Communications to the Editor

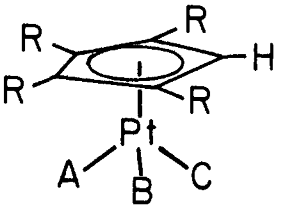
Mechanical Spectroscopy: A New Technique for Measuring Ring Rotation in Organometallic Complexes

Sir:

Interest in the rotation of cyclopentadienyl ligands attached to metals originates with the birth of organometallic chemistry itself.[1] Many methods including NMR of solids[2a] and solutions,[2b] dipole moment studies,[2c] electron,[2d] and X-ray[2e] diffraction have been applied to the investigation of rotation in cyclopentadienyl and arene complexes. Molecular orbital calculations have appeared which attempt to quantify the conformational preferences and rotational barriers observed.[3] We have applied the technique of mechanical spectroscopy, used for many years in the fields of polymer physics and metallurgy, to the study of cyclopentadienyl ring rotation in a series of cyclopentadienyl platinum(IV) complexes embedded in a polystyrene matrix. This method has several advantages and can make valuable contributions to this field.

An introductory review of mechanical spectroscopy[4] has appeared and the details of the experiments will be published later. Briefly, the method consists of codissolving the sample and polystyrene (usually in the weight ratio of 1:9) in benzene and then freeze drying the solution and compression molding the resulting powdery solid solution into a homogeneous rectangular prism. This sample is subjected to a sinusoidal mechanical stress at a fixed frequency and the energy dissipation of the sample is monitored as a function of temperature. When the frequency of motion of a molecule or molecular fragment in the sample matches the frequency of the external mechanical stress, interaction or coupling of the motions occurs resulting in an energy dissipation which is measured. The energy dissipation is expressed as the loss tangent, tan δ.[5] Two instruments have been used in this study: the torsional pendulum[6] twists the sample in a frequency range of 0.3-4.0 Hz while the vibrating reed instrument[7] vibrates the sample in the range 100-10 000 Hz.

The six cyclopentadienyl platinum complexes[8] shown were studied. Complexes **1**, **2**, and **6** are solids while the rest are liquids. A plot of the temperature dependence of the loss tangent obtained by the torsional pendulum and vibrating reed for complex[9] **5** is shown in Figure 1 for three frequencies. Peaks were observed for each compound except **6** between −180 and −160 °C. The intensity of the peak for **2** was shown to be concentration dependent for the range 5-15% by weight, which confirmed that the peak was indeed due to the complex. Polystyrene itself shows no appreciable energy dissipation in that frequency and temperature region.



1 R=H; A=B=C=CH_3
2 R=H; A=B=CH_3, C=C(O)CH_3
3 R=H; A=B=C_2H_5, C=C(O)CH_3
4 R=H; A=B=C_2H_5, C=CH_3
5 R=H; A=CH_3, B=C_2H_5, C=C(O)CH_3
6 R=C_6H_5; A=B=C=CH_3

Table I

complex[a]	T_{max}, °C[b]	ΔH_a[c]	source
$C_5H_5Pt(CH_3)_3$	−188	4.9 ± 0.5	*d*
$C_5H_5Pt(CH_3)_2[C(O)CH_3]$	−173	5.5 ± 0.6	*d*
$C_5H_5Pt(CH_3)(C_2H_5)_2$	−172	5.7 ± 0.6	*d*
$C_5H_5Pt(CH_3)(C_2H_5)[C(O)CH_3]$	−166	5.8 ± 0.6	*d*
$C_5H_5Pt(C_2H_5)_2[C(O)CH_3]$	−155	6.2 ± 0.6	*d*
$(C_5H_5)_2Fe$		2.0	*e*
$(C_5H_5)_2Ru$		4.5	*e*
$(C_6H_6)_2Cr$		4.6	*e*
$C_6H_6Cr(CO)_3$		4.2	*f*

[a] Analyses of the sources of error in the rotating pendulum and vibrating reed measurements have been conducted.[6b,7] Error analysis gave a maximum estimated error of 10% for the ΔH_a values. [b] Temperature at which maximum peak height is obtained at ~3 Hz. [c] In kilocalories/mole. [d] This work. [e] Reference 13. [f] Reference 14.

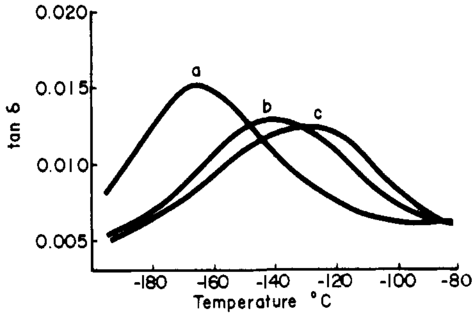


Figure 1. A typical plot of the temperature dependence of tan δ for **5** at three different frequencies: torsional pendulum at 3.6 Hz (a) and vibrating reed at 470 (b) and 3000 Hz (c).

