B, and C can be varied to fit preset values of the barrier height b, the distance between the two minima ΔR, and the curvature at each minimum [or, alternatively, the energy difference between 0 (the average of 0^+ and 0^-) and 1]. R equals 0 for the square configuration of the top of the potential barrier, and ΔR equals 4 times the difference between C—C and C=C.

The cyclobutadiene molecule here is a four-atom system with each carbon atom assigned a mass of 13 daltons. Tunneling is taken as one dimensional corresponding to concerted stretching of bonds 1 and 3 in (1) and an equivalent shortening of bonds 2 and 4 (or vice versa) with the above potential energy. The E_i and ΔE_i values were obtained numerically.[4]

A number of parameter sets were employed for b and ΔR: α[5] – 8.58 kcal/mol, 0.18 Å; β[6] – 12.0 kcal/mol, 0.23 Å; γ[7] – 14.0 kcal/mol, 0.25 Å, δ[8] – 10.8 kcal/mol, 0.198 Å. While no normal coordinate analysis has been carried out here, probably none of the normal modes of cyclobutadiene corresponds quite to the motion of the reaction coordinate. One cannot deduce the appropriate curvature at the minima in the potential directly from the vibrational spectrum of cyclobutadiene. Thus, the curvature at the minima has been varied here to give in various calculations energies for the $0 \rightarrow 1$ transition varying between 800 and 1900 cm^{-1}. Variations corresponding to such a range changed the rates (vide infra) at −10 °C by less than a factor of 3.

Tunneling rates were calculated for each doublet of levels from the ΔE_i values by the formula[9] $k_i = 2\Delta E_i/h$ (i = 0, 1, ...), and the effective tunneling rate is obtained by appropriate Boltzmann averaging.[10] Most of the effective tunneling rate arises from the 0 state, with small contribution from 1 and negligible contributions from higher states. As expected, the highest rates are obtained for α calculations, where ΔE_0 is typically ~ 2 cm^{-1}, and a rate of $\sim 2 \times 10^{11}$ s^{-1} is typically obtained at −10 °C. The lowest rates are given by the γ calculations with $\Delta E_0 \sim 0.009$ cm^{-1} and a rate $\sim 5 \times 10^8$ s^{-1} at −10 °C. β and δ calculations lead to rates of $\sim 3 \times 10^9$ and $\sim 3 \times 10^{10}$ s^{-1}, respectively.

The temperature dependence of the effective tunneling rates is very small, so that between −50 and −10 °C the enthalpy of activation is found to be slightly negative for the various parameter sets, −0.3 to −0.5 kcal/mol. Corresponding entropies of activation are quite negative varying from −8 to −20 kcal/(deg mol). A relatively large negative $\Delta S^{\ddagger}$ value agrees with Carpenter's calculation and also appears to be implied by Whitman and Carpenter's[11] measurements.

The one-dimensional tunneling rates for symmetric potentials here are considerably larger than values evaluated by Carpenter by the TC approximation. On the other hand, it is expected from experience in the NH_3 system[12] that more realistic multidimensional models will tend to yield lower rates. If the double-minimum problem were unsymmetric tunneling rates would decrease.[3a] Possibly such lack of symmetry must be considered for cyclobutadiene in solution. Finally one should note that Whitman and Carpenter's[11] experiment with respect to reaction 1 involved vicinally dideuterated cyclobutadiene. In a one-dimensional calculation, the extra mass does not change the conclusions presented ($\Delta S^{\ddagger}$ tends to decrease by ~ 0.5 cal/(deg mol)). In a multidimensional calculation, conceivably the effect of lack of symmetry caused by isotopic substitution might be nonnegligible.

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Registry No. 1,3-Cyclobutadiene, 1120-53-2.

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[4] The method used here is a one-dimensional version of that used for NH_3 (Bopp, P.; McLaughlin, D. R.; Wolfsberg, M. *Z. Naturforsch., A.* **1982**, *37A*, 398) with the D_{4h} configuration at the top of the potential barrier as the reference configuration and with the normal coordinate of the reference configuration equal to a constant times R here.

[5] Parameter set based on various literature values[1] to yield high tunneling rate.

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

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

[8] Set used in ref 1.

[9] Eyring, H.; Walter, J.; Kimball, G. E. "Quantum Chemistry"; Wiley: New York, 1954.

