8] following excitation by a 530-nm neodymium laser pulse. The depletion of the ground-state absorbance ~450 nm and the increase in absorbance ~360 nm are due to the population of a triplet charge-transfer state of the metal complex.[8]

The triplet decay, back to the original ground-state ion, may be followed by monitoring the 610-nm phosphorescence, the triplet absorbance decay at 360 nm, or the ground-state regeneration at 450 nm. The process was found to be of first order with a lifetime ($\tau = 0.60 \pm 0.06$ μs) which is independent of the $Ru(bpy)_3{}^{2+}$ concentration (in the range 10^{-3}–10^{-5} M) and of the pulse intensity (in the range ~50–5 mJ/cm²). This independence indicates the lack of any substantial triplet quenching effects, either by the ground state or, even under the maximum concentrations and excitation intensities available, by triplet–triplet annihilation.

Above 500 nm a small positive increase in absorbance which is markedly reduced in the presence of N_2O (1 atm) and 0.1 M *tert*-butyl alcohol, is attributed to the low-yield generation of solvated electrons, in keeping with the conclusions of Meisel et al.[9]

Experiments were subsequently carried out with $Ru(bpy)_3{}^{2+}$ solubilized in SDS micelles. Although the transient absorption spectra following laser excitation are identical with those observed in the micelle-free homogeneous aqueous solutions, the decay kinetics of the triplet state are markedly different. A relatively fast nonexponential process is now followed by a slow exponential decay characterized by a lifetime of $\tau = 0.80 \pm 0.08$ μs.

The initial amount of bleaching and the triplet decay kinetics were measured at 450 nm as functions of the intensity of the exciting pulse. The rate of the slow decay process was found to be independent of the excitation intensity. For each intensity value the decay curve corresponding to this process was plotted on a logarithmic scale and extrapolated to zero time. Figure 1 shows the initial amount of bleaching (a) and the initial extrapolated component (b), both as functions of the excitation intensity. The intensity dependence of the absorbance ratio (a/b) shown in Figure 1 clearly indicates that the two decays cannot be represented by two consecutive first-order processes. The observed relationship strongly suggests that the initial component is due to a fast bimolecular triplet–triplet annihilation reaction.

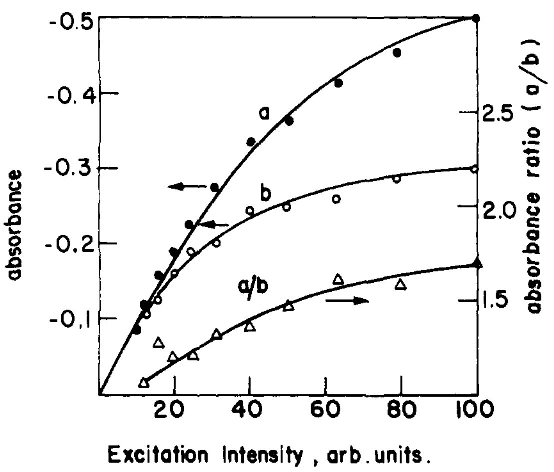

Figure 1. Laser intensity dependence of the amplitudes of the fast and slow triplet decay processes in a solution of 0.98 10^{-4} M $Ru(bpy)_3{}^{2+}$ and 1.0 10^{-2} M SDS. The amplitudes are monitored by the corresponding decrease in absorbance (bleaching) at 450 nm. (a) The initial bleaching at zero time. (b) Value obtained by extrapolation of the slow decay component to zero time. (a/b) The ratio between the former values. (Full intensity scale is equivalent to ~50 mJ/cm².)

