vibronic modes of the coordinated ligands. Therefore, replacement of inner sphere water molecules of the hydrated Cm^{3+} ion by other complexing ligands can cause changes in the life-time of the fluorescence emission, and for a Cm humate an increase of life-time is expected.

In Figure 4, the life-time measurement of Cm humate (T1) complex {plot (a), $[Cm]=6.3\times10^{-8}$ mol/*l*, $[HA]=9.36$ mg/*l*}, and hydrated Cm^{3+} ion {plot (b), $[Cm]=3.7\times10^{-8}$ mol/*l*} are shown. The life-time of the reference hydrated Cm^{3+} ion is found to be 72 μs, which is slightly longer than that reported by Beitz, and this maybe caused by MES buffer. The life-time measurement of Cm humate gave two different time components: 47 μs (minor) and 146 μs (major), as seen by the plot (a) in Figure 4 which shows a discrepancy from the linear line. The minor component of the life-time, 47 μs, is not clearly understood at present and is being further investigated. However, the major life-time component, 146 μs, is comparable to that obtained for the Cm carbonate complex[14], 141 μs.

This preliminary results seem to suggest that the complextion behaviour of humates of differing origins with Cm^{3+} can be investigated at very low concentration for both constituents by TRFLS, thus avoiding the humus aggregation phenomena. All three applications of TRLFS (excitation spectra, emission spectra and life-time of the fluorescence measurement) conclusively show the formation of Cm humate complex. The measured peak shift in the emission spectra and the difference of life-time between the hydrated Cm^{3+} ion and Cm-humate implies a strong inner sphere complexation almost exclusively by the carboxylic groups of the humic acid at pH 6.

Aknowledegement. The author thanks Prof. J. I. Kim, Institute of Radiochemistry at the Technical University of Munich for his support and the use of TRLFS. This work has been funded by the Korea Advanced Institute of Science and Technology.

References

1. J. I. Kim, in "Handbook of physics and chemistry of actinides", Vol. 4, Chap. 7, A. J. Freeman and C. Keller Eds., North-Holland Phys. Publ., Amsterdam (1986).
2. G. R. Choppin, *Radiochim. Acta*, **44/45**, 23 (1988).
3. M. Schnitzer, in Proc. Symposium on soil organic matter studies, Braunchweig, International Atomic Energy, 117, Vienna (1977).
4. J. I. Kim and G. Buckau, Institute fur Radiochemie,TU Munchen, RCM 01588 (1988).
5. M. Caceci, *Radiochim. Acta* **44/45**, 51 (1985).
6. E. Bertha and G. R. Choppin, *J. Inorg. Nucl. Chem.*, **40**, 655 (1978).
7. R. A. Torres and G. R. Choppin, *Radiochim. Acta*, **35**, 143 (1984).
8. V. Moulin, P. Robouch, P. Vitorge, and B. Allard, *Inorg. Chim. Acta* **140**, 303 (1987).
9. J. I. Kim, H. Wimmer, and R. Klenze, *Radiochim. Acta*, submitted for publication (1990).
10. P. Decambox, P. Mauchien, V. Moulin, and C. Moulin, *Radiochim. Acta*, in press (1990).
11. J. V. Beitz, *Radiochim. Acta*, in press (1990).
12. W. T. Carnal and K. Rajnak, *J. Chem. Phys.*, **63**, 3510 (1975).
13. J. V. Beitz and J. P. Hessler, *Nucl. Technol.* **51**, 169 (1980).
14. R. Klenze, J. I. Kim and H. Wimmer, *Radiochim. Acta*, in press (1990).
15. J. V. Beitz, D. L. Bower, M. M. Doxtader, V. A. Maroni, and D. T. Reed, *Radiochim. Acta* **44/45**, 87 (1988).
16. H. Moon, M. H. Lee, and T. H. Yoon, *Bull. Korean Chem. Soc.*, **12**, 2 (1990).
17. S. Hufner, in "Optical spectra of transparent rare earth compounds", Academic Press, New York, London, 38 (1978).

Substituent and Solvent Effects on the Excited States of 4,4-Disubstituted Cyclohex-2-enones

Hwa Sung Lee, Kye Sook Namgung, Jung Kyou Sung, and Woo Ki Chae*

Department of Chemistry Education, Seoul National University, Seoul 151-742

Received January 9, 1991

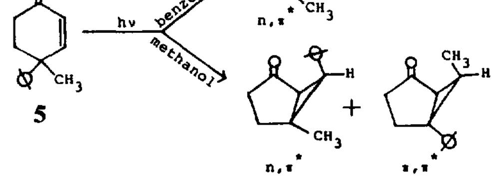
4,4-Disubstituted cyclohex-2-enones can undergo a variety of reactions upon excitation. The choice of reaction pathway by such compounds appears to be dependent upon the character of low-lying triplet states.[1-7]

