

Acknowledgment. This work was supported by the National Science Foundation.

References and Notes

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- (5) Product yields have been measured for every run and will be reported in a full paper.
- (6) A. T. Bell in ref 1, Chapter 1.
- (7) The variation in rate with P and r could come from variations in electron distribution, electron energies, rates of interspecies energy transfer, residence time in the plasma region, or simply from the rate law for the specific reactions. Changes in product composition (ratios) could also arise from all of these factors. In addition, the possibility of converting primary products to other materials has often been suggested and a major change in mechanism with conditions is not unlikely.
- (8) We predict that some dependence of $f(\epsilon)$ on structure will be revealed in more careful and extensive studies and may be present, but obscure, in the present data. Surely, all organics are not exactly the same!

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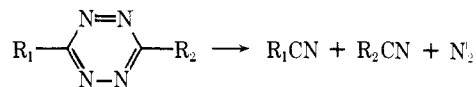
Received April 25, 1977

Measurements of the Relative Chemical Reactivity of Triplet Spin Substates

Sir:

In this communication we report the first direct measurement of relative *chemical reactivity* for separate spin components of a triplet state. The three spin substates, T_x , T_y , and T_z of a triplet state contain differing amounts of singlet character due to the anisotropy in the spin-orbit coupling. In the event that the chemical reactions of the molecule in its triplet state depend on this singlet character, we expect that the reactivity will differ for the three spin substates. One obvious example where such differences might be expected is when the primary step in the reaction involves an intersystem crossing from the triplet state into a highly vibrationally excited singlet ground state, as appears to be one mechanism for some simple molecular predissociations.¹ Recently Leung and El Sayed² have made the first measurements on the *photochemistry* of a triplet state, elegantly showing by microwave techniques how different sublevels of T_1 are photochemically degraded at different rates in $T_1 \rightarrow T_n$ transitions.

In previous work³⁻⁶ we have shown that singlet and triplet excited states of *s*-tetrazine and its derivatives, dimethyl- and phenyl-*s*-tetrazine, undergo an efficient dissociation of the type



Although the dissociation of the triplet state is four to five orders of magnitude slower than the singlet reaction, it is still at least two orders of magnitude faster than the radiative rate calculated from the singlet-triplet absorption strength.³ For the present study we have used dimethyl-*s*-tetrazine for which the conventional phosphorescence decay time of 83 μs is presumed to measure the rate of the photochemical reaction⁷ averaged somehow over the spin substates.

The principle of our experiment is to utilize a combination of low temperature (4.2 K) and relatively high magnetic field (55 kG) to maintain a system of oriented molecules in essentially one spin substate after direct excitation of the lowest triplet with a tunable dye laser. Measurement of the lifetime for radiative decay in the presence of the field then yields the

Table I

Magnetic field orientation ^a ($ \mathbf{B} \cdot \mathbf{x} ^2 = \mu_x^2$)	Lifetime (μs) of phosphorescence ^b
0.65	78.6 \pm 0.4
0.32	107.1 \pm 1.2
0.03	125.2 \pm 1.4
Zero field (4.2 k)	83.2 \pm 0.4

^a Least-squares fit to an exponential over two and one half decades.

^b From optical density measurements on the crystal.

decay for a particular substate. By choosing three mutually perpendicular field orientations, results can be obtained for three orthogonal spin substates. A single crystal of dimethyl-*s*-tetrazine was situated in the field of a superconducting magnet, directly immersed in liquid helium, and irradiated by a nitrogen pumped dye laser at 648 nm. The phosphorescence spectrum originated from a single site with 0-0 band at 13 053 cm^{-1} . The dye laser operated at 50 Hz and signals from $\sim 20\,000$ pulses were averaged to obtain the lifetimes shown in Table I.

For any orientation of the magnetic field, specified by μ , the decay constant of the triplet state resulting from a measurement of the total emitted light, is

