When nonexponential decays were observed for pyrene fluorescence, we could calculate all four rate constants in Scheme I. This made it possible for us to obtain the equilibrium constant for end-to-end cyclization [$\langle K_1 \rangle = \langle k_1 \rangle / k_{-1}$] and ask the important question of whether k_{cy} and K_{cy} have the same dependence upon chain length. Our data indicate that $k_{-1} = (2.7 \pm 0.5) \times 10^6$ s^{-1} at 34.5 °C in cyclohexane for our five lowest molecular weight samples. Since k_{-1} is independent of chain length, K_{cy} must also vary with $M^{-1.62 \pm 0.1}$.

There are two features of this result which should be noted. The first is that polymer chains in Θ solvents are thought to have a Gaussian distribution of end-to-end distances.[15,16] For such a chain, the cyclization probability and thus K_{cy} should vary as $M^{-3/2}$. As in the case of polysiloxanes,[3] this prediction is (within experimental error) verified. The second aspect which we would like to point out is that there is currently some controversy about whether dynamic and thermodynamic behavior of polymers scale according to the same critical exponents.[17] The key aspects of the problem concern the behavior of polymer chains in good solvents, and not in Θ solvents. Our results provide an example in which dynamics and thermodynamics of end-to-end cyclization appear to have the same dependence on chain length in a Θ solvent, and they open the door to similar experiments in solvents where the excluded volume effects on the chains are substantial.

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Electronic Excited-State Analysis by Magnetic Circular Dichroism of d^6 (Alkylamino)pentacarbonyl Complexes, [M(CO)$_5$A]^0 (M = Cr, Mo, W)

Sir:

Transition-metal carbonyls are a class of photochemically and photocatalytically fascinating molecules undergoing diverse excited-state reactions, often with high quantum yields. Yet, the identity of the excited state for light absorption is nearly never directly identified. We report here direct band identifications for several Cr, Mo, and W molecules, [M(CO)$_5$A] (Cr, piperidine, cyclohexylamine; Mo, cyclohexylamine; W, ammonia piperidine, cyclohexylamine), by using magnetic circular dichroism (MCD) spectroscopy as follows.[1,2]

The definitive assignments come from MCD analysis applied to these closed-shell molecules and concern the (i) identification of ^{1}E excited states and their differentiation from excitations to C_{4v} states ^{1}A$_1$, ^{1}A$_2$, ^{1}B$_1$, and ^{1}B$_2$, viz., MCD A terms can occur only for ^{1}A$_1 \rightarrow {}^1$E, and (ii) the *sign* of the A term, since it can reveal the *orbital* fate of the excitation.

Specifically here, we consider the optical bands of M(CO)$_5$A which are to lower energy of the red-most band of M(CO)$_6$ as d–d transitions,[3] since Dq(amine) < Dq(CO). For example, at least bands I (∼430 nm), II (∼400 nm), and II′ (∼380 nm, shoulder) of W(CO)$_5$A (Figure 1) are of d–d type,[3] since W(CO)$_6$ has its two lowest energy bands at ∼350 and ∼310 nm (Figure 1). Furthermore, for interpretation of the d–d transitions of M(CO)$_5$A, the photoelectron spectroscopy (PES) data[4] for amines are of interest here, since they established that the t$_{2g}$ HOMO of the ground state is split into energy order e^4 (∼d$_{xz}$, d$_{yz}$) > b$_{2g}{}^2$ (∼d$_{xy}$). Next, the decision about how to associate the excited-state MOs, a$_1$ (∼d$_{z^2}$ M) or b$_1$ (∼d$_{x^2-y^2}$ M), with a d–d excitation ^{1}A$_1$ → ^{1}E [from e^4 (∼d$_{xz}$, d$_{yz}$ M) → e^3 a$_1{}^1$ (∼d$_{z^2}$ M) or e^4 (∼d$_{xz}$, d$_{yz}$ M) → e^3 b$_1{}^1$ (∼d$_{x^2-y^2}$ M)] can be made directly through MCD, since A/D ratios have opposite signs for the configuration changes, which will be shown subsequently.

