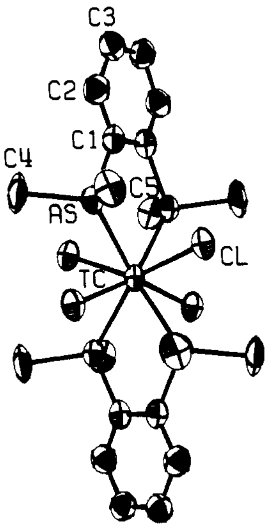

Figure 2. Perspective view of [Tc(diars)$_2$Cl$_4$]$^+$. The ellipsoids represent 50% probability, and hydrogen atoms have been omitted for clarity. Site symmetry, D_2; approximate symmetry, D_{2d}. Bond lengths: Tc(V)-Cl, 2.442 (4); Tc(V)-As, 2.578 (2) Å. Bond angles: As-Tc-As, 129.46 (5), Cl-Tc-Cl, 91.21 (12)°.

radiation]. Final least-squares refinement of 130 parameters (overall scale factor, positional and anisotropic temperature parameters for the nonhydrogen atoms) converged with a conventional discrepancy index[13] of 0.076. The structure of the [Tc(diars)$_2$Cl$_4$]$^+$ cation is shown in Figure 2, the D_{2d} dodecahedral coordination geometry being the same as observed[15-17] in the analogous eight-coordinate titanium(IV) complex Ti(diars)$_2$Cl$_4$. In this geometry the d_{xy} orbital is substantially more stable than any other[18] and therefore it is not surprising that this disposition of ligands can accommodate both a d^0 and a spin-paired d^2 metal center.[1]

Single-crystal X-ray confirmation of the proposed coordination geometries of [Tc(diars)$_2$Cl$_2$]$^+$ and [Tc(diars)$_2$Cl$_4$]$^+$ establishes reaction 1 as the first known example of oxidative addition from a six-coordinate to an eight-coordinate complex. The stability of the eight-coordinate product undoubtedly results in great part from the presence of the diars ligands which are known to promote high coordination numbers.[16,17,19-21] However, even for those reactions in which the eight-coordinate products are metastable or unstable, oxidative addition to six-coordinate technetium complexes has great potential as a synthetic route for the interconversion of octahedral technetium complexes and the ultimate synthesis of new technetium radiopharmaceuticals. Likewise, other large octahedral metal centers such as Mo(II) may also undergo oxidative addition reactions, and synthetic routes based on this chemistry may prove profitable. Reaction 1 is also unusual in that it involves a d^4 starting material, whereas most oxidative addition reactions involve d^8 or d^{10} starting materials;[3] however, it is consistent with Halpern's generalized formulation of oxidative addition reactions[3] in that it involves conversion of an open-shell (16 valence electrons) complex to a closed-shell (18 valence electrons) complex. Studies designed to establish the detailed mechanism of reaction 1 are currently in progress.

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Bond Energy and Conformation of the Molybdenum-to-Molybdenum Triple Bond

Sir:

Recently, thermochemical measurements have been reported for the triply bonded dimers M$_2$(NMe$_2$)$_6$ (M = Mo, W).[1] Although the enthalpy of formation for these systems can be accurately measured, it is difficult to determine the actual M$\equiv$M bond energy because it is not obvious what value to use for the M—NMe$_2$ bond energy. Thus, a range of M$\equiv$M bond energies from weaker than a carbon-carbon single bond to stronger than a nitrogen-nitrogen triple bond are reported. A value of 592 ± 196 kJ mol^{-1} (141 ± 47 kcal mol^{-1}) is suggested for the M$\equiv$Mo bond energy.[1]

We believe that it would be useful to know this value more precisely. Although it is rare to be able to calculate a dissociation energy more accurately than it can be measured, the large error bars on the experimental value for the Mo$\equiv$Mo bond suggest it would be possible for this case. We have used the generalized molecular orbital (GMO) approach in this study.[2] The GMO method consists of a multiconfiguration self-consistent-field calculation followed be a configuration interaction (CI) calculation. All of the orbitals are kept doubly occupied except for those involved in the triple bond. For the six electrons in the triple bond, The GMO wave function consists of the dominant single determinant ($\sigma^2\pi_x{}^2\pi_y{}^2$) plus all paired double excitations, from these bonding orbitals to their antibonding counterparts ($\sigma^*,\pi_x{}^*,\pi_y{}^*$), weighted equally.[2] Application of the variation principle yields a set of primary orbitals ($\sigma,\pi_x,\pi_y,\sigma^*,\pi_x{}^*,\pi_y{}^*$) in which the weakly occupied ones ($\sigma^*,\pi_x{}^*,\pi_y{}^*$) are optimized to correlate the strongly occupied ones (σ,π_x,π_y). The determination of the GMO orbitals is then followed by a full CI calculation in this

