a metal–carbon σ bond with free rotation about the olefinic bond. Thermal *cis*- → *trans*-stilbene isomerization catalyzed by $Fe(CO)_5$ or metal carbonyl thermally catalyzed isomerization of 1,2-dichloroethylene[4] may proceed through a similar intermediate. Very recent work has also implicated the formation of σ-bonded olefins in the thermal decomposition of (*trans*-$CF_3CH{=}CHCF_3$)$Fe(CO)_4$ and related compounds.[18] The difference in the photoassisted isomerization is that the isomerizing configuration is achieved *via* electronic excitation by absorption of light. As pointed out above, the transition responsible for the lowest observed uv absorption of the hexacarbonyls has substantial singlet-to-triplet character. Thus the olefin complex may reach a triplet configuration by direct absorption as well as by intersystem crossing from a singlet. The large spin–orbit coupling of the heavy metal atom facilitates intersystem crossing; in fact, in the case of tungsten, spin–orbit effects could be so large that it becomes meaningless to talk about discrete singlet and triplet excited states. Nonradiative decay from the electronic state achieved in absorption may take the form of intramolecular rearrangement leading to intermediate IV with two unpaired electrons and free rotation about the olefinic bond. Decay to yield a metallocyclopropane intermediate (singlet) would not be expected to result in efficient isomerization.

Acknowledgment. This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research (Contract No. AF OSR-71-1958), and the National Science Foundation.

[18] R. Fields, G. L. Godwin, and R. N. Haszeldine, *J. Organometal. Chem.*, 26, C70 (1971), and references cited therein.

[19] National Institutes of Health Trainee.

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New Aquo Ions of Molybdenum

Sir:

The aquo ion $Cr(H_2O)_6{}^{3+}$, by virtue of its slowness to undergo substitution, has attracted special attention in the past two decades. By contrast, little effort has been devoted to its congener $Mo(H_2O)_6{}^{3+}$, despite the fact that the higher oxidation states of molybdenum are more stable than those of chromium, and $Mo(H_2O)_6{}^{3+}$ thus would seem to offer some unusual opportunities for exploring redox behavior. Hartmann and Schmidt[1] purport to have measured the ligand-field spectrum of $Mo(H_2O)_6{}^{3+}$ in 4 *M* HCl, 4 *M* HBr, and 4 *M* H_2SO_4, and describe the ion as being green. It is difficult to understand why $Mo(H_2O)_6{}^{3+}$ as a member of the second-row transition series should show strong absorption in the region of 600 nm, and, in view of the results we report here, it appears unlikely that Hartmann and Schmidt were actually dealing with $Mo(H_2O)_6{}^{3+}$.

When K_3MoCl_6 is dissolved in acidified water, absorption bands are observed initially at 520 (ϵ 45.3), 416 (61.6), and 308 nm (213). In 6 *M* HCl, the absorption characteristics remain unchanged over a period of 2 days, but when the medium is 1 *M* trifluoromethylsulfonic acid (HTFMS) or 1 *M* *p*-toluenesulfonic acid (HPTS)[2] the red solution changes to yellow, and after 1.5 days absorption in the visible spectral region has disappeared, but a strong band (ϵ 6.0×10^2) develops at 293 nm.

The solution of Mo(III) in HPTS was placed on a cation-exchange column 50W-X2. Analysis of the liquid which passed through, and of the wash water, showed that more than 5 mol of Cl^- had been set free for each mole of Mo(III). By using 0.5 *M* HPTS, a yellow band was eluted from the column, and with 1 *M* HPTS a second band, lighter in color, was slowly eluted. The solution containing the light yellow species was collected. Analysis showed that the average oxidation state of molybdenum was still 3+, and that the solution was free from Cl^-. The analytical evidence and the elution behavior indicate that we have the ion $Mo(H_2O)_6{}^{3+}$ in hand. By following the procedure outlined, about 90% of the total molybdenum is obtained as Mo^{3+}. The conclusion that we have the aquo ion is supported by the measurement of the absorption characteristics. There is no significant absorption in the visible, but strong bands appear at 293 (6.0×10^2) and 253 nm (7.2×10^2) (*cf.* Figure 1.) The same spectrum is obtained if the solution in 1.5 *M* HTMS is kept under argon for 2 days. This indicates that aquation of a dilute solution of $MoCl_6{}^{3-}$ is virtually complete at equilibrium.