The rearrangement of 4,4-diphenylcyclohex-2-enone (**1**) to give bicyclo (3,1,0) hexan-2-one (**2**) is thought to occur from the n, π* triplet state,[2] whereas skeletal rearrangement such as 4,4-dimethylcyclohex-2-enone (**3**) to 6,6-dimethylbicyclo (3,1,0) hexan-2-one (**4**) have been attributed to the π, π* triplet state.[3,4]

In order to evaluate these suggestions, Dauben[4] studied solvent effect on the excited states of 4-methyl-4-phenylcyclohex-2-enone (**5**). Irradiation of **5** in benzene, a nonpolar solvent, gave products arising from n, π* triplet state. The photochemistry of **5** was also investigated in a polar solvent which wouled lower the energy of the π, π* triplet state.

These studies of compound **5** supports the suggestions that rearrangement of the type **1** to **2** results from n, π* triplet state, while rearrangement of the type **3** to **4** results from π, π* triplet state.

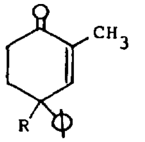
Since the compound **5** is potentially capable of phenyl migration and methyl migration processes, a proximity of n, π* and π, π* triplet states would also be expected.



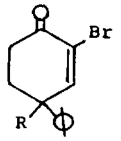
The n, π^* triplet state of **5** causes the phenyl migration, whereas the π, π^* triplet state causes the methyl migration as shown above. But the solvent effect only becomes important when the n, π^* and π, π^* states are very close in energy.[5,6]

Schaffner and Kearns[7] investigated singlet-triplet transition by photoexcitation spectroscopy of some steroids, conjugated enones, in order to acquire detail information on both the nature and location of the low-lying excited singlet and triplet states in these molecules. They also found that the n, π^* and π, π^* triplets are close together in energy and substituents on the α-carbon of the enones lower the π, π^* triplet energy level.

In this paper, we wish to report the photochemical rearrangement of 2-substituted cyclohex-2-enone derivatives (**6**, **7**) to discuss both Schaffner's substituent and Dauben's solvent study on the relative energy levels of the n, π^* and π, π^* triplet states.

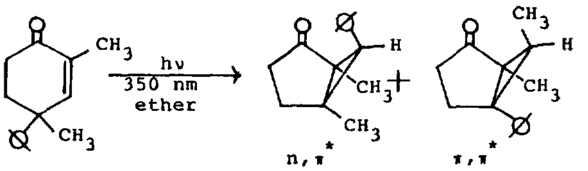


6a:R=methyl
6b:R=phenyl



7a:R=methyl
7b:R=phenyl

Direct irradiation of 2,4-dimethyl-4-phenylcyclohex-2-enone (**6a**) in ether with 16 RPR-3500 Å lamps produced both of methyl and phenyl migrated products as shown below.

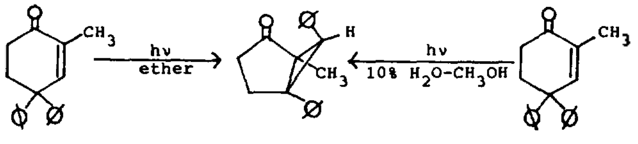


6a 6c 6d

The photoproducts, **6c** and **6d**, were identified by spectroscopic method[8] and the electronic configuration of the responsible triplet states[9] were assigned according to Dauben[4] and Kearns' works.[3]

When more polar solvent, water-methanol, was used for irradiations of **6a**, relative amount and quantum efficiency of **6d** were increased as shown in Table 1. These results indicate, as mentioned earlier, that polar solvent and methyl substituent lower the energy level of π, π^* triplet states and (or) changed the relative energy levels of n, π^* and π, π^* states.

Direct irradiation of 2-methyl-4,4-diphenylcyclohex-2-enone (**6b**) in ether with 16 RPR-3500 Å lamps produced only 5,6-diphenylbicyclo [3,1,0] hexan-2-one (**6e**) resulting from n, π^* triplet state which causes phenyl migration.[4] An increased solvent polarity such as 10% water-methanol also produced **6e** only.



6b 6e 6b

Table 1. Product Distribution on the Irradiation of **6** in Different Solvent Polarity

Solvents	Φ		Relative ammounts(%)	
	6c	**6d**	**6c**	**6d**
Ether	0.001	0.0001	91	9
10%-H_2O-CH_3OH	0.0009	0.0005	64	36
30%-H_2O-CH_3OH	—[a]	—[b]	62	38

[a,b]not determined; Φ: quantum efficiency of product appearance.

