

Some MNDO SCF-MO Computations on Proton-transfer Systems

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The MNDO SCF-MO method has been used in a study of a few potential-energy surfaces for the proton abstraction from carbon acids by anionic bases. The calculated force-constant matrices of the reactant and the transition state have been used for the computation of the semiclassical and tunnelling contributions to the overall primary proton/deuteron isotope effect. The variation in this effect caused by reasonable degrees of energetic unsymmetry in the reaction is similar to that observed experimentally. Both contributions vary and are of comparable importance for not too unsymmetric reactions.

Proton-transfer systems have been studied quantitatively for a long time but there are still aspects of the reaction about which there is no consensus of opinion. The experimentally well-established isotope-effect maximum for energy-balanced reactions¹ may thus be due either mainly to the semiclassical (tunnel-correction-free) isotope effect² or mainly to the tunnel effect^{3,4} or, finally and perhaps most likely, to finite contributions from both.⁵ In simple discussions based on the three-atom model as well as in rather complete computer calculations of isotope effects the crucial force constants in the transition state have originated from pure guesswork or the application of simple rules of thumb. It is obvious that little real progress in this field can be made without better knowledge concerning the shape of the potential-energy surface at the transition state. Such knowledge has to be gained by means of quantum-mechanical computations. The semiempirical methods MINDO/3 and MNDO have already been shown to reproduce kinetic isotope effects satisfactorily for some reactions.⁶⁻⁹

In order to obtain full compatibility between

model and reality in solution reactions, solvating molecules have certainly to be introduced into proton-transfer models. In this respect the semiempirical methods seem less promising, being unable to reproduce intermolecular nonbonded interactions in a reliable way. This shortcoming and the fundamental fact that the parameters of semiempirical methods like MNDO¹⁰ (Modified Neglect of Diatomic Overlap) are calibrated by means of data for stable molecules tend to discourage their use with transition states. On the other hand, if *ab initio* methods are to be used, reliable results claim also inclusion of configuration interaction, and the computation becomes lengthy and expensive if molecules of the size of interest to the organic chemist are to be handled. In MNDO electron-correlation effects are at least partly taken care of in the calibration procedure, but only for ordinary, stable molecules,¹⁰ and it is likely that such effects manifest themselves differently in transition states with their looser structures. (See, however, Ref. 11.)

In spite of the expected shortcomings of the simpler methods when applied to proton-transfer transition states we decided to make a modest attempt to scan the field by computations according to the ordinary MNDO scheme on reactions between some simple carbon acids and a few simple bases. It is hoped that the results will at least inspire future investigations of the same systems by more reliable methods, because the variety in behavior found already in this limited study seems quite interesting, if real.

METHOD

The calculations were performed according to the semiempirical scheme devised by Dewar and

Thiel.¹⁰ The actual computer programs used were MNDO by Thiel¹² and a program for calculations of force constants on a MNDO potential surface by W. Thiel, Y. Yamaguchi, G. Ford and S. Olivella, kindly provided by Dr. H. S. Rzepa. (See also Ref. 13).

The latter program was written in FORTRAN for a CDC computer and needed some modifications in order to run on the IBM 3030 N computer at Gothenburg Universities Computing Centre.

For calculations of energy balances the energy of each stable species was computed separately with optimization of all geometric parameters (bond lengths, bond angles and twist angles).

The location of the transition state was determined by the following procedure. The two distances between the proton in flight and its nearest neighbors were assumed to be the major components of the minimum-energy path. When one of these is large compared to its expected value in the transition state it is probably dominating. It is fixed at such a value while all the other geometric parameters are optimized by minimization of the energy. In this way the value of the distance between the proton and its other neighbor is found, and all the structure obtained should not differ too much from one on the minimum-energy path. By observing the variation of the minimized energy and the last-mentioned distance as functions of the predetermined one the approach toward the transition state may be followed. The procedure is then repeated with the roles of the two pertinent distances interchanged. The interrelation between the two distances obtained in this way is best studied in a diagram with the distances as axes. From such a diagram and the energy values for different points in it *approximate* distance values for the transition state may be estimated. Nine pairs of distance values corresponding to a