When solutions containing Mo(III) are stored for a time (see below), a green color develops. Earlier efforts[4] to produce $Mo(H_2O)_6{}^{3+}$ by reduction of Mo(VI) also yielded green solutions. (Those described by Hartmann and Schmidt were obtained by reduction.) It seems likely that the green species is a condensation product of Mo(III).

We turn now to describe a method for the preparation of the aquo ion of Mo(II), which, in contrast to Cr(II), exists in the dimeric form. Attempts to prepare $Mo_2{}^{4+}$(aq), reducing $MoCl^{2+}$(aq) by the method[5] which yielded $Rh_2{}^{4+}$, were only partially successful. A solution containing $MoCl^{2+}$(aq)[6] and dilute Cr^{2+} shows mainly the color of Cr^{2+}, but turns green after a few days. The same color change takes place even without Cr^{2+}. When EDTA is added to a mixture of $MoCl^{2+}$ and Cr^{2+}, immediate reaction occurs, producing a reddish brown solution and a precipitate of the same color. Taking note of the color, we surmise that some $Mo_2{}^{4+}$ is formed by this method, but it is clear that the reaction is by no means quantitative. An alternative method (to be described) of preparing $Mo_2{}^{4+}$ showing promise, we gave up further work attempting to reduce $MoCl^{2+}$(aq). It should be noted that a method for preparing $Mo_2{}^{4+}$ which is dependent on cation-exchange separation, as is the case with the

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[1] H. Hartmann and H. J. Schmidt, *Z. Phys. Chem.* (*Frankfurt am Main*), **11**, 234 (1957).

[2] It has been shown[3] that when a solution of $Cr(H_2O)_6{}^{3+}$ is made 6 *M* in HTFMS, complex formation is negligible. There is no reason to believe that Mo(III) will have a higher affinity for $TFMS^-$ than does Cr(III), and our experience indicates that even with PTS^-, which is expected to be somewhat more nucleophilic than $TFMS^-$, complex formation at the 1 *M* level is negligible.

[3] A. Scott and H. Taube, *Inorg. Chem.*, 10, 62 (1971).

[4] A. B. Hoffman and H. Taube, unpublished observations.

[5] F. Maspero and H. Taube, *J. Amer. Chem. Soc.*, 90, 2361 (1968).

[6] The species $MoCl^{2+}$(aq) is separated by cation exchange from a solution of K_3MoCl_6 in 1 *M* TFMS which had been allowed to aquate for *ca.* 12 hr.

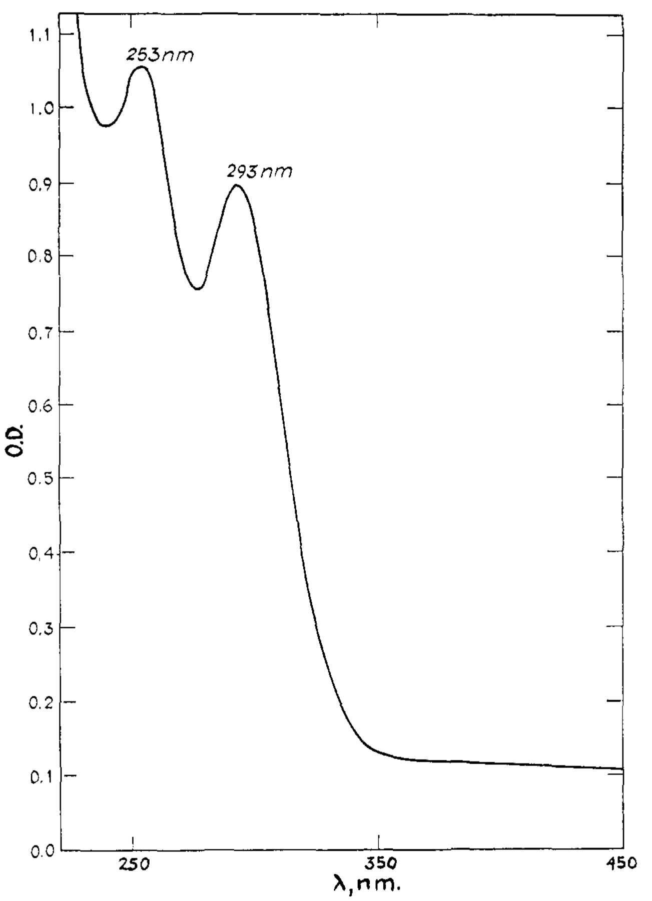

Figure 1. Mo(III) (1.33×10^{-3} *M*) eluted from a cation-exchange column by 1 *M* trifluoromethylsulfonic acid.