$$k_\mu = Z^{-1} \sum_{m_s} k_\mu^{(m_s)} e^{-g\beta B_0 m_s / kT} \quad (1)$$

where $g \simeq 2$, β is the Bohr magneton, B_0 the applied field strength, Z is the partition function for the spin sublevels, and $m_s = 0$ and ± 1 . $k_\mu^{(m_s)}$ is the total decay constant for sublevel m_s at field orientation μ . For $B_0 = 55$ kG, $2\beta B_0/hc = 5.13$ cm^{-1} , whereas $kT/hc = 2.92$ cm^{-1} ; thus it is a reasonable first approximation to take $Z \simeq 1$ and consider only the $m_s = -1$ sublevel. In eq 1 we have assumed rapid achievement of a Boltzman distribution amongst the spin sublevels, consistent with our observation of exponential decays for all field orientations. The decay of the light signal is therefore a measure of $k_\mu^{(-1)}$. The three orthogonal directions (μ) for the magnetic field in the table are referred to the out-of-plane (x) molecular axis. The ${}^1\text{B}_{3u} \leftarrow {}^1\text{A}_g$ transition of the tetrazine is known to be out of plane polarized;^{4,5,8} so the trichroism of the single crystals provides the approximate absolute value of the cosines of the angles between the three principal absorption axes of the needle-like crystals and the x axis of the molecules. The magnetic field was directed along each of these three axes. The results of our measurements are shown in the table.

The T_x , T_y , and T_z content of the $m_s = -1$ sublevel depends on μ ; the probability of measuring T_ζ ($\zeta =$ molecular axis; x , y , or z) in $m_s = -1$ is zero when μ is parallel to ζ , and 0.5 when μ is perpendicular to ζ . It is apparent from the data shown in Table I that the longest lifetime occurs when B_0 is nearly perpendicular to x and the shortest lifetime occurs when B_0 is closest to x . This result implies that the T_x substate undergoes chemistry⁷ substantially more slowly than either T_y or T_z . In the case that the triplet state decay occurs into pure singlet vibronic levels, the specific rate for a particular $m_s = -1$ sublevel is given by

$$k_\mu^{(-1)} = \frac{1}{2}[(1 - \mu_x^2)k_x + (1 - \mu_y^2)k_y + (1 - \mu_z^2)k_z] \quad (2)$$

also

$$3k = \sum_{\zeta} k_{\zeta} = \sum_{\mu} k_{\mu}^{(m_s)} \quad (3)$$

where k is the decay constant at zero field with equilibrated spin substates, and μ_ζ is the cosine of the angle between the field and the ζ axis. Our measurements yield 1.2×10^4 s^{-1} for the decay at zero field and 1.0×10^4 s^{-1} for $3\sum_{\mu} k_\mu^{(-1)}$, neglecting the population of the $m_s = 0$ sublevel. This discrepancy is

significant and might imply that, although the zero field populations are the same at all times (exponential decay), they are not equal. Such a situation can arise when there is anisotropic energy transfer occurring in the crystal.⁸

Of the three spin components at zero field only the T_x substate does not have the symmetry of a pure π -electron state of the molecule. The $n\pi^*$ state has strong (one-center) spin-orbit coupling only with π states. Therefore, we have found evidence indicating in this instance that the chemistry of the triplet state⁷ is controlled by the singlet admixture in the various substates. A simple spin orbit coupling calculation yields $k_y \approx k_z$ and our result can be used along with eq 2 to show that k_x is $\sim 10^{-3}$ of k_y or k_z . Thus the effect reported here is substantial.

We are presently pursuing zero field approaches to measuring the chemistry of different spin substates as well as a detailed structural analysis of dimethyl-*s*-tetrazine that will allow a more complete picture of the contributions from each spin substate to the relative reactivity of the triplet state.

Acknowledgments. It is a pleasure to acknowledge the partial support of this investigation by the National Science Foundation (No. CHE 75-16177) the National Institutes of Health (GM12592), and the Materials Research Laboratory at the University of Pennsylvania (No. DMR 76-00678).

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Received May 16, 1977

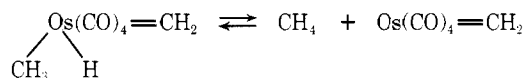
Mechanism of Reductive Elimination. 3.¹

Methyl Radical Elimination from *cis*-Dimethyltetracarbonylosmium

Sir:

Reported work on the decomposition of polymethyl transition-metal compounds, while extensive, has rarely offered definitive conclusions. For example, many workers have suggested the involvement of methyl radicals²⁻⁶ on the basis of observed methane formation. However, the process of α elimination, which has been suggested by many workers^{2a,c} and for which reasonable evidence has recently been published,⁷ offers an alternative pathway for elimination of methane from two methyl ligands: it would leave a coordinated methylene carbene *without* a methyl radical intermediate. Such a mechanism has recently been proposed for the thermal decomposition of $(\text{CH}_3)_2\text{Co}[\text{P}(\text{OCH}_3)_3]_4^+$.⁸

We have therefore investigated in detail the formation of methane from $\text{Os}(\text{CO})_4(\text{CH}_3)_2$.^{9,10} Despite the extraordinary thermal stability of this compound (considerable undecomposed material can be recovered after 1 week at 162.5 °C), methane elimination is irreversible once it occurs. The presence of 0.2 atm of CH_4 has no significant effect on the rate of decomposition (gas phase) of $\text{Os}(\text{CO})_4(\text{CH}_3)_2$, nor is any H found in $\text{Os}(\text{CO})_4(\text{CD}_3)_2$ recovered after partial decomposi-



tion in the presence of 1 equiv of CH_4 . Thus neither a reversible α elimination nor any other reversible process is occurring.