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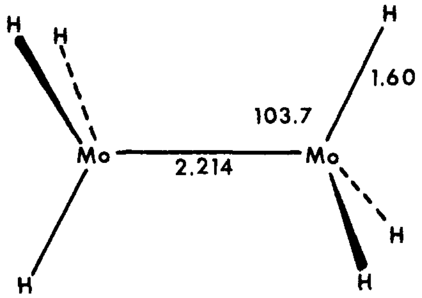

Figure 1. Structure of Mo_2H_6. The bond distances are in angstroms; the bond angle is in degrees.

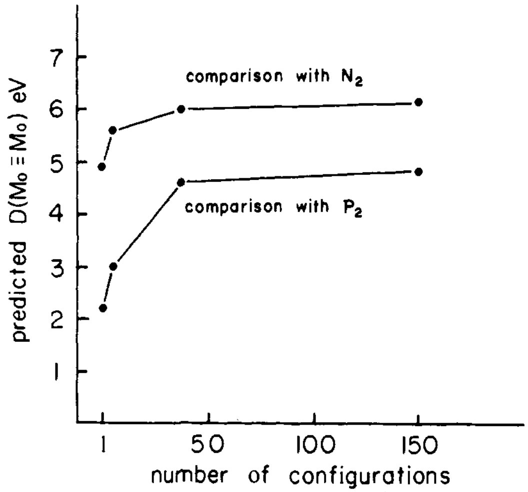

Figure 2. Bond energy of Mo≡Mo from comparative calculations on N_2 and on P_2 at various levels of configuation interaction.

restricted orbital space. The dissociation energy of N_2 calculated by this approach in a large Gaussian basis [4s,3p,1d][3] is 8.82 eV, while the single determinant Hartree-Fock value is only 4.98 eV. The GMO-CI value is only 10% less than the experimental value and only 1% less than that obtained in a similar basis with the GVB-CI approach.[4]

Because of the size of the molybdenum system, some additional approximations have been made. We have replaced the NMe_2^- ligands with H^-. Although this appears to be a severe approximation, the Mo≡Mo bond distance and, presumably, the bond energy are relatively insensitive to the ligands.[5] Even with this reduction in the size of the molecule, we have not been able to employ as accurate a basis set as in the N_2 study mentioned above. For this reason we have done comparative calculations on the series of triply bonded molecules Mo_2H_6, N_2, and P_2 in equivalent basis sets[6] and with an identical GMO-CI procedure. The bond distances and angles for the Mo_2H_6 model system are shown in Figure 1.

The results are shown in Figure 2 where we have plotted the dissociation energy of Mo_2H_6, D(Mo≡Mo), as predicted by its comparison with N_2 and with P_2[7] at various levels of CI. The calculations range from the single determinant, through GMO and GMO-CI, to a polarization CI calculation, where one electron is allowed outside the GMO orbital space. If the comparison with N_2 and P_2 were working perfectly, we would expect the same prediction for D(Mo≡Mo) from both. Although they are not identical, the predictions at the most accurate level differ by only 1.3 eV. Thus, our best estimate of D(Mo≡Mo) from the average of the two comparisons is 526 ± 63 kJ mol^{-1} (126 ± 15 kcal mol^{-1}). We believe the correct value is within this range although our "error bars" are simply the average deviation from two comparisons. These results place the bond energy of Mo≡Mo between that of C═C and O═O. The W≡W bond, which is stronger by 183 kJ mol^{-1},[1] would then be the third strongest homonuclear bond known behind N≡N and C≡C.

Table I. Mo_2H_6 Total Energies and Their Difference for the Staggered and Eclipsed Conformers

	HF	GMO	GMO-CI
staggered, au	−7897.1755	−7897.2332	−7897.3623
eclipsed, au	−7897.1771	−7897.2335	−7897.3622
Δ, kcal/mol	+1.0	+0.2	−0.1

We will avoid speculating on whether the correct value for the bond energy is nearer the upper or lower extreme of our estimate. However, we would like to mention some of the problems with the present calculations, which we are working to overcome. The basis set is smaller than one would like to employ; for the model compound Mo_2H_6, larger basis set calculations are possible and should reduce our error bars. We do not know the effect of replacing the NMe_2^- ligands with H^-, but we are investigating the complex $Mo_2(NH_2)_6$ which is a somewhat more realistic model.[8] The Mo≡Mo triple bond is more highly correlated than either N≡N or P≡P. This can be seen in Figure 2, where the predicted dissociation energy of Mo_2H_6 increases as one introduces correlation into the wave function. This is also reflected in the wave function, where for Mo_2H_6 the triply bonded determinant ($\sigma^2\pi^4$) is only 80% of the total wave function, while for N_2 and P_2 it is >90%. Although we are employing the same configurations in the comparative CI calculations, it is not clear that we are recovering an equivalent fraction of the correlation energy.