[10] ΔE_i values are calculated only for those levels lying below the top of the barrier. While Harmony[3b] has indicated how to include the classical rate (over the top of the barrier) in the total rate constant, this process is unnecessary here because this classical rate is negligible on account of the adverse Boltzmann factor.

[11] Whitman, D. W.; Carpenter, B. K. *J. Am. Chem. Soc.* **1982**, *104*, 6473.

[12] Bopp, P.; McLaughlin, D. R.; Wolfsberg, M. *Z. Naturforsch., A* **1982**, *37A*, 398.

Tunneling Dynamics of Cyclobutadiene

Michael J. S. Dewar,* Kenneth M. Merz, Jr., and
James J. P. Stewart

Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712

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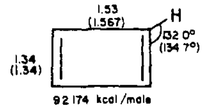
It is now generally accepted that cyclobutadiene (**1**) has a rectangular singlet ground state, the square structure (**2**) being the transition state (TS) for automerization of **1** (i.e., **1** to **2**). Estimates[1–6] of the barrier height range from 8 to 15 kcal/mol, implying that is should be possible to freeze out a single isomer at low temperatures.

Recently, however, Carpenter[7] has proposed on the basis of a rather simplistic model that the automerization may take place predominantly by tunneling, a rather striking suggestion because it has always been assumed that heavy-atom tunneling can be neglected. Here, however, the distance (<0.2 Å) the carbon atoms move during the reaction is comparable with the de Broglie wavelength[14] of carbon, suggesting that tunneling may in fact play the role Carpenter suggests. To test this, we have now carried out detailed calculations for the automerization of **1** and its tetradeuterio (**3**) and tetra ^{13}C (**4**) derivatives, and also for the (square) TS, **2**, **5**, and **6**, for their automerizations. The calculations were carried out using the "half-electron" version (MINDO/3/HE) of MINDO/3 with 3 × 3 CI because the square



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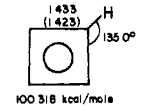

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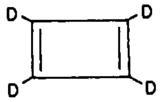

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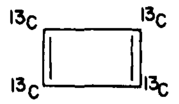

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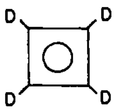

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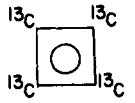

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[11] The parameters for MINDO/3 and MNDO are chosen to fit the calculated total energies to observed heats of formation. The calculated "total energies" therefore contain implicit corrections for thermal contributions.

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Table I. Calculated Splitting Values for the Cyclobutadiene Automerization

compd GS	compd TS	$\hbar\omega_F$, cm^{-1}	$\hbar\omega_i$, cm^{-1}	ΔE, cm^{-1}	$10^{11}\omega_T$, s^{-1}
1	**2**	1764	1929*i*	9.03	5.39
1^a	**2**^{a}	1588	1736*i*	3.80	2.28
3	**5**	1700	1929*i*	7.87	4.71
3^a	**5**^{a}	1530	1736*i*	3.28	1.96
4	**6**	1698	1853*i*	6.63	3.96
4^a	**6**^{a}	1528	1668*i*	2.71	1.62

^{a} 10% correction of the calculated vibrational frequency (see ref 8).

structures, **2**, **5**, and **6**, would be expected to be biradicals. Our results differ little from those given earlier by straightforward MINDO/3 calculations, implying that **3** is not a real biradical.[1]

The geometries and heats of formations (kcal/mol) calculated for **1** and **3** are shown on and below the formulas with values for high-level ab initio calculations in parenthesis. The barrier height calculated by MINDO/3/HE/CI (8.1 kcal/mol) is less than that from the ab initio calculation (12.0 kcal/mol), as expected (see below).

Since the vibrational frequencies differed only a little from the earlier MINDO/3 values[1] they are supplied as supplementary material, together with comparisons with experiment[9] and ab initio[10] calculations.

Since MINDO/3 contains an implicit allowance of vibrational/rotational energy via its parametrization,[11] it should give a good estimate of the barrier height for automerization of **1**, whereas the ab initio one corresponds to a reaction where neither **1** nor **2** has any vibrational energy. The ab initio value therefore has to be corrected for the loss of zero point energy corresponding to the transition coordinate. From the calculated vibrational frequencies this is estimated to be 3.6 kcal/mol, almost exactly the difference between the MINDO/3 (8.1 kcal/mol) and ab initio (12.0 kcal/mol) barriers.