three times three rectangular array around the most likely location of the transition state are then fixed, and the energy is minimized, this time with the *two* distances being held at the predetermined values and optimizing all the other geometric parameters. The resulting nine energy values are then used as input values in a two-dimensional treatment of the type suggested by McIver and Komornicki.¹⁴ The outcome of this is an improved pair of distance values for the transition state, and generally this single improvement afforded values accurate enough for defining the transition state. The final structure of the transition state was obtained by a complete optimization of all variables but the two distances obtained according to the procedure outlined above.

In calculations of kinetic isotope effects the force constant matrices of the transition states and the corresponding reactants were used as input to the BEBOVIB IV program.¹⁵

The tunnel correction factor Q was computed according to the ordinary Bell formula, for the present purpose written in the form

$$Q = \frac{\frac{1}{2}u_t}{\sin \frac{1}{2}u_t} - \sum_{n=1}^{\infty} (-1)^n \times \left[\exp \left(\frac{u_t - 2n\pi}{u_t} \alpha \right) / \frac{u_t - 2n\pi}{u_t} \right]$$

where $u_t = h|v^*|/kT$ and $\alpha = E/kT$, h and k being Planck's and Boltzmann's constants, respectively, $|v^*|$ the absolute value of the imaginary frequency along the reaction co-ordinate, T the absolute temperature, and E the height of the barrier.

RESULTS AND DISCUSSION

Before considering reaction profiles for the proton-transfer systems studied, it is of interest to

Table 1. Calculated and experimental energies for some proton-transfer equilibria in the gas phase.

Equilibrium	Reaction energy/kJ mol ⁻¹		Exp. (ΔH) ^c
	MNDO ^a	<i>Ab initio</i> ^b	
HO ⁻ + CH ₃ CN ⇌ H ₂ O + ⁻ CH ₂ CN	-177.4	-99.7	-78
HO ⁻ + HC≡CH ⇌ H ₂ O + ⁻ C≡CH	-34.5	-74.1	-68
CH ₃ O ⁻ + CH ₃ CN ⇌ CH ₃ OH + ⁻ CH ₂ CN	-20.1	-32.1	-29

^a Present work. ^b Calculated from values (4-31G) in Refs. 18 and 19. ^c From Fig. 3 in Ref. 20.

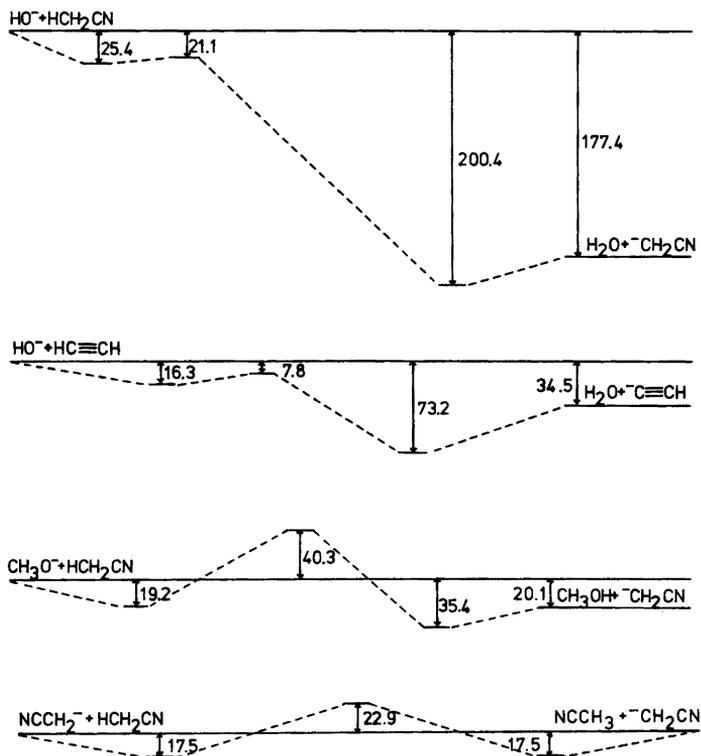


Fig. 1. Energy profiles for some proton-transfer reactions in the gas phase as calculated by the MNDO method. Energies in kJ mol^{-1} .

