

Intramolecular Hydrogen Tunneling in Malonaldehyde

Eugene M. Fluder and Jose R. de la Vega*

Contribution from the Department of Chemistry, Villanova University, Villanova, Pennsylvania 19085. Received May 13, 1977

Abstract: Ab initio SCF calculations using an extended basis set were performed in order to determine the tunneling frequency of the interconversion between the two asymmetric forms of β -hydroxyacrolein. Along the reaction coordinate, a double minimum profile with a barrier of 11.6 kcal/mol is found. Due to the value of the effective mass involved in the exchange along the reaction coordinate, the tunneling frequency that results is one order of magnitude less than the experimental value. The double minimum profile obtained when all the atoms but the intervening hydrogen are kept in the average position gives a tunneling frequency which is of the same order as the experimental value. This proton exchange mechanism also explains the change in tunneling frequency when an isotopic species is used.

Introduction

The molecule of malonaldehyde has recently been the subject of intensive experimental and theoretical study. Particular attention has been given to the intramolecular hydrogen bond in the enol form of the molecule (β -hydroxyacrolein). Recently published theoretical calculations^{1,2} indicate that the structure of minimum energy corresponds to the asymmetric form of the enol molecule, while the symmetric intermediate has definitely higher energy.

The interconversion between the two asymmetric forms requires a long amplitude nonharmonic oscillation, the profile of which shows a double minimum potential. The reaction coordinate for this interconversion is one of the $3N - 6$ internal coordinates of the molecule. In general, the long amplitude nonharmonic interconversion is not rigorously separable from either the rotational motion or the remaining $3N - 7$ small amplitude harmonic vibrations.

The microwave spectrum of β -hydroxyacrolein led Wilson and co-workers³ to conclude that the interconversion between the two asymmetric C_s forms has a frequency of $16 \pm 14 \text{ cm}^{-1}$ and is faster than molecular rotations. The difference in magnitude between the rates of molecular rotation and interconversion between the two asymmetric forms permits the study of the two motions separately.

The interconversion frequency is from one to two orders of magnitude smaller than the estimated or expected frequencies^{4,5} for the small amplitude harmonic vibrations of the molecule. This difference justifies the separation of the coordinate representing the interconversion from the $3N - 7$ small amplitude vibrations allowing the interconversion to be studied using a one-dimensional potential function. Wilson and co-workers³ believe that the interconversion profile has a "double minimum potential surface with a relatively low barrier between the two minima so that rapid tunneling occurs".

Thus it seems appropriate to use a recently published method^{6,7} for describing the motion of the system in a double minimum potential.

Calculations

The sum of a parabola and a Gaussian or two Morse functions⁸ may be used to represent the double minimum profile. At least three parameters are needed to fit the symmetric energy profile properly to the parabola-Gaussian potential or to the two Morse functions: the energy barrier E , the interminimal distance D , and the curvature at the minima k_m . Ab initio values for E and D along the reaction coordinate have been reported;¹ however, not enough points on the potential energy surface have been published to provide for the proper evaluation of k_m at the minima. Besides, if tunneling is to occur, symmetric double minimum profiles other than the profile

provided by the reaction coordinate must be explored. In such cases, additional points in the potential energy surface are needed. To obtain the necessary information, ab-initio self-consistent field, extended basis set, known as 4-31G, calculations were used.^{9,10} The energies and geometries for the initial and final asymmetric structures as well as the symmetric intermediate of minimum energy (col or saddle point along the reaction coordinate) coincide with those reported by Karlström.¹ Table I shows the Cartesian coordinates of the initial and final states and of the symmetric intermediate, referred to the center of gravity of the molecule after separation of rotational displacements. The numbers used to identify the atoms in the table are shown in Figure 1. It is observed that in the exchange between the two C_s geometries of minimum energy along the reaction coordinate all atoms in the molecule move, most of all the two oxygens and the intervening hydrogen (Figure 2). The energy at various points along the reaction coordinate are given in Table II along with the two hydrogen-oxygen distances. The double minimum energy profile is depicted in Figure 3A. The profile can be fitted to a parabola-Gaussian potential:

$$V = a_2x^2 + v_0e^{-\alpha x^2} \quad (1)$$

The parameters in this potential are calculated from the interminimal distance D , the energy barrier E , and the curvature at the minima k_m . The effective mass used to calculate the tunneling frequency was obtained as the ratio of the components along the reaction coordinate of the contravariant metric tensor \mathbf{a}^{ii} and the contravariant kinetic tensor \mathbf{g}^{ii} .¹¹ All these values are included in Table II. A tunneling frequency of $2.25 \times 10^{10} \text{ s}^{-1}$, corresponding to a wavenumber of 0.75 cm^{-1} , was obtained. This value is lower than the wavenumber given by Wilson et al.³