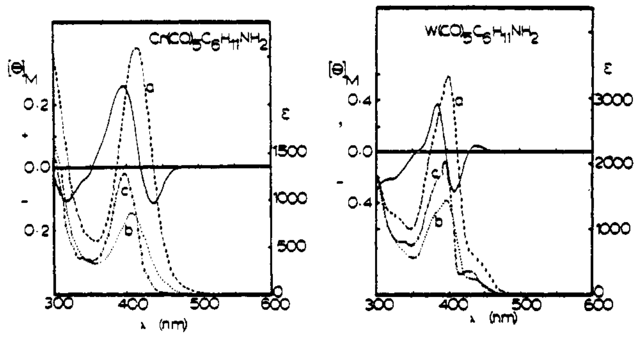
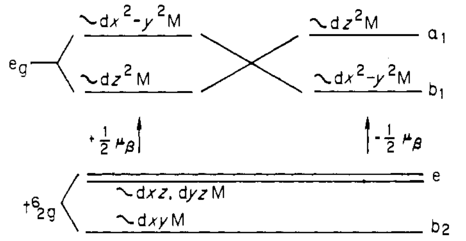


Figure 1. Optical and magnetic circular dichroism spectra of M(CO)$_5$ (cyclohexylamine): (a) MCD and optical spectra in dichloromethane at 300 K, (b) in EPA at 300 K, and (c) in EPA at 77 K (uncorrected for volume contractions). The solid line spectrum is the MCD of [M(CO)$_5$A]. $[\theta]_M$ is the molar ellipticity per gauss.



D is the electric dipole strength for the transition from the ground state (state function a) to the excited state (state function j), i.e., $D(a \rightarrow j)$ equals $1/d_a \sum_{a,j} |\langle a|m|j\rangle|^2$, or $|\langle {}^1\text{A}_1 \| m \| {}^1\text{E}\rangle|^2$, m is the electric dipole operator ($m_x + m_y$), a is ^{1}A$_1$, and j is ^{1}E, and $\langle {}^1\text{A}_1 \| m \| {}^1\text{E}\rangle$ is basis free.[5] Also, with a and j in the complex basis and μ and m real, the MCD A term equals $^1/_2 \sum \langle j|\mu|j\rangle \cdot Im\langle a|m|j\rangle \times \langle j|m|a\rangle$, or $-2^{-3/2} i \langle \text{E}\|\mu\|\text{E}\rangle |\langle \text{A}_1 \| m \| \text{E}\rangle|^2$, so that A/D equals $-2^{-3/2} i \langle {}^1\text{E}\|\mu\|{}^1\text{E}\rangle$, where $\langle {}^1\text{E}\|\mu\|{}^1\text{E}\rangle$ is a basis-free magnetic dipole state integral[2,5] which we evaluate ($\mu_z = \beta \text{L}_z$) as in eq 1.

$$\langle {}^1\text{E}\|\mu\|{}^1\text{E}\rangle = (\beta) 2^{1/2} \langle {}^1\text{E}_x|\text{L}_z|{}^1\text{E}_y\rangle \qquad (1)$$

Evaluation[6] of ⟨L⟩ for four electrons of ^{1}E[e^3 (∼d$_{xz}$, d$_{yz}$ Cr) a$_1{}^1$ (∼d$_{z^2}$)] or ^{1}E[e^3 b$_1{}^1$ (∼d$_{x^2-y^2}$)] simplifies to the one-electron integrals, as already shown (eq 2 and 3).[7] Furthermore, we will

$$\langle {}^1\text{E e}^3 \text{ a}_1{}^1(z^2) \| \text{L} \| {}^1\text{E e}^3 \text{ a}_1{}^1(z^2)\rangle = \langle \text{e}\|l\|\text{e}\rangle \qquad (2)$$