see if the MNDO method is capable of reproducing the experimental values of the overall energy change in such reactions. We have therefore calculated these energy changes, and the results for three proton-transfer processes can be seen in Table 1 together with the experimental gas-phase data. The results from the present MNDO calculations are in agreement with data published by Dewar *et al.*^{10,16}

There are examples in the literature showing that the MNDO method gives rather reliable results for reaction energies.¹⁷ None of these reactions are, however, of the proton-transfer type and it is interesting to note that it seems as if the MNDO method gives reasonable results for the reactions given in Table 1, too. The values calculated by the MNDO method are at least of the same magnitude as the ones calculated by *ab initio* methods at the 4-31G level, also listed in Table 1.

A simplified picture of the energy profiles for

the reactions studied so far is presented in Fig. 1.

In all four reactions the reactants form a hydrogen-bonded type of ion-molecule complex* in which the distance between the accepting oxygen/carbon and the proton to be abstracted lies in the range 0.25–0.29 nm. Corresponding complexes are also formed on the product side of the reaction. For the three unsymmetric reactions the carbon-hydrogen distance lies in the range 0.19–0.32 nm. The minima corresponding to the ion-molecule complexes have been found by complete optimization of all variables and thus correspond to true minima. It should be added that in a calculation (unpublished results) on proton-transfer from acetylene to acetylide ion a completely symmetric ion-molecule complex was formed with no barrier for the proton-transfer step.

* This is a common phenomenon in gas-phase reactions and has been noted earlier both in calculations and in gas-phase experiments.

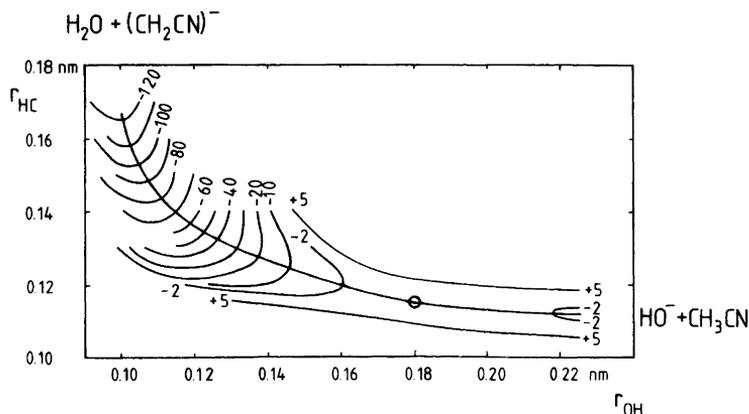


Fig. 2. Potential-energy map for the reaction between acetonitrile and hydroxide ion. Position of the activated complex is denoted by the circle. Energies in kJ mol^{-1} relative to the energy of the activated complex.

In most cases the effort was concentrated upon finding only the stationary points, and thus the horizontal axes in Fig. 1 have no exact physical meaning. Only in the case of the reaction between hydroxide ion and acetonitrile a more thorough mapping of the potential-energy surface was performed, and part of the calculated surface is shown in Fig. 2.

The geometries obtained for the transition states of the four proton-transfer reactions are given in Fig. 3. That these structures correspond to transition states can be seen from Table 2. Only one imaginary frequency of any appreciable size has been found for each transition state. The frequencies corresponding to the three translational and three rotational modes are all rather small and we consider them sufficiently small for the present explorative study. The error in the $3N-7$ real vibrational frequencies should be of little importance.

The calculated geometric data of the neutral reactant molecules are also given in Fig. 3 for

comparison. They were obtained by complete optimization of all variables.