Loss tangent vs. temperature curves were obtained at three different frequencies for each complex. The relationship between log (frequency) and the inverse of the peak temperature is linear in all cases, permitting Arrhenius-type activation energies to be calculated (Table I).

The peaks observed for these complexes could in principle be due to molecular relaxation or group relaxation.[10] However, consider the following: (1) the $C_5H_5^-$ group is the only ligand common to complexes **1-5**, (2) when four phenyl groups, which should lock the ring in the matrix, are attached, as in complex **6**, no peak is observed, (3) dielectric studies[10a,c,11] on polar molecules embedded in polystyrene indicate that the activation energy for rotation of small or disk shaped molecules is ~5.5 kcal/mol while that for larger molecules was >7 kcal/mol. Therefore we feel the absorption can be assigned to $C_5H_5^-$ ring rotation.[12]

The activation energies obtained for ring rotation in complexes **1-5** are slightly larger than those found by NMR techniques for ferrocene,[2a] ruthenocene,[2a] dibenzenechromium,[2a] and benzenetricarbonylchromium[13] (Table I) but still of the same order of magnitude.[14] The trend in the variation of the activation energies for the five complexes correlates roughly with the steric bulk of the PtABC tripod with **3** being the most bulky and having the highest energy. It is known that the barrier to cyclopentadienyl ring rotation in the solid is largely due to nonbonded intermolecular interactions,[2a,3] in this case between the ring and the polystyrene matrix.[15] Therefore, it is reasonable to conclude that the relative differences are due to some intramolecular phenomenon. Mo-

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lecular orbital calculations on molecules of the type $C_5H_5M(CO)_3$ give tiny barrier values.[3] Thus, it is unlikely that the differences in the activation energies between **1** and **4**, for example, are due to electronic effects. Therefore these differences are probably due to the relative steric interactions between the three types of substituents on the platinum atom and the ring. Relative contributions for $C(O)CH_3$ (0.6 kcal/mol) and for C_2H_5 (0.3 kcal/mol) with respect to CH_3 can be derived from comparing **1, 2,** and **5** and used to calculate activation energies for **4** (5.5 kcal/mol) and for **3** (6.1 kcal/mol) which agree well with the measured values.

Mechanical spectroscopy appears to be a promising technique with which to examine ring rotation in organometallic compounds. It has the advantage that both solid and liquid compounds can be examined if they are soluble in benzene (and most are). The temperature used to mold the sample (~80 °C) is low enough not to cause decomposition.[16] The polystyrene environment is probably close to being isotropic with respect to nonbonded intermolecular interactions allowing comparisons of a series of molecules to be made. Finally the instruments are fairly simple and inexpensive making this method most attractive.[17]

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References and Notes

(1) R. B. Woodward, M. Rosenblum, and M. C. Whiting, *J. Am. Chem. Soc.*, **74,** 3458 (1952).

(2) (a) A. J. Campbell, C. A. Fyfe, D. Harold-Smith, and K. R. Jeffrey, *Mol. Cryst. Liq. Cryst.*, **36,** 1 (1976); (b) F. van Meurs, J. M. vander Toorn, and H. van Bekkum, *J. Organomet. Chem.*, **113,** 341 (1976); (c) H. H. Richmond and H. Freiser, *J. Am. Chem. Soc.*, **77,** 2020 (1955); (d) N.-S. Chiu, L. Schäfer, and R. Seip, *J. Organomet. Chem.*, **101,** 331 (1975); (e) M. J. Bennett, W. L. Hutcheon, and B. M. Foxman, *Acta Crystallogr., Sect. A.*, **31,** 488 (1975).

(3) T. A. Albright, P. Hofmann, and R. Hoffmann, *J. Am. Chem. Soc.*, **99,** 7546 (1977).

(4) A. Eisenberg and B. C. Eu, *Annu. Rev. Mat. Sci.*, **6,** 335 (1976).

(5) H. Markovitz, *J. Appl. Phys.*, **34,** 21 (1963).

(6) (a) A general description of the instrument is given by L. E. Nielsen, *Rev. Sci. Instrum.*, **22,** 690 (1951). (b) Our specific instrument is described by B. Cayrol, Ph.D. Thesis, McGill University, 1972.

(7) J. Williams, Ph.D. Thesis, McGill University, 1978.

(8) A. Shaver, *Can. J. Chem.*, **56,** 2281 (1978).

(9) The concentration was 10% by weight of complex in polystyrene.

(10) (a) M. Davis and J. Swain, *Trans. Faraday Soc.*, **67,** 1637 (1971). (b) C. K. McLellen and S. Walker, *Can. J. Chem.*, **55,** 583 (1977). (c) A. Lakshmi, S. Walker, and N. A. Weir, *J. Chem. Soc.*, Faraday *Trans. 2*, **74,** 727 (1978); *J. Chem. Phys.*, **68,** 4662 (1978).

(11) (a) S. P. Tay, S. Walker, and E. Wyn-Jones, *Adv. Mol. Relaxation Interact. Processes*, **13,** 47 (1978); (b) S. P. Tay and S. Walker, *J. Chem. Phys.*, **63,** 1634 (1975). (c) M. Davies and A. Edward, *Trans. Faraday Soc.*, **63,** 2163 (1967).