$$\langle {}^1\text{E e}^3 \text{ b}_1{}^1(x^2 - y^2) \| \text{L} \| {}^1\text{E e}^3 \text{ b}_1{}^1(x^2 - y^2)\rangle = -\langle \text{e}\|l\|\text{e}\rangle \qquad (3)$$

be selecting the z component, l_z, for purposes of evaluating $\langle \text{e}\|l\|\text{e}\rangle$ as $-2^{1/2}\langle \text{e}_x|l_z|\text{e}_y\rangle$. Dominant contributions to MOs with transformation behavior of e$_x$, e$_y$ will be assumed to come from d$_{yz}$, d$_{xz}$ orbitals of the metal,[6] on which operator l_z is based, so $\langle \text{e}_x|l_z|\text{e}_y\rangle$

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(1) A. F. Schreiner, S. Amer, W. M. Duncan, R. M. Dahlgren, and J. Zink, presentation at the 178th National Meeting of the American Chemical Society, Washington, D.C., Sept 1979; Abstr. 219, Inorganic Chemistry. This constitutes the first MCD report of molecules [M(CO)$_5$A].

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equals ca. $\langle d_{yz}|l_z|d_{xz}\rangle$. Converting to the complex basis in which l_z is diagonal, and since l_z operates only on $\Phi(\phi)$, we obtain eq 4. Similarly, for transition $\sim d_{xz}, d_{yz}$ Cr → $\sim d_{x^2-y^2}$ Cr, we obtain

$$\langle e_x|l_z|e_y\rangle \simeq -\langle d_{yz}|l_z|d_{xz}\rangle = -\left\{\frac{2^{1/2}}{2}i\left(\langle 2,1| - \langle 2,-1|\right) \times |l_z|\frac{2^{1/2}}{2}(|2,1\rangle + |2,-1\rangle)\right)\right\} \langle R(r,d_{yz})|R(r,d_{xz})\rangle = i \quad (4)$$

$A/D = -{}^1/_2\beta$. The sign difference of the A terms for $^1A_1 \rightarrow {}^1E$ will therefore differentiate between transitions to the two different orbital types. This applies to the present data as follows.

The dominant optical band II, and the one of great photochemical interest,[8–12] at ~400 nm of each compound has a distinct MCD A term of positive sign (Figure 1). These bands are therefore directly assignable to $^1A_1 \rightarrow {}^1E_1$. Additionally, the orbital character can be assigned, from the *sign* of the A term, e.g., to e^4 ($\sim d_{xz}$, $\sim d_{yz}$ Cr) → $e^3\,a_1^{\,1}$ ($\sim d_{z^2}$ Cr) (A/D positive), ruling out the $\sim d_{xz}, d_{yz}$ Cr → $\sim d_{x^2-y^2}$ Cr assignment (A/D negative). Thus, excited state *and* excited orbital assignments are made directly for this photochemically important band II.

Bands III at 350 (Cr) and ~340 nm (Mo and W) are tentatively assigned to the vibronically allowed transition $^1A_1 \rightarrow {}^1A_2$ (T_{1g} $[t_{2g}{}^5e_g{}^1]$) since (i) for the first time fine structure is observed here at 80 K, and (ii) their intensities decrease in going from room temperature to 80 K.

Band types I and III are clearly and distinctly present only in the $W(CO)_5A$ complexes, band I is present weakly in $Mo(CO)_5A$ and absent in $Cr(CO)_5A$, and band II′ is absent in Cr and Mo complexes. Therefore, band I is assigned to the spin-forbidden transition $^1A_1 \rightarrow {}^3E$ of the e^3 ($\sim d_{xz}, d_{yz}$) $a_1^{\,1}$ ($\sim z^2$) excited orbital origin. Since the appearance of band II′ (blue shoulder of band II) follows that of band I, band II′ is also attributed to a spin-orbit-allowed transition, perhaps of $^1A_1 \rightarrow {}^3A_2$ origin, whose spin-allowed partner would be band III. Such assignments were offered for similar molecules.[8,9]