Anomalous geometries. As a test of the procedure outlined in the Method section we also tried some odd starting geometries in the optimization.

In one such case the abstracted hydrogen was placed at an 85° angle to the carbon-carbon bond, 1. The distances between this hydrogen

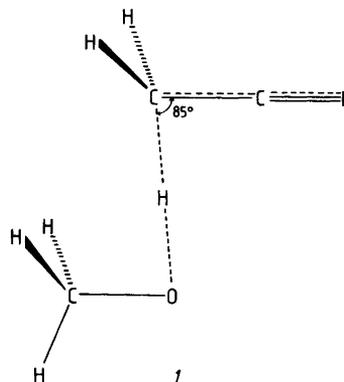


Table 2. The imaginary frequency ν^* of the decomposition mode and the six spurious frequencies ν corresponding to translation and rotation for each transition state.

Transition state	ν^*/cm^{-1}	ν/cm^{-1}					
HO-HCH ₂ CN	196.6i	13.1i	1.5i	0.3i	2.0	7.3	16.0
HO-HCCH	249.1i	6.3i	3.4i	1.0i	0.9	5.9	94.7
CH ₃ O-HCH ₂ CN	1339.1i	54.1i	5.2i	0.0i	0.0i	2.3	15.8
NCCH ₂ -H-CH ₂ CN	1007.9i	10.9i	0.5i	0.0i	0.0	7.8	14.6

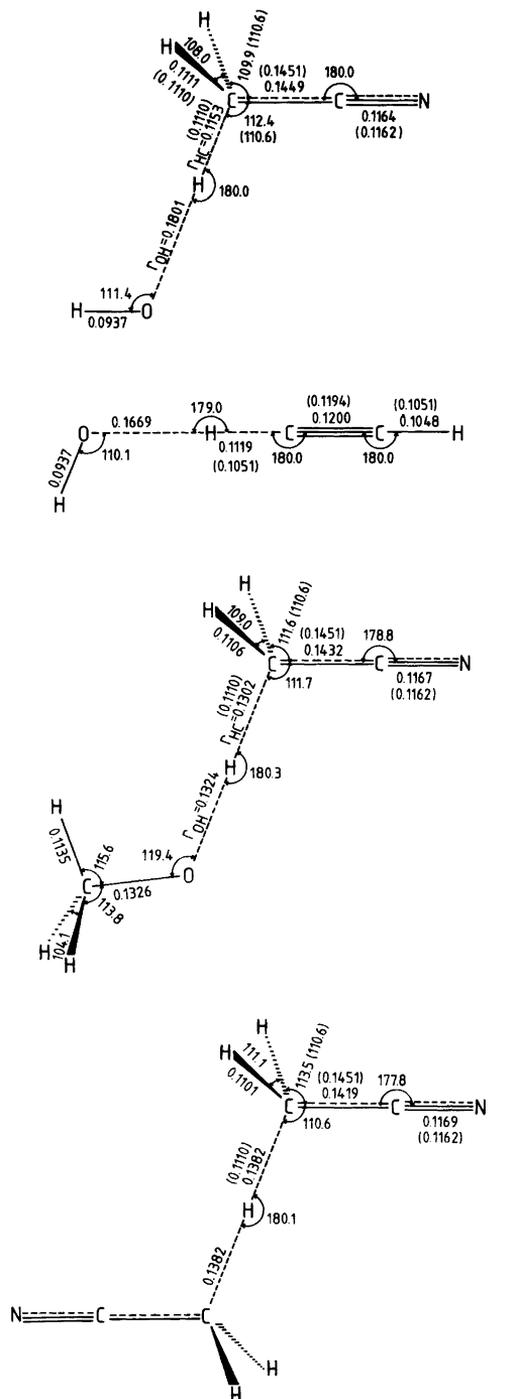
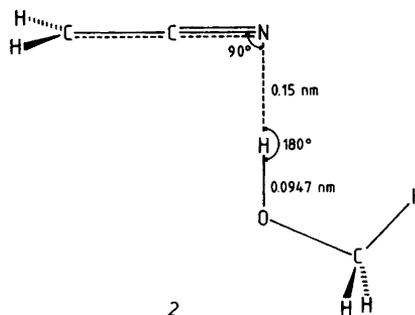


Fig. 3. Optimized transition-state structures. Bond lengths in nm. Values in parentheses correspond to reactant values.

