efforts for the low-temperature matrix isolation of oxirenes were unsuccessful.

Further studies are in progress.

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Heavy-Atom Tunneling as the Dominant Pathway in a Solution-Phase Reaction? Bond Shift in Antiaromatic Annulenes

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It is probably fair to say that many organic chemists view the concept of tunneling, even of hydrogen atoms, with some skepticism.[1] Heavy-atom tunneling is thus considered to be of negligible significance to chemical reactions.[1] The purpose of this communication is to point out that the bond shift reaction of [4*n*]annulenes could proceed by a mechanism that is *primarily* heavy-atom tunneling and that for cyclobutadiene in particular the *tunneling process could constitute >97% of the total rate constant below 0 °C*! The tunneling mechanism leads to the prediction of abnormally low activation entropies for the bond-shift reactions, in accord with experimental observation.

The reaction coordinate for automerization of cyclobutadiene can be approximated by a single stretching motion. This is equivalent to treating cyclobutadiene as homonuclear diatomic molecule with the two pseudoatoms each having a mass[2] of 26 daltons (see Figure 1).

The potential-energy profile for the bond-shifting reaction can be approximated as an intersection between two harmonic potential functions whose minima are separated on the reaction coordinate by a distance equal to the difference in length between the long and the short carbon–carbon bonds of cyclobutadiene. One could guess that this difference (ΔR) would be about 0.18 Å, given typical lengths of 1.52 and 1.34 Å for the long (single) and short (double) bonds respectively. Recent molecular orbital calculations[3-5] suggest that ΔR is about 0.198 Å.

In the model used here the height of the potential-energy barrier is determined by ΔR and the force constant for the stretching vibration. If one assumes a plausible value of 1000 cm^{-1} for the in-plane rectangular deformation[6] (symmetry b_{1g}), then the force constant for the pseudodiatomic molecule is calculated to be 1.532×10^6 dyn/cm. This leads to a calculated potential barrier of 10.8 kcal/mol for the automerization reaction, which perhaps by coincidence is near the middle of the range (8.3–14 kcal/mol) obtained from the most sophisticated quantum mechanical calculations.[4,5,7]

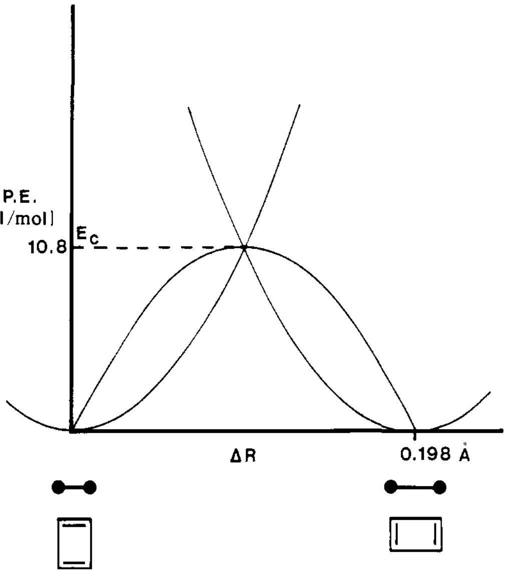

Figure 1. Model potential-energy functions for the automerization of cyclobutadiene.

In order to carry out the tunneling calculations one must represent the potential barrier by some analytical function. In the interests of preserving the simplicity of this model, I have chosen the truncated parabola form.[8] As shown in Figure 1, the parabola that passes through the point (0.099, E_c) and the minima of the harmonic potentials is probably somewhat too wide, and so the contribution from tunneling will tend to be *underestimated*. Nevertheless, *the width is nearly an order of magnitude smaller than that for most organic reactions. It is the extreme narrowness of the barrier that makes bond-shifting reactions especially susceptible to tunneling.*

The energy levels of the pseudodiatomic molecule can be calculated from the usual harmonic oscillator formula,[9,10] and the probability of transmission through the barrier $G(E)$ at each of these levels can be calculated from the Bell formula:[11]

$$G(E) = \frac{1}{1 + \exp[2\pi(E_c - E)/h\nu_t]}$$

$$\nu_t = \frac{1}{\pi a}\left(\frac{E}{2\mu}\right)^{1/2}$$

where μ is the reduced mass of the oscillator and the width of the barrier at its base is $2a$. The microcanonical tunneling-rate constant for each level is then taken to be the product of $G(E)$ and the oscillator frequency.

Finally, one can calculate the unimolecular tunneling-rate constant at various temperatures by imposing a Boltzmann population on each of the energy levels of the oscillator.[12] This is equivalent to assuming that the experiment is conducted at the

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[1] There are, of course, some exceptions. See, for example: Kaldor, S. B.; Saunders, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 7594–7599. Buchwalter, S. L.; Closs, G. L. *Ibid.* **1975**, *97*, 3857–3858. Especially relevant to the present problem: Fong, F. K. *Ibid.* **1974**, *96*, 7638–7646.

[2] The real normal coordinate will consist of some C–H motion in addition to the predominant C–C motion. This means that the effective masses of the pseudoatoms in the diatomic model should be somewhat less than 26. By use of the highest value the tendency will be to *underestimate* the tunneling contribution.