It is not necessary, when tunneling occurs, that the system moves along the reaction coordinate. Nonclassical behavior may occur by direct transfer from the initial to the final states. Table I shows that, for a direct transfer, the intervening hydrogen is the only atom which moves significantly; the displacement of the other atoms in the molecule is negligible. Therefore, the effective mass of the system will be the mass of the hydrogen atom, although a higher energy barrier and larger interminimal distance will result. Here the initial and final states have the same minimal energy (C_s) geometry as before, but the intermediate state, instead of having the minimal energy (C_{2v}) geometry which corresponds to the saddle point along the reaction coordinate, has, for all atoms but the intervening hydrogen, coordinates which are averages between those in the initial and final states. For the intervening hydrogen the point on the symmetry axis which gives the lowest energy barrier was found. A barrier of 0.035724 au resulted.

Table I. Cartesian Coordinates for the Initial (C_s), Transition (C_{2v}), and Final (C_s) States. Referred to the Center of Gravity and after Separation of Rotational Displacements^a

			initial	transition	final	difference	S(I,T)	S(I,F)
1	H	X	0.43908	0.00000	-0.43908	-0.43908	0.45129	0.8782
		Y	1.30158	1.19730	1.30158	-0.10429		
2	O	X	-1.32136	-1.14637	-1.30536	0.17499	0.17802	0.0501
		Y	0.82291	0.8556	0.87043	0.03274		
3	C	X	-1.23992	-1.17100	-1.19742	0.06892	0.07008	0.0632
		Y	-0.41441	-0.42710	-0.46120	-0.01270		
4	C	X	0.02813	0.00000	-0.02813	-0.02813	0.05398	0.0563
		Y	-1.12992	-1.17599	-1.12992	-0.04607		
5	C	X	1.19742	1.17100	1.23992	-0.02642	0.04313	0.0632
		Y	-0.46120	-0.42710	-0.41441	0.03410		
6	O	X	1.30536	1.14637	1.32136	-0.15899	0.15967	0.0501
		Y	0.87043	0.85566	0.82291	-0.01477		
7	H	X	-2.17108	-2.14098	-2.12583	0.03019	0.06185	0.0683
		Y	-1.00001	-0.94602	-1.05117	0.05399		
8	H	X	0.03131	0.00000	-0.03131	-0.03131	0.05571	0.0626
		Y	-2.22992	-2.27599	-2.22992	-0.04608		
9	H	X	2.12583	2.14089	2.17108	0.01506	0.10622	0.0683
		Y	-1.05117	-0.94602	-1.00001	1.10515		

^a All distances are in ångström units. The last two columns give the linear displacement between the initial and transition states, S(I,T), and the initial and final states, S(I,F).

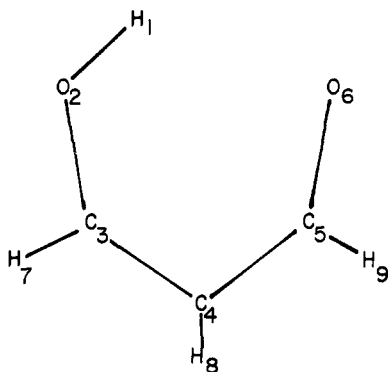


Figure 1. Minimum energy geometry of β -hydroxyacrolein. The numbers correspond to those used in the tables and the text.