It is much harder to demonstrate that methane formation is *not* occurring *irreversibly* from an intermediate formed by α elimination. As such a process would give only CH_4 and CD_4 from $\text{Os}(\text{CO})_4(\text{CH}_3)_2$ and $\text{Os}(\text{CO})_4(\text{CD}_3)_2$, respectively, a mixture of those two compounds was decomposed at 162.5 °C. All possible isotopically substituted methanes (CH_4 , CH_3D , CH_2D_2 , CHD_3 , CD_4) were formed.¹¹ These results offer no support for an irreversible process via α elimination, but they do not disprove it. The observation of CH_2D_2 suggests instead that methane is attacked during the decomposition process.

Other observations confirm this inference. CD_3H is observed¹² in the methane atmosphere resulting from both the partial decomposition of $\text{Os}(\text{CO})_4(\text{CD}_3)_2$ in the presence of 1 equiv of CH_4 , described above, and the decomposition of $\text{Os}(\text{CO})_4(\text{CH}_3)_2$ in the presence of 1 equiv of CD_4 .

These results require the irreversible formation of methane via a species capable of reacting with it and suggest the intermediacy of a methyl radical.^{13,14} Solvent attack is thus predicted when the reaction is run in solution. Indeed, CD_3H is formed upon thermolysis of $\text{Os}(\text{CO})_4(\text{CD}_3)_2$ in a wide variety of solvents at 162.5 °C:¹⁵ mesitylene, dodecane, di-*n*-pentyl ether, phenetole, *sec*-butylbenzene, 2-octanone, acetophenone, and 1,2,3,4-tetramethylbenzene. Some CD_4 is also formed, e.g., $\text{CD}_4/\text{CD}_3\text{H} = 0.18$ in di-*n*-pentyl ether.

The isotopic selectivity $k_{\text{H}}/k_{\text{D}}$, required to demonstrate that the intermediate is in fact a methyl radical, thus cannot be determined from a single experiment in which solvent H and solvent D compete for the intermediate; some of the CD_4 will be the result of attack by the intermediate on the starting material, not on the solvent. A solution to this problem is suggested by the following general rate equations

$$\frac{d[\text{CD}_4]}{dt} = k_{\text{D}}[\text{I}][\text{R-D}] + \text{rate of formation of } \text{CD}_4 \text{ directly from } \text{Os}(\text{CO})_4(\text{CD}_3)_2 \quad (1)$$

$$\frac{d[\text{CD}_3\text{H}]}{dt} = k_{\text{H}}[\text{I}][\text{R-H}] \quad (2)$$

where R-D and R-H are deuterated and nondeuterated solvent and I is the reactive intermediate, presumably (but not necessarily) arising from a process first order in $\text{Os}(\text{CO})_4(\text{CD}_3)_2$. If temperature (162.5 °C), initial concentration of $\text{Os}(\text{CO})_4(\text{CD}_3)_2$ (0.03 M), and reaction time (20% completion) are held constant, then [I] and the "rate of formation of CD_4 directly from $\text{Os}(\text{CO})_4(\text{CD}_3)_2$ " are constant, and for a series of reactions with different mole fractions of deuterated solvent

$$\frac{[\text{CD}_4]}{[\text{CD}_3\text{H}]} = k_{\text{D}}/k_{\text{H}}([\text{R-D}]/[\text{R-H}]) + \text{a constant} \quad (3)$$

Thus from the slope of a plot of $[\text{CD}_4]/[\text{CD}_3\text{H}]$ against $[\text{R-D}]/[\text{R-H}]$, $k_{\text{H}}/k_{\text{D}}$ can be obtained.¹⁶

Results from the thermolysis of $\text{Os}(\text{CO})_4(\text{CD}_3)_2$ in mixtures of *n*- $\text{C}_{12}\text{H}_{26}$ and *n*- $\text{C}_{12}\text{D}_{26}$ are shown in Figure 1. The value of $k_{\text{H}}/k_{\text{D}}$ which results, 5.3 ± 0.9 , provides quantitative verification of our hypothesis that methyl radicals are involved. Similar selectivities (the numbers quoted have been extrapo-