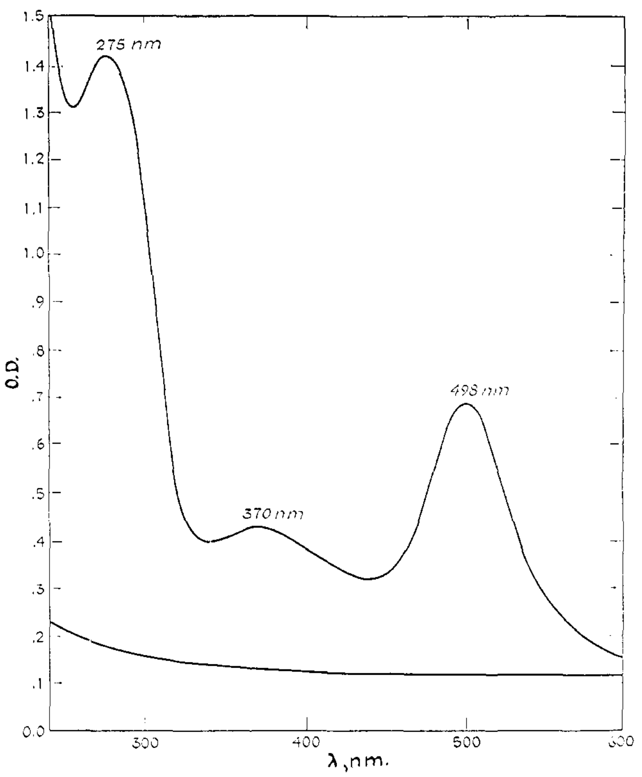

Figure 2. The spectrum of Mo_2^{4+} as prepared from $K_4Mo_2(SO_4)_4$. [Mo_2^{4+}] = 2.7×10^{-4} *M* in 0.5 *M* HTFS. Lower curve is 0.5 *M* HTFS.

Cr^{2+}–$MoCl^{2+}$ procedure, is tedious and inconvenient because the ion Mo_2^{4+} is very difficult to elute from a column.

A convenient method which we believe does produce Mo_2^{4+} is described herewith. A solution *ca.* 0.01 *M* in $K_4Mo_2Cl_8 \cdot 2H_2O$[7] and 0.25 *M* in TFMS was prepared and kept under Ar for 3 hr. (The solution remained red during this interval of time, but there was some change in hue.) It was then saturated with K_2SO_4, whereupon a reddish pink precipitate formed (the solution itself turned green at this point). The solid was collected in the absence of oxygen; it was washed and then dried *in vacuo*. *Anal.* Calcd for $K_4Mo_2(SO_4)_4$: K, 21.4; Mo, 26.2; SO_4^{2-}, 52.4. Found: K, 21.0; Mo, 25.9; SO_4^{2-}, 52.0. The ir spectrum was taken and indicated that the sulfate in the solid is bidentate.

The red-pink solid, when dissolved in 1 *M* HTFMS, shows absorption bands at 512 and 382 nm. When it is made 0.1 *M* in $Ba(TFMS)_2$, $BaSO_4$ forms, the precipitation being complete within 30 min. After removal of the sulfate, the species shows absorption bands at 498 (ϵ 248), 370 (108), and 275 nm (434) (*cf.* Figure 2).

By using Fe^{3+} as oxidant, and determining the total Mo, the average oxidation state of Mo in the red species was found to be 2+. The product of the oxidation of Mo_2^{4+} by excess Fe^{3+} is Mo(VI). The species is very strongly held by cation-exchange resin, and is not elutable by 1 *M* HTFMS. To elute it, unless very high concentration of electrolyte is to be used, resort must be had to cations of higher charge. It is eluted by 0.02 *M* La^{3+} and by 3 *M* H_2SO_4 (in the latter case, complex formation with SO_4^{2-} undoubtedly plays a role in the elution process).