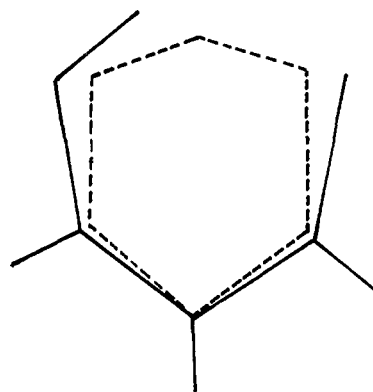


Figure 2. Initial and intermediate configuration of β -hydroxyacrolein. It is noteworthy that in the change from the C_s initial (solid line) state through the C_{2v} intermediate (broken line) state to the C_s (not shown) final state, all the atoms move. In such cases, the effective mass used for the motion of the system along the reaction coordinate is calculated as the ratio of the component along the reaction coordinate of the contravariant metric tensor a^{ij} and that of the tensor g^{ij} .¹⁰

The sum of a parabola and a Gaussian does not fit this profile and the sum of two Morse curves was used instead.⁸ This potential becomes

$$V = v_0 - (2v_0e^{-\beta x_0}) \cosh \beta x - (v_0e^{-2\beta x_0}) \cosh 2\beta x \quad (2)$$

The energy values, the two hydrogen-oxygen distances, parameters, and other results are given in Table III. A wavenumber of 0.663 cm^{-1} resulted which is similar to that along the reaction coordinate.

In a recent report on further work¹² Wilson and co-workers observed nonrigid rotor effects in the spectrum when heavy isotopic species were used. Such effects have not been reported previously.³ The larger effective mass brought the tunneling frequency down to the nonrigid rotor region. For this to occur, the tunneling frequency must be reduced by approximately one order of magnitude. This seems to eliminate the interconversion along the reaction coordinate, as the effective mass will only increase from 4.288 to 5.045. In this case a tunneling frequency reduction by 0.54 is obtained, as shown in Table II. The necessary reduction in tunneling time by one order of magnitude is obtained, however, when the effective mass is doubled. This reduction will occur if, and only if, the intervening hydrogen is the only atom involved in the interconversion while the rest of the atoms move so fast about their equilibrium positions that they may be considered as stationary when the motion of the

intervening proton is studied. This fact is consistent with the difference in order of magnitude between the frequency of interconversion and the $3N - 7$ small amplitude vibrations. It justifies using a profile which has all the atoms but the intervening hydrogen in the average position, not only in the intermediate state (as done above) but also in the initial and final states. The results are displayed in Table IV and the profile in Figure 3C. For hydrogen, the tunneling time is found to be $7.03 \times 10^{-12} \text{ s}$ indicating that the proton oscillates between the two wells with a frequency of $0.711 \times 10^{11} \text{ s}^{-1}$ or a wavenumber of 2.4 cm^{-1} . This value is technically in agreement with the range of frequencies reported by Wilson and co-workers from the statistical treatment of intensity data.³ Substitution of hydrogen by deuterium reduces the tunneling frequency by 0.05, one order of magnitude lower than the value calculated for hydrogen.

Discussion

Various energy profiles for the exchange between the two asymmetric forms of β -hydroxyacrolein and the corresponding

Table II. Energy Profile and Tunneling Frequency along the Reaction Coordinate^a

symmetry	energy, au	O ₂ -H ₁ distance, Å	O ₆ -H ₁ distance, Å
C _s	0.001643	0.926377	1.950066
C _s	0.000417	0.946777	1.887208
C _s	0.000000	0.967642	1.824355
C _s	0.000595	0.988940	1.761506
C _s	0.001963	1.010646	1.698663
C _s	0.009052	1.077955	1.510169
C _s	0.016173	1.148099	1.321750
C _{2v}	0.018513	1.196194	1.196194

For hydrogen $m^{\ddagger} = 7877.89 \text{ au} = 4.288m_{\text{H}}$

For deuterium $m^{\ddagger} = 9267.67 \text{ au} = 5.045m_{\text{H}}$

$$\begin{aligned}
 D &= 0.863609 \text{ au} & a_2 &= 0.127864 & E_g &= 0.003999 \text{ au} \\
 k_m &= 0.540693 \text{ au} & v_0 &= 0.064901 & E_u &= 0.004002 \text{ au} \\
 E &= 0.018513 \text{ au} & \alpha &= 5.667804 & \bar{\nu}_{\text{H}} &= 0.75 \text{ cm}^{-1} \\
 & & \bar{\nu}_{\text{D}}/\bar{\nu}_{\text{H}} &= 0.54 & &
 \end{aligned}$$

^a Self-consistent-field energy at the minimum is -265.237486 au . The sum of a parabola and a Gaussian was fitted to the profile for the calculation of the tunneling frequency.