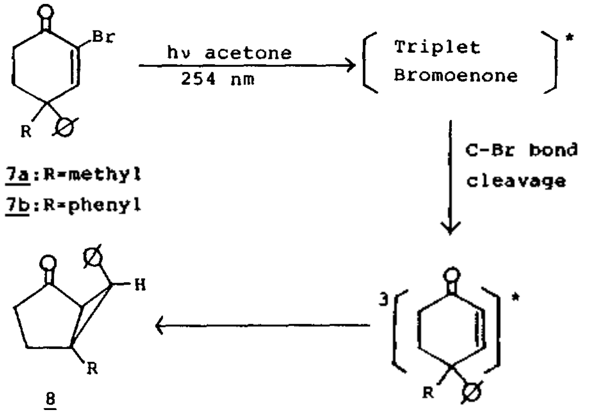
These results, as Zimmerman's works,[2] indicate that the triplet energies of n, π^* and π, π^* are not close enough to change the relative energy levels by the solvent polarity.

Irradiation of 2-bromo-4-methyl-4-phenylcyclohex-2-enone (**7a**) and 2-bromo-4,4-diphenylcyclohex-2-enone (**7b**) in benzene respectively with medium pressure Hg-arc lamp showed no reactions. During the irradiation of **7a** and **7b** for 44 hours, both reactants remained unchanged. The stability of **7a** and **7b** against photons would be explained by increased radiationless decay efficiency of excited states which have a heavy atom on α-carbon of the enones **7**.

Givens and co-workers[10] suggested that heavy atoms could increase the importance of the radiationless decay pathway of triplet excited state, and the radiationless decay processes of singlet excited state by heavy atom was also shown by Foster and Dudley.[11]

Since heavy atom could increase the efficiency of the both singlet and triplet radiationless decay, **7a** and **7b** were sensitized by acetone to see the expected n, π^* and π, π^* triplet products.

Acetone sensitized irradiation of **7a** and **7b** showed a secondary photoproduct after C-Br bond cleavage as shown below.:



7a:R=methyl
7b:R=phenyl

8

It was concluded that the singlet excited state of enone **7** undergo fast radiationless decay to the ground state and C-Br bond cleavage occurs in the triplet excited state, then undergo to the enone photo-rearrangement.[4]

Methyl substituent on α-carbon of the enone **5** and solvent polarity, however, lower the energy π, π^* triplet state or changed the relative energy levels of n, π^* and π, π^* triplet states of enone **6a**.

Acknowledgement. This work was supported by the Basic Science research Institute Program (1990), Ministry of Education and in part from the Daewoo Research Fund in SNU (1988).

References

1. (a) H. E. Zimmerman, X. Jian-hua, R. K. King, and C. E. Caufield, *J. Am. Chem. Soc.*, **107**, 7724 (1985); (b) H. E. Zimmerman and R. K. King, *ibid*, **107**, 7732 (1985); (c) H. E. Zimmerman and D. C. Lynch, *ibid*, **107**, 7745 (1985).
2. H. E. Zimmerman and K. G. Hancock, *J. Am. Chem. Soc.*, **90**, 3749 (1968).
3. K. Schaffner, D. R. Kearns, and D. Bellus, *Helv. Chim. Acta*, **52**, 971 (1969).
4. W. G. Dauben, W. A. Spitzer, and M. S. Kellog, *J. Am. Chem. Soc.*, **93**, 3674 (1971).
5. K. Schaffner, D. R. Kearns, and G. Marsh, *Helv. Chim. Acta*, **51**, 1890 (1968).
6. A. A. Lamola, *J. Chem. Phys.*, **47**, 4810 (1967).
7. K. Schaffner, D. R. Kearns, and G. Marsh, *J. Am. Chem. Soc.*, **93**, 3129 (1971).
8. Spectral data for **6c**: NMR ($CDCl_3$) δ 1.4 (singlet, 3H) 1.48 (singlet, 3H) 1.7-2.5 (multiplet, 5H) 7.27 (singlet, 5H); IR (KBr) 3050 cm^{-1}, 1705, 1600; Mass (m/e) 91, 128, 129, 143, 158, 200; Anal Calcd. $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83,78; H, 7.72. Spectral data for **6d**: NMR ($CDCl_3$) δ 1.05 (doublet, 3H) 1.65 (doublet, 3H) 1.8-3.1 (multiplet, 5H) 7.0-7.5 (multiplet, 5H); IR (neat 3050, 1705, 1650, 1600; Mass (m/e) 77, 91, 115, 129, 143, 158, 200; Anal. Calcd. $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.61; H, 7.70.
9. The Reactions were quenched by naphthalene.
10. (a) R. S. Givens and Woo Ki Chae, *J. Am. Chem. Soc.*, **100**, 6278 (1978); (b) R. S. Givens, Woo Ki Chae, and B. Matuszewski, **104**, 2456 (1982).
11. L. S. Forster and D. Dudley, *J. Phys. Chem.*, **66**, 838 (1962).