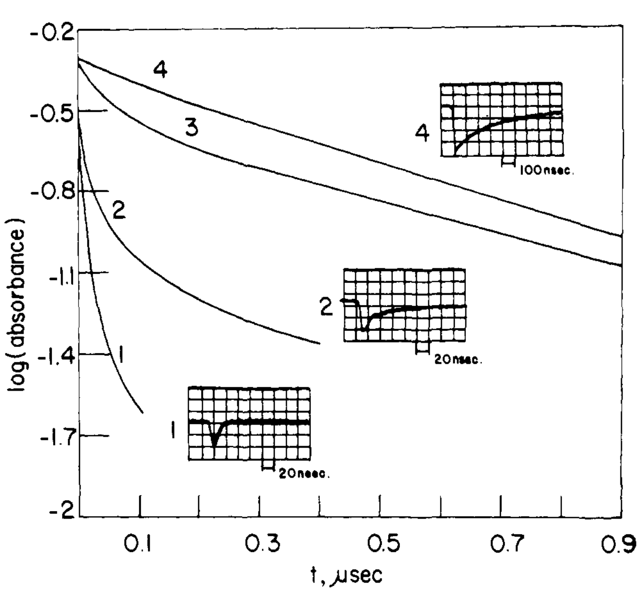

Figure 2. Characteristic oscillograms (upper trace monitoring light off, lower trace monitoring light on) of the bleaching at 450 nm and corresponding absorbance decay curves, showing the effects of varying the SDS concentration at a constant pulse intensity (~50 mJ/cm²) on the decay of the triplet state in 1.0 10^{-4} M $Ru(bpy)_3{}^{2+}$ solutions. SDS concentrations are (1) 3.1 10^{-3} M, (2) 6.3 10^{-3} M, (3) 1.3 10^{-2} M, (4) 3.2 10^{-2} M.

To further confirm this conclusion and also to discriminate between inter- and intramicellar annihilation reactions, relatively high-intensity experiments were carried out in solutions with varying micelle concentrations in the presence of a constant amount of $Ru(bpy)_3{}^{2+}$. The observations are summarized in Figure 2. At very low micelle concentrations (i.e., when the number of $Ru(bpy)_3{}^{2+}$ ions per micelle is high) the lifetime of fast component is so fast ($\tau < 5$ ns) as to essentially follow the laser pulse profile. Under such conditions the amplitude (b) of the slow decay is negligible. When the micelle concentration increases and, consequently, there are less $Ru(bpy)_3{}^{2+}$ ions per micelle, the lifetime of the fast decay increases and its amplitude decreases, while that of the slow process becomes more pronounced.

These observations are consistent with a scheme in which intramicellar triplet-triplet annihilation competes with the unimolecular decay of triplet ($\tau = 0.8\ \mu s$) in the micelle. Although the exact composition and structure of the present SDS-Ru(bpy)$_3^{2+}$ micelles are still unclear, the results lead to the general conclusion that it is possible to enhance the yield of triplet-triplet interactions by orders of magnitude (at least 3 in the present study) by incorporating molecules in micelles. The search for systems in which a large fraction of the energy of the two interacting excited states is trapped and used before dissipation may be the subject of future research, also in relation to the use of solar radiation.

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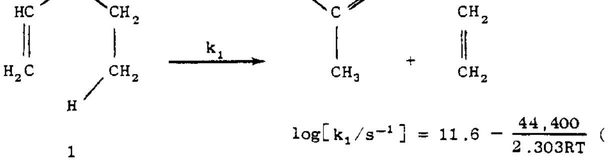
Infrared Photodecomposition of Ethyl Vinyl Ether. A Chemical Probe of Multiphoton Dynamics

Sir:

Chemistry following multiphoton absorption[1] may, in general, involve collisionless *and* collision-induced processes.[2] The dynamics and time regimes associated with these processes remain to be well characterized experimentally. We report here the CO_2 TEA-laser photolysis of ethyl vinyl ether (EVE, **1**) and its relevance to these questions.