Table III. Direct Proton Transfer from the Initial Minimum Energy C_s Geometry to the Final Minimum Energy C_s Geometry

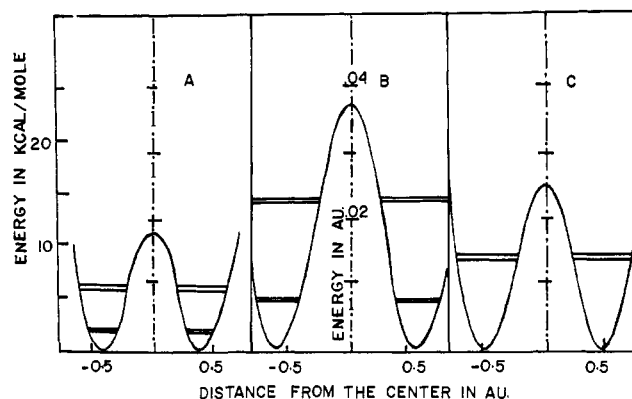
symmetry	energy, au	O ₂ -H ₁ distance, Å	O ₆ -H ₁ distance, Å
C _s	0.001432	1.008860	1.780612
C _s	0.000000	0.967642	1.824355
C _s	0.001525	0.926725	1.868147
C _{2v}	0.038568	1.389912	1.389912
C _{2v}	0.035724	1.360468	1.360468
C _{2v}	0.037476	1.337869	1.337869

$$\begin{aligned}
 E &= 0.035724 \text{ au} & \beta &= 0.59761 \text{ au} \\
 D &= 1.484323 \text{ au} & x_0 &= 1.31932 \text{ au} \\
 k_m &= 0.535900 \text{ au} & E_g &= 0.008271 \text{ au} \\
 m &= 1837.0 \text{ au} & E_u &= 0.008275 \text{ au} \\
 v_0 &= 8.647460 \text{ au} & \bar{\nu} &= 0.663 \text{ cm}^{-1}
 \end{aligned}$$

^a The last three rows in the table correspond to a profile along the axis of symmetry of the molecule. A sum of two Morse curves was used for the profile with the 0.035724 barrier.

tunneling times were calculated. The exchange along the reaction coordinate results in a tunneling frequency one order of magnitude less than the accepted experimental value. The low value is explained by the rather large effective mass involved in the motion along the reaction coordinate. A result technically in agreement with the experimental value is obtained by using a profile based on moving only the intervening proton while the other atoms are kept in the average positions. The mechanism agrees with the observed reduction of tunneling frequencies when heavy isotopic species are used.

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**Figure 3.** Energy profile for (A) the transfer of the system along the reaction coordinate, (B) the direct transfer between the initial and final C_s states, and (C) the transfer of the intervening hydrogen along the path of minimum energy while the remaining atoms in the molecule are kept in the average position.**Table IV.** Energy Profile for the Direct Proton Transfer When All Atoms, Except the Intervening Hydrogen, Remain in the Average Position of the Two Minimum Energy C_s Forms^a

symmetry	energy, au	O ₂ -H ₁ distance, Å	O ₆ -H ₁ distance, Å
C _s	0.001727	1.818332	0.914995
C _s	0.000000	1.798721	0.933462
C _s	0.004181	1.651935	1.073713
C _s	0.018507	1.505783	1.216292
C _{2v}	0.025468	1.360468	1.360468

$$\begin{aligned}
 E &= 0.025468 \text{ au} & \beta &= 6.98518 \text{ au} \\
 D &= 1.655970 \text{ au} & x_0 &= 0.82799 \text{ au} \\
 k_m &= 2.516090 \text{ au} & E_g &= 0.0151824 \text{ au} \\
 m &= 1837.0 \text{ au} & E_u &= 0.0151930 \text{ au} \\
 v_0 &= 0.05137 \text{ au} & \bar{\nu}_{\text{H}} &= 2.37 \text{ cm}^{-1} \\
 & & \bar{\nu}_{\text{D}}/\bar{\nu}_{\text{H}} &= 0.05
 \end{aligned}$$

^a The energy in the minimum is -265.227229 au .

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