The cation-exchange behavior shows the new species to have a charge of greater than 3+ per molecule. The general resemblance of the spectrum to that of freshly dissolved $K_4Mo_2Cl_8$ [in 6 *M* HCl this has maxima at 518 (3.4×10^2) and 420 nm (1.6×10^2) and a very weak band at 745 nm (1.82)] shows that the Mo–Mo bond, present[7] in the species $Mo_2Cl_8^{4-}$, is retained in the aquo ion. On the basis of the evidence outlined, we take the species to be Mo_2^{4+}.

If oxygen is excluded, Mo_2^{4+} in acid solution can be kept for long periods of time. After a month in the dark, some oxidation appears to have taken place. The species is quite tractable, and promises to have an extensive chemistry.[8] Thus we have prepared a solid answering closely to the composition $Mo_2(en)_4Cl_4$. This dissolves in acidic solution with yellow-orange color, and shows the long-wavelength maximum now shifted to 474 nm. The species, which is presumed to be $Mo_2(en)_4^{4+}$, is much more resistant to attack by O_2 than is Mo_2^{4+}(aq).

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(7) J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **8**, 7 (1969).

(8) This potential is already implied by the successful conversion of $Mo_2(OAc)_4$ to $Mo_2Cl_8^{4-}$ by concentrated HCl.[7] A large number of salts containing the ion $Mo_2Cl_8^{4-}$, as well as some containing $Mo_2Cl_8^{3-}$, have been described by Cotton and coworkers. References can be found in the latest paper of a series: J. V. Brencic and F. A. Cotton, *ibid.*, **9**, 351 (1970).

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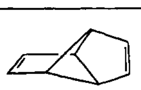
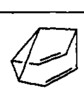
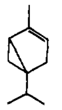
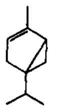
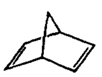
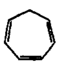
Linear Relationship between Ultraviolet Absorption Transition Energies and Activation Energies for Thermal Isomerization of Cyclic Olefins[1]

Sir:

We have observed an unusually low-energy ultraviolet transition for bicyclo[2.1.0]pent-2-ene (**1**), $\lambda^{\text{gas}}_{\text{max}}$ 263 nm (ϵ ~440).[2,3] This highly strained bicyclic olefin undergoes facile thermal isomerization to cyclopentadiene (**2**) (E_a = 26.9 kcal mol^{-1})[4] and is the most paramagnetic cyclic olefin yet subjected to molecular rotational Zeeman effect studies: $(2\chi_{cc} - \chi_{aa} - \chi_{bb}) = +3.6 \times 10^{-6}$ erg G^{-2} mol^{-1}.[5,6] 2-Methylbicyclo[2.1.0]pent-2-ene (**3**) has been shown to rearrange thermally to 1-methylcyclopentadiene (**4**), presumably through a symmetry-allowed but rarely encountered $[_\sigma 2_s + _\sigma 2_a]$ cycloreaction.[7]

Table I. Ultraviolet Absorption Maxima and Activation Energies for Rearrangement of Cyclic Olefins

Olefin	Product	$\lambda_{\max}$, nm	$\tilde{\nu}$, cm^{-1} $\times 10^{-3}$	E_a, kcal mol^{-1}
		300[a]	33.3	~22[a,b]
		263[c]	38.0	26.9[d]
		250[e]	40.0	~31[b,f]
		226[g]	44.2	35.2[h]
		~213[i]	46.9	43.4[j]
		189[k]	52.9	51.6[l]
		175[m]	57.1	57.3[n]