The reaction dynamics of the automerization were then studied by using the procedures of Bicerano et al.,[12] based on the method of periodic orbits described by Miller.[13] This treats the system in terms of a double-minimum model, analogous to that used in discussing inversion of ammonia. Tunneling leads to a splitting of the energy levels, the ground states splitting being given by

$$\Delta E = (h\omega_F/(2\pi^2))e^{-\theta} \tag{1}$$

where ω_F is the frequency of the normal mode of vibration (F) leading to reaction and for the Eckart[14] barrier θ is given[13] by

$$\theta = [V_{\text{eff}} - (E_0 V_{\text{eff}})^{1/2}]4\pi^2/(h\omega_i) \tag{2}$$

where V_{eff} is the effective barrier height, ω_i is the value of the (imaginary) frequency corresponding to the transition coordinate in the TS, and $E_0 = h\omega_F/(4\pi)$. In the present treatment,[12,13] all vibrations except that (F) leading to reaction are assumed to contribute adiabatically, so V_{eff} is given in terms of V_0, the barrier on the potential surface, by

$$V_{\text{eff}} = V_0 + \sum_{k=1}^{3n-6} (h\omega_k^{\ddagger} - h\omega_k)/4\pi \tag{3}$$

where the $\omega_i^{\ddagger}$ are the vibration frequencies of the TS. In MINDO/3, however, the zero point energy is taken into account via the parameterization so the second term in eq 3 should be neglected. The MINDO/3 values for the relevant quantities in eq 1–3 are (for **1**)

$$V_{\text{eff}} = V_0 = 8.14\ \text{kcal/mol}\ (2856\ \text{cm}^{-1}) \tag{4}$$

$$E_0 = h\omega_F/(4\pi) = 882\ \text{cm}^{-1} \tag{5}$$

$$h\omega_i = 1929i(\text{cm}^{-1})2\pi \tag{6}$$

The ground-state splittings estimated for **1** and its isotopically substituted isomers, **3** and **4**, are shown in Table I, together with tunneling rates (ω_T) calculated from the following expression:[14,13]

$$\omega_T = 2\Delta E/h \tag{7}$$

Table II. Calculated Classical Rate Constants

temp, K	ΔS, cal/(mol K)	A, s^{-1}	k, s^{-1}
100	−1.33	2.89×10^{12}	4.58×10^{6}
350	−0.28	1.72×10^{13}	1.41×10^{8}

Using our calculated enthalpy and entropy of activation values, we arrive at the estimates of the classical rates of automerization shown in Table II. Comparison of Tables I and II shows that the rate of tunneling is greater by 3 powers of 10 even at 350 K.

The ground-state splitting we calculate for **1** (Table I) is large enough to be observed experimentally, in the form of an absorption in the microwave spectra of **1**. Since the relevant vibrational frequency is IR inactive this splitting will not appear in the IR spectrum of **1**.

We are currently studying the possibility of analogous tunneling in other automerization processes.

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Supplementary Material Available: Tables I–VII of de Broglie wavelengths, MINDO/3 and ab initio results, calculated and theoretical vibrational frequencies for D_{2h} and D_{4h} states, splitting values, and rate constants (4 pages). Ordering information is given on any current masthead page.

Photochemistry of $H_4Ru_4(CO)_{12}$ in Rigid Alkane Matrices at Low Temperature: Spectroscopic Detection and Characterization of Coordinatively Unsaturated $H_4Ru_4(CO)_{11}$

James G. Bentsen and Mark S. Wrighton*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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We wish to report the spectroscopic detection and characterization of a reactive intermediate from the photoexcitation of $H_4Ru_4(CO)_{12}$ showing that loss of CO, eq 1, is the only net

$$H_4Ru_4(CO)_{12} \xrightarrow{h\nu} H_4Ru_4(CO)_{11} + CO \tag{1}$$

chemical result of near-UV irradiation of $H_4Ru_4(CO)_{12}$ in an alkane matrix at 77 K. While light-induced loss of CO from mononuclear and dinuclear complexes is known,[1-5] our new results constitute the first direct observation of the cluster product from light-induced loss of CO from a high nuclearity metal carbonyl complex with retention of the cluster core, providing a possible

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