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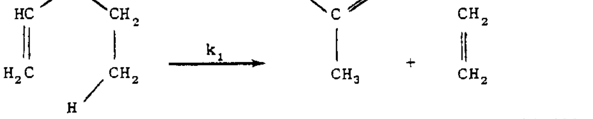
Infrared Photodecomposition of Ethyl Vinyl Ether, A Chemical Probe of Multiphoton Dynamics

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.

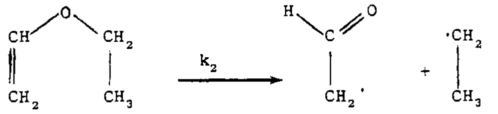
Conventional pyrolysis[3] of EVE yields ethylene and acetaldehyde by a retro-ene molecular elimination (eq 1).



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

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.



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

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 $\sim 10^6$–$10^7\ s^{-1}$, 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 $\sim 1\ J\ cm^{-2}$, 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

and extending our experiments to include the collisionless regime by increasing fluence and decreasing pressure.

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(5) The Arrhenius parameters shown in eq 2 were estimated using methods described in S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1976.
Similar effects are noted in the IR–laser photolysis of alkyl iodides.

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(7) The average rate of a process i, $\langle k_i(E) \rangle$, can be formulated using a generalized Lindemann model.[8] The resulting expression depends on the rates of radiative and collisional activation and deactivation, decomposition, laser power, and pulse width. The time evolution of $k_i(E)$ depends on the relative rates of laser pumping, energy pooling, deactivation, and reaction and can be determined using a kinetic master equation. Work in this regard is in progress in our laboratories.

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Mixed-Metal Clusters via Metal Hydride Coupling. New Rhenium-Osmium Clusters and the Crystal Structure of $H_2Re_2Os_3(CO)_{20}$

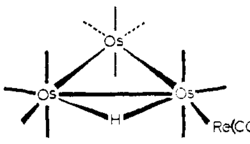
Sir:

The systematic preparation of metal carbonyl cluster compounds combining two or more different metals is a challenging synthetic problem and is potentially of practical importance in the generation of supported bimetallic catalysts.[1] Heterometallic bond formation via the displacement reaction of a metal carbonyl anion with a metal halide compound is the most predictable of the known procedures.[2] Other methods involving either the copyrolysis of different homometallic carbonyl units[2,3] or the combination of a metal carbonyl anion and a neutral metal carbonyl[4,5] can be selective but frequently afford a mixture of products. The metal hydride coupling reaction shown in

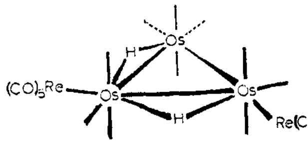
$$L_nM_xS + HM'L_m \rightarrow L_nM_x \cdot\cdot H \cdot\cdot M'L_m \text{ or } L_nM_x(H)M'L_m + S \quad (1)$$

is a relatively unexplored approach to heterometallic cluster compounds.[6] Loss of the two-electron donor ligand S from the metal center M generates a vacant site that may interact with the H–M′ bond to form either a stable M··H··M′ three-center two-electron bond (as in $HMnRe_2(CO)_{14}$[7]) or new M–H and M–M′ bonds (as suggested for formation of $H_2Os_2(CO)_8$[8]). We have recently shown that the labile derivatives $Os_3(CO)_{12-x}S_x$ (x = 1, 2; S = cyclooctene or acetonitrile) can be prepared and used for substitution reactions.[9] Combining these derivatives with $HRe(CO)_5$ as in eq 1 has allowed us to prepare the compounds $Os_3(CO)_{12-x}[HRe(CO)_5]_x$ (x = 1, 2).

Treatment of the cyclooctene complex $Os_3(CO)_{10}(C_8H_{14})_2$[9] with an excess of $HRe(CO)_5$ in benzene[10] provided a single product, isolated as a yellow solid in 90% yield after thin-layer chromatography. The electron impact mass spectrum of this material is consistent with the formulation $H_2Re_2Os_3(CO)_{20}$.[12] In its ^{1}H NMR spectrum two hydride signals are observed at τ 26.9 and 28.1 (CH_2Cl_2) with J_{HH} = 2 Hz. The $^{13}C\{^1H\}$ NMR spectrum of the compound, prepared from ^{13}CO-enriched $Os_3(CO)_{10}(C_8H_{14})_2$, displays at 33 °C three singlets of intensity 2 C and four singlets of intensity 1 C.[13] These data are consistent with a structure that retains the basic Os_3 triangle of $Os_3(CO)_{12}$, but with two rhenium carbonyl groups substituted unsymmetrically for two equatorial carbonyl ligands (cf. $Os_3(CO)_{10}(PEt_3)_2$[14]). The data do not determine whether the rhenium carbonyl groups are bound to the Os_3 triangle by Os–H–Re or Os–Re bonds. However, a single-crystal x-ray diffraction study of $H_2Re_2Os_3(CO)_{20}$ has established the latter mode together with the probable positions of the hydrogen ligands as in structure II.



I



II

The $H_2Re_2Os_3(CO)_{20}$ molecule crystallizes in the monoclinic space group *Cc* with a = 9.248 (2) Å, b = 23.010 (4) Å, c = 29.665 (5) Å, β = 104.59 (1) °, V = 6109 (2) Å^3, and π (calcd) = 3.27 g cm^{-3} for M = 1505 and Z = 8. Diffraction data were collected with a Syntex P2$_1$ automated diffractometer using Mo Kα radiation and an ω-scan technique. Data were corrected for absorption (μ = 205 cm^{-1}); the structure was solved by Patterson methods (which indicated the lower space group *Cc*, rather than the centrosymmetric *C2/c*) and refined by full-matrix least-squares methods (409 variables; 2764 data in the range 3° < 2θ < 40° with $F > \sigma(F)$) using the Syntex XTL system to final discrepancy indices of R_F = 4.5% and R_{wF} = 4.9%. All atoms other than hydrogen atoms have been located and refined. Metal atoms were assigned anisotropic thermal parameters, while all other atoms were restricted to isotropic thermal parameters. The crystallographic asymmetric unit consists of two molecules of $H_2Re_2Os_3(CO)_{20}$ related to each other by a (local) pseudoinversion center at a *general* position in the unit cell. The two molecules have identical connectivities and their bond lengths and angles are identical with the limits of experimental error. One such molecule is illustrated in Figure 1.

The metal core consists of a triangle of osmium atoms with