In a letter just preceding the thermochemistry of these molecules, Albright and Hoffmann[9] suggest that these triply bonded dimers should be eclipsed, and that it is only the steric bulk of the ligands which gives rise to the observed staggered geometry. Using extended Hückel (EH) calculations, these authors predict that the eclipsed geometry is favored by 46 kJ mol^{-1} (11 kcal mol^{-1}) in M_2H_6. Our results for the eclipsed and staggered conformers are shown in Table I. At the single determinant level the eclipsed conformer is prefered, for just the reasons cited by Albright and Hoffmann, but by only 4.2 kJ mol^{-1} (1.0 kcal mol^{-1}). When correlation is introduced into the triple bond this small preference vanishes, and the Mo_2H_6 system shows essentially free rotation. Thus, the conformation of the dimers is determined solely by the ligands, but there is no barrier to overcome in forming a staggered geometry. We believe the barrier from the EH calculations is too large because this approach overestimated the hybridization of the ML_3 fragments. Our results suggest almost pure 4d π bonding in Mo_2H_6.[10]

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(7) Dissociation energies are notoriously difficult quantities to calculate. Because of the small basis sets emplyed in these calculations, the absolute errors are substantial. For calculations at the GMO-CI level, the error in the dissociation energy of N_2 is 5.3 eV compared to an error of 1.1 eV for

our larger basis set. The corresponding error in P_2 is 3.9 eV. Since these errors appear to be independent of the magnitude of the dissociation energy, we assumed that we could estimate the dissociation energy of Mo_2H_6 by using these errors as additive corrections.
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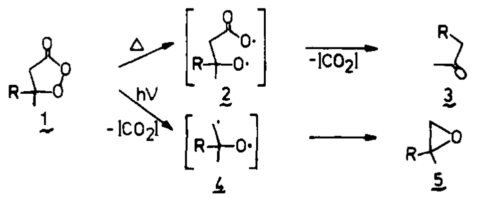
On the Mechanism of β-Peroxylactone Decarboxylation[1]

Sir:

Previous work suggested that the thermolysis[2] of β-peroxylactones **1** affords the ketone **3** as major product via the 1,5 diradical **2**, while photolysis[3] leads predominantly to the epoxide **5** via the 1,3 diradical **4** (eq 1). Herein we present

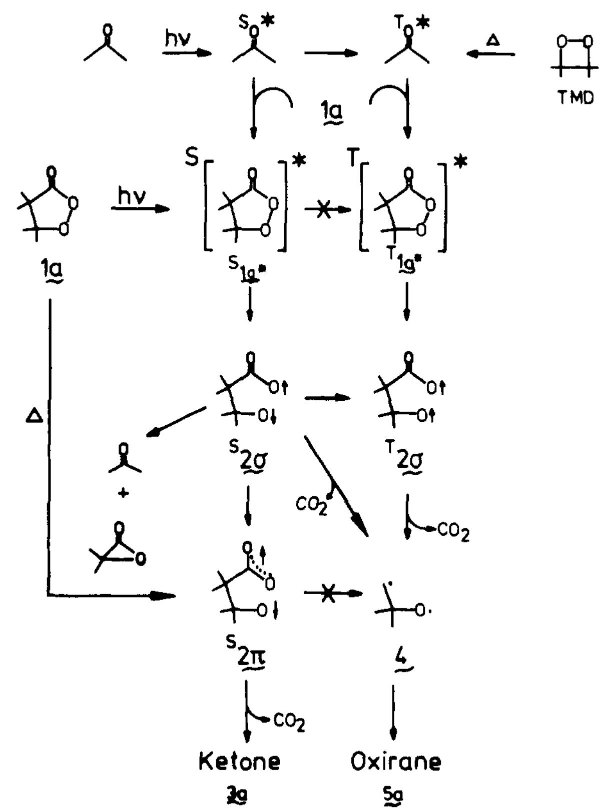


(1)