(12) Although the evidence strongly supports our assignment it does not conclusively eliminate whole molecule tumbling or PtABC-tripod rotation as possible sources of the absorption. Experiments are in progress which will, it is hoped, unambiguously settle the question.

(13) P. Delisle, G. Allegra, E. R. Mognaschi, and A. Chierico, *J. Chem. Soc., Faraday Trans. 2*, **71,** 207 (1975).

(14) (a) There is evidence that energy barrier data for certain organic molecules obtained by both dielectric studies on polystyrene matrices and by NMR studies on solids are similar.[10a] A preliminary study[14b] on benzenetricarbonylchromium gave an activation energy of 4.8 kcal/mol in fairly good agreement with the NMR value[13] of 4.2 kcal/mol. (b) T. Tsutsui, A. Eisenberg, and A. Shaver, work in progress.

(15) A slight concentration dependence of the peak temperatures for **2** suggests that the physical state of the matrix may have some influence on the barrier to ring rotation. Since the comparison is done at uniform concentration (10%), this should not affect the relative differences.

(16) All of the complexes **1–6** are air stable; thus inert atmosphere techniques were not used but they could easily be applied.

(17) Both of the instruments used in this study were designed and built within our department at an estimated total price of $15,000.

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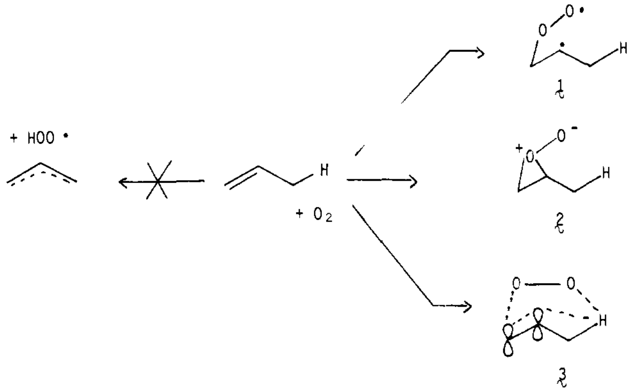
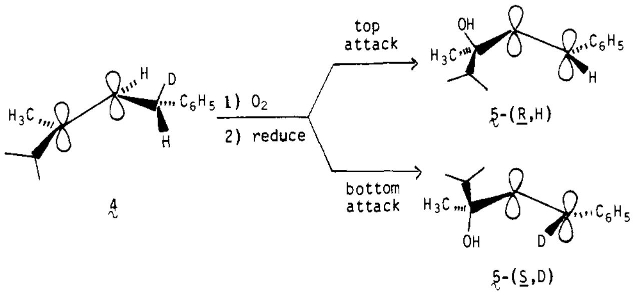
Stereochemistry of the Singlet Oxygen Olefin-Ene Reaction

Sir:

Most of the convincing demonstrations of mechanism in potentially concerted reactions have involved combinations of kinetic-energetic considerations and stereochemical studies. In the singlet oxygen-ene reaction, the finding of low activation enthalpies[1] (<10 kcal/mol) eliminates rate-determining hydrogen abstraction, but is less useful in deciding between other competing mechanisms, e.g., diradical **1,** perepoxide **2,** or concerted pathway **3.** We report here a study of reaction stereochemistry and isotope effects for this reaction. The reactive trisubstituted olefin, **4,** is ideally suited for this purpose. Compound **4** can be prepared in high geometrical and known optical purity.[2] The product, **5,** is obtained in high yield (only 18% $-CH_3$ hydrogen abstraction and no isopropyl CH abstraction) and only the trans-allylic alcohol shown is found in the mixture. The expectations for a concerted, or similarly highly organized, reaction pathway are shown. Approach of oxygen from above would form the *R* tertiary alcohol, and, to produce trans olefin, would remove D. Approach from below would form the *S* alcohol and remove H. These two products are labeled **5**-(*R*-H) and **5**-(*S*-D). With this mechanism, one could obtain crossover products (*R*-D and *S*-H) only to the extent that the other olefin isomer or opposite enantiomer is present in the starting material.





Examination of both the methyl and the olefinic protons of **5** by NMR reveals that both are measurably diastereotopic in the presence of $Eu(tfc)_3$, even at 60 MHz. Thus, it is simple to demonstrate that one enantiomer of the product **5** has only H at the crucial vinyl position, while the other has only D. High analytical precision can be claimed in this measurement, since, starting with materials of lower optical and geometrical purity, we find precisely the expected quantity of the "crossover products", *R*-D and *S*-H, in the resulting allylic alcohol.

We find no isotope discrimination in this reaction, *R*-H and *S*-D being produced in equal yield. Thus, while the reaction is highly stereospecific, it does not display the isotope effect one might anticipate for a *normal* ene reaction.

A conceptually simple way of viewing this result is via irreversibly formed perepoxide intermediates. One would an-

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