[3] Dewar, M. J. S.; Komornicki, A. *J. Am. Chem. Soc.* **1977**, *99*, 6174–6179.

[4] Newton, M. D.; Jafri, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 5012–5017.

[5] Borden, W. T.; Davidson, E. R.; Hart, P. *J. Am. Chem. Soc.* **1978**, *100*, 388–392.

[6] Schaad et al. calculate a frequency of 978 cm^{-1} for this mode: Schaad, L. J.; Hess, B. A.; Ewig, C. S. *J. Org. Chem.* **1982**, *47*, 2904–2906.

[7] Kollmar, H.; Staemmler, V. *J. Am. Chem. Soc.* **1977**, *99*, 3583–3587.

[8] Bell, R. P. *Trans. Faraday Soc.* **1959**, *55*, 1–3.

[9] Schutte, C. J. H. "The Wave Mechanics of Atoms, Molecules and Ions"; Arnold: London, 1968; p 50.

[10] Actually there should be some splitting of the energy levels due to interaction between the wave functions for the two oscillators (see ref 9, pp 69 ff) but this has been neglected for the present purposes.

[11] Bell, R. P. "The Proton in Chemistry", 2nd ed.; Cornell University Press; Ithaca, NY, 1973; p 274.

[12] In fact the populations of these levels should be divided by vibrational partition function for the true molecule and not for the diatomic model. The reported unimolecular rate constants were calculated in this way although the effect is small: with the vibrational frequencies from ref 6, the vibrational partition function is calculated to be 1.14 at −50 °C and 1.27 at −10 °C.

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high-pressure limit, which seems to be reasonable if one is interested in reactions in a condensed phase.

The calculated rate constants for tunneling at −50 and −10 °C are 8.08×10^4 and 4.65×10^5 s^{-1}, respectively. These are to be compared with the classical rate constants[13] of 1.01×10^2 and 4.82×10^3 s^{-1} at the same temperatures. The startling conclusion is that, assuming the validity of this model, *tunneling accounts for >97% of the total reaction below 0 °C.*

The combined tunneling and classical rate constants correspond to the activation parameters $\Delta H^{\ddagger} = 4.6$ kcal/mol, $\Delta S^{\ddagger} = -15$ cal/(mol K). Recent experiments suggested that the activation parameters for cyclobutadiene automerization,[14] measured over the same temperature span, must be in the range $1.6 \leq \Delta H^{\ddagger} \leq 10$ kcal/mol and $-32 \leq \Delta S^{\ddagger} \leq -17$ cal/(mol K). Given the crudity of the model used here and the probable underestimate of the tunneling contribution, the agreement seems to be quite good.

Two features of this analysis should be emphasized. First, the most striking consequence of the tunneling mechanism is the abnormally low activation entropy that one calculates. Second, the apparent $\Delta H^{\ddagger}$ for the reaction cannot be equated with the potential barrier calculated by any molecular orbital technique.

For the conclusions drawn here to be *qualitatively* incorrect, the model used for the calculation of the tunneling-rate constants would have to be seriously in error (and there is substantial experimental evidence to suggest that it is not[15]) or the numerical parameters (barrier width and oscillation frequency) would have to be wrong by considerable amounts.

While the discussion to this point has centered on cyclobutadiene, there is reason to believe that the bond-shift reaction in cyclooctatetraene might have a significant tunneling contribution as well. The activation entropy was recently measured[16] and found to be −9.7 cal/(mol K). While this is not as low as the one for cyclobutadiene, it must still be considered abnormal for a reaction in which no rotations are frozen out and no especially low-frequency vibrations are lost in the transition state. It is possible that the higher temperatures at which the measurements were made resulted in a larger contribution from the classical mechanism in this case.

When one considers the effect of substituents on the tunneling efficiency, it becomes clear that sterically demanding groups, which tend to force a planar annulene toward the regular polygonal structure,[17] should further reduce the barrier width and increase the tunneling rate constant.[18] This could be the reason that the automerization of tri-*tert*-butylcyclobutadiene cannot be frozen out in the ^{13}C NMR even at −185 °C.[19] Substituents seem to have a profound effect on the $\Delta S^{\ddagger}$ for bond shifting in cyclooctatetraenes[20] with values ranging from +2.3 to −23.6 cal/(mol K). Here, too, the effect could be a geometrical one in which the substituents increase or decrease the amount of tunneling by changing the effective barrier width in the planar structure.

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(13) In order to calculate the classical rate constant a value of $\Delta H^{\ddagger} = 10.8$ kcal/mol was used. The value for $\Delta S^{\ddagger}$ was calculated to be −0.4 cal/(mol K), reflecting a vibrational contribution of +1.0 (calculated from vibrational frequencies listed in ref 3 and 6) and a rotational contribution of −1.4 cal/(mol K). The latter was due in large part to the change in symmetry number during the bond-shift reaction.

(14) Whitman, D. W.; Carpenter, B. K. *J. Am. Chem. Soc.* **1982**, *104*, 6473–6474. This experiment was actually conducted on cyclobutadiene-d_2, but the extra mass makes a negligible contribution to the overall effect.