[a] J. Meinwald and H. Tsuruta, *J. Amer. Chem. Soc.*, **91**, 5877 (1969); **92**, 2579 (1970). [b] Estimated from the Arrhenius equation assuming log A = 14. [c] This work and ref 2. [d] Reference 4. [e] J. Meinwald and B. E. Kaplan, *J. Amer. Chem. Soc.*, **89**, 2611 (1967); M. B. Robin, H. Basch, N. A. Kuebler, B. E. Kaplan, and J. Meinwald, *J. Chem. Phys.*, **48**, 5037 (1968). [f] J. Meinwald and D. Schmidt, *J. Amer. Chem. Soc.*, **91**, 5877 (1969). [g] J. Meinwald and F. Uno, *ibid.*, **90**, 800 (1968). [h] H. M. Frey, R. G. Hopkins, H. E. O'Neal, and F. T. Bond, *Chem. Commun.*, 1069 (1969). [i] Unpublished observations on a sample of 6-methylbicyclo[3.1.0]hex-2-ene kindly provided by R. S. Cooke. [j] W. v. E. Doering, Lecture, Twenty-First National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June 18, 1969. [k] K. Stich, G. Rotzler, and T. Reichstein, *Helv. Chim. Acta*, **42**, 1480 (1959). [l] J. H. Birely and J. P. Chesick, *J. Phys. Chem.*, **66**, 568 (1962). [m] C. Heathcock, unpublished observations, private communication, Oct 1970. [n] C. A. Wellington, *J. Phys. Chem.*, **66**, 1671 (1962).

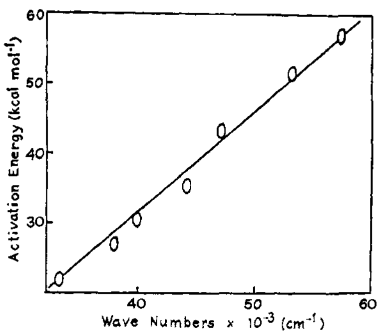
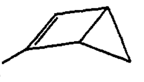
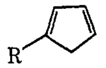


Figure 1. Empirical correlation between Arrhenius activation energy for thermal rearrangement and $\tilde{\nu}$ of the $\pi \rightarrow \pi^*$ electronic transition for the cyclic olefins of Table I.



1, R = H
3, R = CH$_3$



2, R = H
4, R = CH$_3$

A number of other cyclic olefins known to suffer formally analogous thermal rearrangements display a linear correlation between ultraviolet absorption transition energies and activation energies. The data are gathered in Table I and plotted in Figure 1; the dimensionless slope of the correlation is 0.5.

Expressions for the diagonal matrix elements in the diamagnetic and paramagnetic molecular magnetic susceptibility tensors are available.[8,9]

$$\chi^{d}_{aa} = -\frac{e^2}{4mc^2}\langle 0|\sum_i (b_i^2 + c_i^2)|0\rangle \qquad (1)$$

$$\chi^{p}_{aa} = -\frac{\beta^2}{2\hbar^2}\sum_{k>0}\frac{|\langle 0|L_a|k\rangle|^2}{E_0 - E_k} \qquad (2)$$

$$\chi_{\text{total}} = \chi^{d} + \chi^{p} \qquad (3)$$

In eq 1 and 2, b_i and c_i are the coordinates of electron i, and L_a is the projection of electronic angular momentum along the a axis.

The diamagnetic contribution, χ^d, depends solely upon the electron density of the ground state, while the paramagnetic contribution to χ_{total} depends on mixing of ground and excited states by the electronic orbital magnetic moment operator. Thus, as noted by

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(1) This work was supported by National Science Foundation Grant No. GP 9259, the Cities Service Oil Co., and the Du Pont Co.

(2) Initially reported in conjunction with the microwave spectroscopic studies of **1**: A. H. Andrist, S. L. Hsu, T. D. Gierke, R. C. Benson, W. H. Flygare, and J. E. Baldwin, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, No. PHYS 184.

(3) This observation has been corroborated by an independent study: J. I. Brauman, private communication, March 1970.

(4) D. M. Golden and J. I. Brauman, *Trans. Faraday Soc.*, **65**, 464 (1969).

(5) S. L. Hsu, A. H. Andrist, T. D. Gierke, R. C. Benson, W. H. Flygare, and J. E. Baldwin, *J Amer. Chem. Soc.*, **92**, 5250 (1970).

(6) Compare this value with those presented in Table V of R. C. Benson and W. H. Flygare, *ibid.*, **92**, 7523 (1970).

(7) J. E. Baldwin and A. H. Andrist, *Chem. Commun.*, 1561 (1970).

(8) J. R. Eshbach and M. W. P. Strandberg, *Phys. Rev.*, **85**, 24 (1952).

(9) W. H. Flygare and R. L. Shoemaker, *Symp. Faraday Soc.*, No. 3, 119 (1970).