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and the adjacent carbon and oxygen were kept at the transition state values, while all other parameters were optimized. This procedure led to the same structure and energy as for the corresponding transition state in Fig. 3.

In another trial the optimization was started with the methanol molecule placed at the nitrogen end of the acetonitrile anion, 2. Initially



the nitrogen-hydrogen distance was set to 0.15 nm. Full optimization resulted in the formation of an ion-molecule complex with an N-H bond length of 0.27 nm and an O-H bond length of 0.095 nm. The O-H bond of this complex is pointing toward the nitrogen atom, and the HNC angle is 151°. This ion-molecule complex is somewhat higher in energy (0.6 kJ/mol) than the one indicated to the right in Fig. 1. In the latter the abstracted proton is at a distance of 0.31 nm from the acetonitrile carbon and the CHO angle is 144.2°.

Force constants, frequencies and isotope effects. A crucial point in calculating properties of potential-energy surfaces is the determination of the curvature at the stationary points of the surface. It has been pointed out, however, that the MNDO method overestimates the frequencies of stretching vibrations by about 10%.¹³ The same is also true for more sophisticated methods as 3-21 G.²¹

In Fig. 4 a histogram is shown of the relative frequency differences for the four stable molecules water, methanol, acetylene and acetonitrile, studied in the present calculations. The number of normal frequencies represented by the four molecules is 28 (degenerate frequencies counted once). It is easily seen that both methods overestimate the frequencies, even if the *ab initio* method seems to give rise to a somewhat smaller spread.

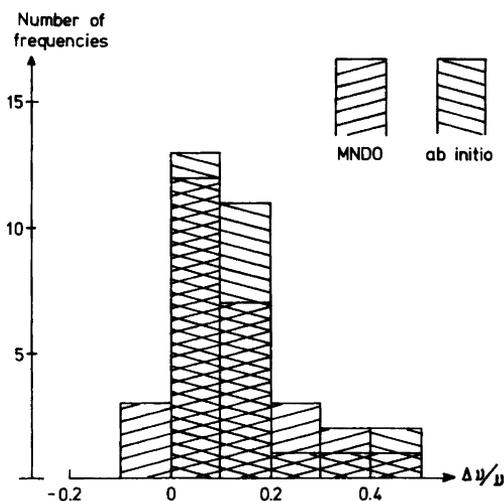


Fig. 4. Histogram showing the relative frequency differences for the four molecules water, methanol, acetylene and acetonitrile. $\Delta\nu/\nu = (v_{\text{calc}} - v_{\text{exp}})/v_{\text{exp}}$. Experimental values from Ref. 22, MNDO values from Ref. 23, *ab initio* data from Ref. 21.

The force-constant matrix obtained originally refers to cartesian co-ordinates but has been transformed into an internal co-ordinate force-constant matrix. The latter force constants are more easily interpreted in terms of changes in bond lengths, bond angles, *etc.* The diagonal ones for reacting bonds in the reactions are given in Table 3.

It is quite remarkable how different in magnitude the force constants of the reacting bonds are. This is in sharp contrast to the results from an electrostatic model for a proton-transfer reaction used by Bell and co-workers.⁴ In the case of hydroxide ion and acetonitrile the calculated

force constant of the incipient O–H bond in the transition state is even negative.