(15) For an example and some leading references see: Brunton, G.; Griller, D.; Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 6803–6811.

(16) Naor, R.; Luz, Z. *J. Chem. Phys.* **1982**, *76*, 5662–5664.

(17) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1980**, *102*, 7958–7960.

(18) The increase in the effective reduced mass of the tunneling groups will tend to counterbalance the reduction in barrier width, but model calculations suggest that the net effect should still be an increase in the tunneling-rate constant.

(19) Maier, G.; Kalinowski, H.-O.; Euler, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 693–694.

(20) Paquette, L. A. *Pure Appl. Chem.* **1982**, *54*, 987–1004.

The Novel Reaction of Metal–Metal Triple-Bonded Complexes and Nitro Compounds. Decarbonylation and the Formation of High Oxidation State Molybdenum and Tungsten Complexes Bearing Bridging and Terminal Oxygen Ligands

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The fascinating chemistry of complexes containing metal–metal multiple bonds has been a subject of great interest in recent years.[2,3] One of the most widely investigated class of compounds is the (cyclopentadienyl)molybdenum dicarbonyl dimer and related complexes.[4] The metal–metal bond in such complexes undergoes intriguing reactions with nucleophilic (e.g., isocyanides)[5] and electrophilic (e.g., α-halo ketones)[6] reagents.

The reaction of nitro compounds with $[C_5H_5M(CO)_2]_2$ has not been investigated. It seemed conceivable that the nitro group would add to the triple bond to give a complex in which cleavage of at least one nitrogen–oxygen linkage has taken place. The occurrence of such a process is of relevance to the metal carbonyl catalyzed reduction[7] and reductive carbonylation[8] of nitro compounds. We now report the remarkable reaction of nitro compounds with $[(C_5H_4R)M(CO)_2]_2$, where M = Mo, W and R = H, CH_3.

Addition of *p*-nitrotoluene (**1**, Ar = *p*-$CH_3C_6H_4$, Scheme I) to an equimolar amount of the (cyclopentadienyl)molybdenum dicarbonyl dimer (**2**, M = Mo, R = H) in toluene at room temperature afforded the molybdenum complex **3**, M = Mo, R = H, Ar = *p*-$CH_3C_6H_4$. This reaction, and others described below, are exceedingly facile since they are essentially complete in 5 min (infrared spectral determination), although they generally were stirred for 3 h. Complex **3** could also be prepared by refluxing a mixture of **1** and (cyclopentadienyl)molybdenum tricarbonyl dimer overnight in toluene (**2** is generated under these conditions). The infrared spectrum of **3** (M = Mo, R = H, Ar = *p*-$CH_3C_6H_4$) showed $\nu_{Mo=O}$ at 895 cm^{-1} while the μ-Mo–O stretching band appeared at 817 cm^{-1}.[9] The nuclear magnetic resonance spectral data (Table I) of the complex are also in accord wth structure **3**.

In order to establish the structure unambiguously, an X-ray determination[10] of **3**, M = Mo, R = H, Ar = *p*-$CH_3C_6H_4$, was

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(1) E. W. R. Steacie Fellow, 1980–1982.

(2) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

(3) Chetcuti, M. J.; Chisholm, M. H.; Folting, K.; Huffman, J. C.; Janos, J. *J. Am. Chem. Soc.* **1982**, *104*, 4684.

(4) Curtis, M. D.; Messerle, L.; Fotinos, N. A. In "Reactivity of Metal–Metal Bonds"; Chisholm, M. H., Ed.; American Chemical Society: Washington, D.C., 1981; ACS Symp. Ser. No. 155.

(5) Adams, R. D.; Katahira, D. A.; Yang, L.-W. *Organometallics* **1982**, *1*, 231.

(6) Petrignani, J. F.; Alper, H. *Organometallics* **1982**, *1*, 1095.

(7) Alper, H.; Amaratunga, S. *Tetrahedron Lett.* **1980**, 2603.

(8) Alper, H.; Hashem, K. *J. Am. Chem. Soc.* **1981**, *103*, 6514.

(9) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds"; 3rd ed.; Wiley: New York, 1978.

(10) Single crystals of $(\mu\text{-}NC_6H_4CH_3)(\mu\text{-}O)([C_5H_5]MoO)_2$ were monoclinic, space group $C2/c$, with $a = 14.796$ (1) Å, $b = 15.999$ (1) Å, $c = 7.692$ (1) Å, and $\beta = 109.44$ (1)°. ρ_{calcd} $(Z = 4) = 1.838$ g cm^{-3}. X-ray diffraction intensity data were collected by the line profile analysis of 1517 reflections $(3° < 2\theta < 50°)$ measured on a Picker FACS-I diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.7093$ Å). Non-hydrogen atoms were located by conventional methods and refined with anisotropic temperature factors. H atomic coordinates were determined geometrically but were not refined. An absorption correction ($\mu = 14.5$ cm^{-1}) was applied. Block-diagonal refinement of 108 variables [using 1364 reflections with $I > 2.30\sigma(I)$] gave $R = 0.022$, $R_w = 0.035$.

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