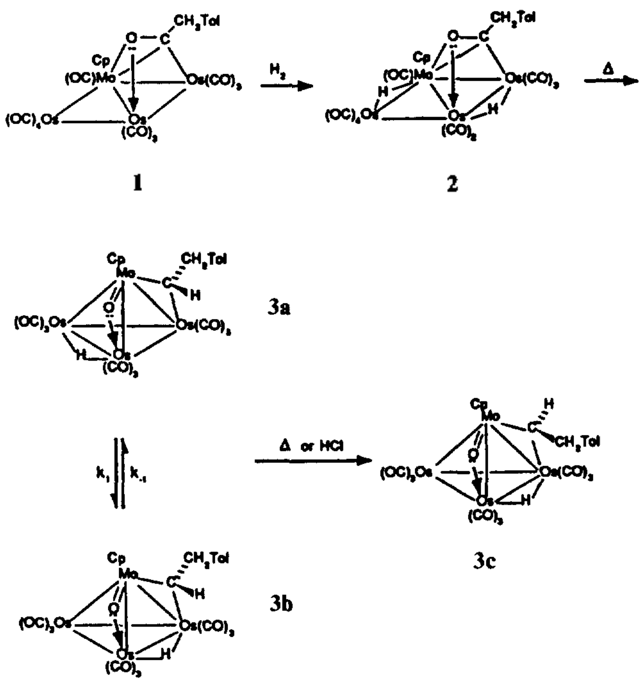
Internal Hydride Assisted C-O Bond Scission of a μ_3-η^2-Coordinated Acyl and an Apparent Rotation of μ-Alkylidene Carbon in Molybdenum-Triosmium Cluster Compounds

Joon T. Park*, Kang M. Chun†, Sock S. Yun†,
and Sangsoo Kim‡

Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejeon 305-701
†*Department of Chemistry, Chungnam National University, Taejeon, 305-701*
‡*Lucky Ltd., R & D Center, Taejeon 305-343*

Received January 14, 1991

It has been suggested that the direct C-O bond scission in acyl species[1a] may play a significant role in hydrocarbon chain growth during Fischer-Tropsch synthesis. We have now extended our studies on the μ_3-η^2-acyl groups as potential surface intermediates to investigate the reactivity of acyl ligand on a molybdenum-triosmium mixed metal cluster framework. It has been reported that the tungsten-triosmium cluster compound $CpWOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol](Cp=\eta^5\text{-}C_5H_5,\ Tol=p\text{-}C_6H_4Me)$ undergoes facile thermal μ_3-η^2-acyl C-O bond scission yielding the oxo-alkylidyne complex $CpWOs_3(CO)_9(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$.[1] This oxo-alkylidyne complex has, in turn, been shown to undergo hydrogenation to provide a mixture of two isomers of the hydrido-oxo-alkylidene complex $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$.[1a,2] We here report that an analogous molybdenum-triosmium acyl compound undergoes the acyl C-O bond scission assisted by internal hydride ligands and that an apparent rotation of μ-alkylidene carbon is directly observed on the molybdenum-triosmium cluster framework.



Scheme 1.

The triply-bridging acyl complex $CpMoOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$(**1**)[3] is isolated as the major product in 60% yield from a Stone reaction,[4] the reaction of $H_2Os_3(CO)_{10}$ with the molybdenum alkylidyne complex $Cp(CO)_2Mo(CTol)$ under mild conditions (5-20℃). Initial decarbonylation of compound **1** with $Me_3NO/MeCN$ followed by reaction with dihydrogen (50 psig, toluene, 80℃, 1 h) gives the dihydride complex $CpMoOs_3(CO)_{10}(\mu\text{-}H)_2[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$(**2**)[5] in a quantitative yield (Scheme 1). Thermolysis of compound **2** (toluene, 100 ℃, 1h) now induces scission of the acyl C-O bond to afford three isomeric hydrido-oxo-alkylidene complexes $CpMoOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ [**3a** and **3b** (59%) and **3c** (18 %)].[6] Complex **3c** is produced as well either by thermolysis of a mixture of **3a** and **3b** in toluene for a prolonged period (61%, 100℃, 19h) or by treatment with hydrochloric acid in acetone (72%, 56℃, 14h).

The molecular configuration of **2** is shown in Figure 1.[7] The tetrametallic molecule contains a planar triangulated rhomboidal arrangement of metal atoms, with Mo and Os(2) atoms at the bridge-head positions. The present molecule has an μ_3-η^2-acyl group,[8] C(2)-O(1), associated with the triangular Os(1)-Os(2)-Mo face. The C(2)-O(1) bond length is