The main conclusion is that MCD directly assigns band II, the band of great photochemical interest.[8–12] Our measurements were carried out as previously described.[13]

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Organic Photochemistry with 6.7-eV Photons: Rigid Homoallylic Alcohols. An Inverse Norrish Type II Rearrangement

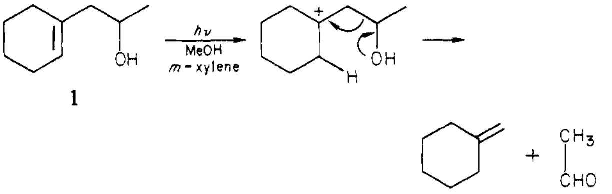
Sir:

There are numerous examples of the photoprotonation of six- and seven-membered cyclic alkenes, which takes place on sensitized photolysis in an appropriate solvent.[1] Kropp and co-workers,[2–4] who have studied this process extensively, have proposed that photoprotonation is preceded by a light-induced cis → trans isomerization of the olefin, and protonation occurs as a secondary ground-state reaction of the highly strained trans olefin. In the case of homoallylic alcohols,[5] this reaction proceeds as in eq 1.[6]

Table I. Rates and Compositions of Aldehydic Products from Homoallylic Alcohols **2**–**5**[a]

reactant	ratio 6/7	ratio 8/9	total rate of aldehyde formation, mol/L/min
2	1.6		7.0×10^{-6}
3	1.0		5.3×10^{-6}
4		2.1	3.2×10^{-6}
5		1.0	1.4×10^{-6}

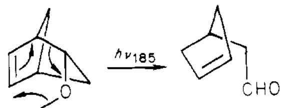
[a] For reaction conditions, see ref 9.



(1)

On direct irradiation with an unfiltered mercury arc, a homoallylic alcohol with a cyclohexene group underwent a similar fragmentation, but one with a cyclopentene group did not.[7] These results will be discussed later.

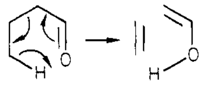
In this communication, we show that direct irradiation of homoallylic alcohols which incorporate the olefinic group in a rigid, bicyclic framework results in an intramolecular process which leads to an isomeric, monocyclic, unsaturated aldehyde. In the case of bicyclo[2.2.1]hept-5-en-2-ol (**2**), this reaction can be represented as in eq 2. Since this reaction formally involves the abstraction of a hydrogen from a hydroxyl group by an olefin possibly via a six-membered cyclic intermediate to yield a carbonyl group, it can be viewed as the inverse of the Norrish type II process (compare eq 2 to eq 3).[8]



major product

2

(2)



(3)

The homoallylic alcohols **2**–**5** exhibit ultraviolet absorptions (solvent: pentane) which are indistinguishable from those of the

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(1) For reviews, see (a) P. J. Kropp, C. Ouannes, and R. Beugelmans in "Elements de Photochimie Avancée", P. Courtot, Ed., Hermann, Paris, 1972, pp 229–288; (b) P. J. Kropp, *Mol. Photochem.*, **9**, 39 (1978–1979).

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(6) In the case of cholesterol in which the –OH group is bound to the cyclohexene by a fused ring, a similar reaction leads predominantly to oxetanes which are derived by the intramolecular addition of the aldehyde to the exo methylene olefin [Y. Kondo, J. A. Waters, B. Witkop, D. Guenard, and R. Beugelmans, *Tetrahedron*, **28**, 797 (1972)].

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(8) A purely formal view can be confusing as there is also a thermal reaction of homoallylic alcohols which is formally similar to reaction 2 [R. T. Arnold and G. Smolinsky, *J. Am. Chem. Soc.*, **82**, 4918 (1960)]. The deuterium labeling experiments which are described later in this communication show that the view of reaction 2 as the inverse of the Norrish type II process is not merely a formalism but duplicates the latter in detail.

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