Although the present computations refer to solvent-free systems, it is very tempting to try to draw conclusions concerning the expected behavior under the more familiar solution conditions. In doing this it is assumed that the vibrational analyses are still valid for (solvated) reactants and transition states in solution. It is further assumed that the barrier height which is needed in tunnel-correction computations is equal to the difference in energy level between the transition state and the reactant molecule-ion complex according to Fig. 1.* This is a very rough way to simulate the effect of the solvation, which causes a drastic change in the relative energy levels and, in particular, lowers the level of the reactants in the cases with oxygen bases. Since the main effect is due to solvation of the reactant base ion (which is non-isotopic in the isotope-effect systems concerned), it may still be hoped that the much weaker solvation effects on the neutral reactant and the large transition-state ion do not completely invalidate the conclusions drawn from these computations on a gas-phase model.

Table 4 shows the semiclassical isotopic rate ratio obtained from the vibrational analyses on

* The barrier height should include the difference in zero-point energy between the transition state and the reactant, which difference is generally larger in the deuterated system than in the protiated one. This isotopic difference in barrier height has been neglected here, because the weak isotopic dependence of $|v^*|$ in the two first reactions in Table 3 indicates a strong dependence of the real frequencies of the transition state, tending to cancel the barrier difference, and an addition of about 4.5 kJ to the deuterium barrier affects only the third decimal in Q_D in the third case and not even that in the fourth case.

Table 3. Stretching force constants (in N cm^{-1}) of reacting bonds in proton-transfer reactions in the gas phase.

$\text{B}^- + \text{H} \xrightarrow{F_{\text{AH}}} \text{A} \longrightarrow [\text{B} \overset{F_1}{\text{---}} \text{H} \overset{F_2}{\text{---}} \text{A}]^{\ddagger} \longrightarrow \text{B} \overset{F_{\text{BH}}}{\text{---}} \text{H} + \text{A}^-$						
B^-	H–A	$\Delta E/\text{kJ mol}^{-1}$ ^a	F_{AH}	F_1	F_2	F_{BH}
HO^-	H–CH ₂ CN	–177.4	6.02	–0.03	4.85	9.26
HO^-	H–C≡CH	–34.5	7.55	0.01	5.25	9.26
CH_3O^-	H–CH ₂ CN	–20.1	6.02	0.47	2.67	8.99
NCCH_2^-	H–CH ₂ CN	0	6.02	1.56	1.56	6.02

^a Energy change in completed reaction calculated by the MNDO method.

Table 4. Kinetic isotope effects at 25 °C and reaction co-ordinate frequencies for some proton/deuteron-transfer reactions.

Reactants	ΔE^a kJ mol ⁻¹	$(k_H/k_D)_s^b$	$ v_H^{\ddagger} ^c$ cm ⁻¹	$ v_D^{\ddagger} ^c$ cm ⁻¹	$E^{\ddagger,d}$ kJ mol ⁻¹	Q_H^e	Q_D^e	Q_H/Q_D	k_H/k_D^f
HO ⁻ +CH ₃ CN	-177.4	1.69	196.62	191.99	4.3	1.0385	1.0367	1.002	1.7
HO ⁻ +HCCH	-34.5	1.87	249.06	242.91	8.5	1.0628	1.0596	1.003	1.9
CH ₃ O ⁻ +CH ₃ CN	-20.1	5.77	1339.1	1007.5	59.5	34.03	3.724	9.14	53
NCCH ₂ ⁻ +CH ₃ CN	0	4.93	1007.9	789.9	40.4	3.703	2.018	1.83	9.0

^a Energy change in completed reaction calculated by the MNDO method. ^b Semiclassical isotopic rate ratio. ^c Imaginary frequency along the reaction co-ordinate, absolute value. ^d Assumed effective barrier height. ^e Tunnel correction factor. ^f Overall isotopic rate ratio.