experimental evidence for the tetramethyl-β-peroxylactone (**1a**), which obliges us to modify this mechanistic interpretation. We postulate that in both decarboxylation modes 1,5 diradicals **2** of different electronic configurations intervene. Our evidence includes the following facts (cf. Table I): (i) thermolysis (125°C) gives exclusively pinacolone (**3a**); (ii) tetramethyl-1,2-dioxetane (TMD) chemienergization (60 °C) leads exclusively to tetramethyloxirane (**5a**); (iii) direct photolysis (355 nm) affords both pinacolone (**3a**) as major and tetramethyloxirane (**5a**) as minor products; (iv) acetone-sensitized photolysis (313 nm) results predominantly in tetramethyloxirane (**5a**), but the pinacolone product (**3a**) increases with increasing concentration of β-peroxylactone **1a**; (v) photolysis (355 nm) in the presence of piperylene (Pip) causes no alteration of the product composition; (vi) quantum yield of β-peroxylactone disappearance is 100%.

The mechanism which in our opinion accommodates best these unusual results is given in Scheme I. We postulate that the thermolysis gives rise to the singlet state π-type 1,5 diradical $^{S}\mathbf{2}\pi$, the triplet acetone-sensitized process (either via TMD chemienergization[4] or via photoenergization) leads to the triplet state σ-type 1,5 diradical $^{T}\mathbf{2}\sigma$ via the triplet excited β-peroxylactone $^{T}\mathbf{1a}^{*}$, while the direct photolysis affords the singlet state σ-type 1,5 diradical $^{S}\mathbf{2}\sigma$ via the singlet excited β-peroxylactone $^{S}\mathbf{1a}^{*}$. Intersystem crossing between $^{S}\mathbf{1a}^{*}$ and $^{T}\mathbf{1a}^{*}$ appears unlikely because the product compositions of the direct photolysis in the absence and presence of the triplet-state quencher piperylene (facts iii and v, respectively; cf. entries 3 and 5 in Table I) remained constant within experimental error, the TMD chemienergized process gave only oxirane **5a** (fact ii; cf. entry 2 in Table I), and the quantum yield of disappearance of the singlet excited β-peroxylactone is 100% (fact vi), which suggests that the weak peroxide bond in $^{S}\mathbf{1a}^{*}$ cleaves prior to any spin reorganization.

Scheme I



The fate of the singlet-state π-type 1,5-diradical $^{S}\mathbf{2}\pi$ in the thermolysis is exclusive formation of the rearrangement product pinacolone (fact i; cf. entry 1 in Table I). Although acyloxy radicals decarboxylate considerably more readily than alkoxy radicals undergo β scission,[5] theoretical considerations[6] imply that the resonance-stabilized π-type carboxylate radicals should be relatively reluctant in decarboxylating. Since no oxirane **5a** product was formed in the thermolysis, the decarboxylation process $^{S}\mathbf{2}\pi \rightarrow \mathbf{4}$ is not taking place. In fact, the

Table I. Product and Quantum Yields for the Decarboxylation of β-Peroxylactones **1a**

process	conditions	yields, %			
		ketone **3a**	oxirane **5a**	acetone	total
thermolysis[a]	125 °C, c-C_6H_{12}	100 ± 0.5	0.0	0.0	100 ± 0.5
TMD energized[a,b]	60 °C, n-C_6H_{14}	0.9 ± 0.1	97 ± 2	c	98 ± 2
photolysis[d,e] (direct)	355 nm, n-C_6H_{14}	49 ± 3	22 ± 1	26 ± 4	97 ± 4
photolysis[a,d-f] (sensitized)	313 nm, acetone	32 ± 1	44 ± 1	c	76 ± 2
photolysis[d,e] (1.0 M Pip)	355 nm, n-C_6H_{14}	50 ± 2	20 ± 2	25 ± 5	95 ± 5

[a] Product yields were determined by GLC. [b] 72 mmol of **1a** and 172 mmol of tetramethyl-1,2-dioxetane in 2 mL of Spectrograde n-hexane. [c] In the latter case the acetone product yield could not be determined since acetone was the solvent. Besides, as shown, the acetone yields are essentially constant in those cases in which it could be determined. [d] Quantum yields were determined by GLC for 15-20% consumption of **1a**; remaining **1a** was destroyed by catalytic hydrogenolysis. [e] To minimize product-sensitized decarboxylation of **1a**, we irradiated at as long a wavelength as was feasible. Furthermore, we measured the quantum yields for up to 15-20% β-peroxylactone **1a** consumption. Before GLC quantitation, the excess **1a** was destroyed by catalytic hydrogenolysis. [f] The [**3a**]/[**5a**] ratio was 0.08 and 0.70 at 0.01 and 0.10 M [**1a**], respectively.

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