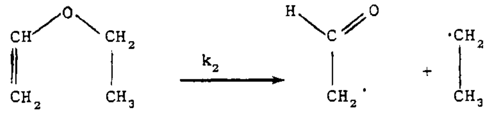
Conventional pyrolysis[3] of EVE yields ethylene and acetaldehyde by a retro-ene molecular elimination (eq 1).



$$\log[k_1/\mathrm{s}^{-1}] = 11.6 - \frac{44{,}400}{2.303RT} \quad (1)$$

1

Decomposition with a focused laser yields not only these conventional products but also comparable amounts of ketene, ethane, and butane.[4] This suggests that a simple bond fission process[5] (eq 2) competes effectively with eq 1 upon multiphoton excitation.[6] Ketene is formed by subsequent disproportionation reactions of $\cdot CH_2CHO$ and the ratio $[CH_3CHO]/[CH_2CO]$ provides a measure of the relative rates of processes 1 and 2. This ratio, as a function of pressure, is as follows: 1.89 (440 Torr), 1.89 (280), 1.64 (230), 1.45 (25), 1.44 (20), 1.71 (11), 1.79 (10), 1.86 (10), 1.84 (5), and 1.75 (10 + 40 torr of He). Thus, $k_1 \simeq 0.37\ k_2$ over the pressure range studied. Irradiation with an unfocused beam yields only ethylene and acetaldehyde.



$$\log[k_2/\mathrm{s}^{-1}] = 15 - \frac{65{,}800}{2.303RT} \quad (2)$$

1

The two reactions compete at high energies since the reaction channel density for eq 2 exceeds that for eq 1 (as reflected in their A factors). A number of molecules will exhibit similar behavior if their lowest thermal path involves a cyclic transition state,[6] but EVE is especially interesting since the difference in activation energies for its two lowest energy channels is large, thereby increasing the dynamic range available for studying the energy distribution of reacting molecules.

Our experimental results can be considered in terms of the following steps: laser pumping, $A(E) \rightarrow A(E')$ $\{k_p(I,E)\}$; collisional energy pooling or deactivation, $M + A(E') \rightarrow M + A(E'')$, $\{k_c\}$; and, reaction via channel i, $A(E) \rightarrow (\text{products})_i$, $\{k_i(E)\}$. Such a scheme calls attention to the various competitive processes, each of which may dominate under different experimental conditions.[7]

In our pressure range, ~1-100 collisions occur during the laser pulse. The observed lack of pressure dependence thus suggests that most the chemistry occurs after the pulse. Furthermore, assuming the applicability[7,9,10] of a quantum RRK model,[11] we find that $k_1(E)$ and $k_2(E)$ are comparable at $\sim 10^6$-$10^7\ \mathrm{s}^{-1}$, which is $\lesssim$ collision frequency, implying that our results are predominantly collisional. Collisions between molecules in the irradiated region occur rapidly compared with escape and subsequent cooling, since the mean free path is small at our pressures. (Isotopic specificity may still obtain under these conditions since collisions with "cold" molecules are simply deactivating.) Therefore, in our experiments, the chemistry appears to be that of a collisionally (V-V) thermalized system. This is also consistent with recent experiments[10] which suggest that, at energy fluences of ~1 J cm^{-2}, although considerable excitation occurs, only a small fraction of excited molecules react. The low conversions typically observed in this regime are thus consistent with an energy distribution function that decreases monotonically above E_c, the threshold for reaction. Consequently, the collisional nature of this chemistry indicates the Arrhenius forms of k_1 and k_2 can be used in expressing the yield ratio, giving a temperature of ~1600 K. The temperature dependence of k_1/k_2 (for T = 300, 1000, 2000 K, $k_1/k_2 = (0.55 \times 10^{12}, 18.94, 8.68 \times 10^{-2})$ indicates the sensitivity of the branching ratio of EVE as a probe of excitation. The cleanliness of IR-laser photolysis relative to the high temperature pyrolysis[3] of EVE suggests this is an attractive alternative to conventional activation techniques. Evidence indicates that increasing fluence will raise the apparent "temperature" [11] so that eq 2 would compete more effectively with eq 1.

In summary, we have developed a sensitive chemical probe of energy distribution applicable to bulk and collisionless systems. Our results are consistent with recent studies[10-12] in terms of lifetimes and energy distribution functions. We are currently studying the intensity and buffer dependence of k_1/k_2