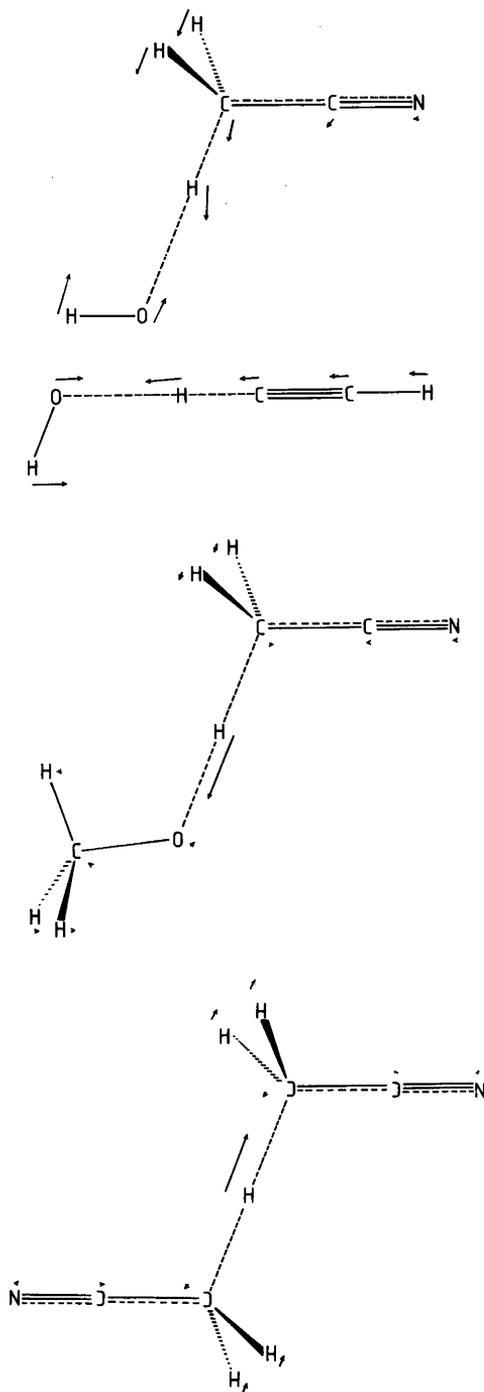


Fig. 5. Relative displacements (not mass-weighted, proton case) of the atoms for the decomposition mode of the four transition states.

reactant and transition state assuming the transferred particle to be a proton/deuteron. The strengthening of the isotope effect on approaching an energy-balanced reaction is evident. (The type of base used in the fourth reaction is different from that in the other three, and hence too much attention should not be paid to the fact that the trends discussed in this paragraph do not place the third and fourth reactions exactly in the order expected from their ΔE values.) The decomposition frequencies are also given, and they increase in the same direction. It is also evident that the isotopic difference in these frequencies increases, absolutely as well as relatively, and these facts together with an increase in barrier height make the tunnel-effect contribution to the isotopic rate ratio increase very rapidly and even surpass the semiclassical one. The last column in Table 4 shows the overall isotopic rate ratio. It should be noted that these ratios could be somewhat too large due to the overestimation of the vibrational frequencies by the MNDO method mentioned above.

Fig. 5 shows the decomposition mode of the four transition states.

Conclusions. There are certainly shortcomings in the application of the MNDO method to transition states, and the quantitative significance of the results obtained in the present calculations is, of course, open to discussion. Still it is hoped that the results considered in a more qualitative way may be instructive and more reliable than any results obtained from classical models.

The overall isotope effect varies with the energetic symmetry in the way shown by several experimental systems, and for reasonably symmetric reactions the semiclassical and tunnelling contributions are of comparable importance, at least according to calculations based on current theories. The potential-energy surface seems to behave as assumed by Melander and Saunders in their discussion of the hydrogen transfer as a three-center reaction.²⁴ Disregarding any entropy contributions, the reaction energies given in Table 4 correspond to an equilibrium constant of 10^{31} , 10^6 , $10^{3.5}$ and 1 at 25 °C, thus at least in the second and third cases to reasonable degrees of unsymmetry. The fact that the equilibrium points in the direction opposite to that expected for a system in solution does not necessarily mean that the distortion of the potential-energy surface caused by energetic unsymmetry comes out in an

unrealistic way. The same principles are probably valid for a distortion in either direction.

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