Concerted Synchronous Two-hydron Transfer within the Formic Acid Dimer. A Kinetic Isotope Effect Study using *Ab initio* Calculations

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Calculated isotope effects on the two-hydron transfer within the formic acid dimer calculated at different levels of theory including perturbational electron correlation correction (MP2) together with normal mode analysis form a basis for the interpretation of isotope effects in two-hydron transfer reactions.

Isotope effects are of great importance in the mechanistic investigations of two-hydron transfer reactions.[1,2] Ultimately it would be desirable to be able to make predictions of transition-state structures from isotope-effect data. The success of such predictions is, however, severely hampered by the lack of useful theoretical models for isotope effects on two-hydron transfer reactions. Recently some theoretical calculations on isotope effects in dihydrogen transfer reactions have been performed.[3]

In order to assist the interpretation of observed isotope effects we have started some theoretical studies using *ab initio* methods. In our first investigation the predicting power of a simple vibrational model was investigated by calculations on the formamidine system at the Hartree–Fock/STO-3G level of theory. At this level the two hydrons are transferred concertedly and synchronously.[4] It was later shown that with more extended basis sets the minimum energy path for the two-hydron transfer in this system corresponds to a stepwise mechanism.[5]

In the present communication we present some data on the formic acid dimer system. This system shows a concerted and synchronous transfer of the two hydrons at all computational levels that have been used.

The formic acid dimer system has been subject to many experimental and theoretical investigations and a recent theoretical study[6] treats the potential energy surface for the two-hydron transfer up to double-ζ plus polarization (DZ + P) level of theory. In the present calculations Pople's split-valence basis set[7] up to and including polarization functions on both hydrogens and heavy atoms has been used.

Table 1. Energies (kcal mol^{-1}; 1 cal = 4.184 J) for two isolated monomers (2M) and the transition state (TS) relative to the stable dimer (D).[a]

Computational level	$E_{2M}-E_D$	$E_{TS}-E_D$
RHF/STO-3G	15.2	5.2
RHF/6-31G	19.1	15.6
RHF/6-31 + G**	13.6	17.1
RMP2/6-31G**	18.4	8.0

[a] Total energies (a.u.) for D at computational levels given in the table (from top to bottom): −372.45992, −377.36144, −377.57674, −378.57113.

Diffuse functions[7] on the heavy atoms have been included to give a better description of the lone pair regions. For the first time the effect of electron correlation (MP2)[8] has been investigated for this type of reaction.

Symmetry-restricted geometry optimization followed by analytical second-derivative calculations were performed to obtain and characterize the stationary points at all levels of theory. We have used Gaussian 86[9] for the Hartree–Fock calculations and CADPAC[10] for calculations at MP2 level of theory. Semiclassical isotope effects were calculated from the geometries and the force constants of the initial state (IS) and the transition state (TS) respectively.

The geometries at the MP2 level are given in Figure 1. Our results on geometries and energies (Table 1) are, at all comparable levels, in good agreement with those in ref. 6.

The results in Table 1 show that the barrier height is extremely sensitive to the choice of basis set and that it changes dramatically with the inclusion of electron correlation. The effect of electron correlation (MP2) is almost as

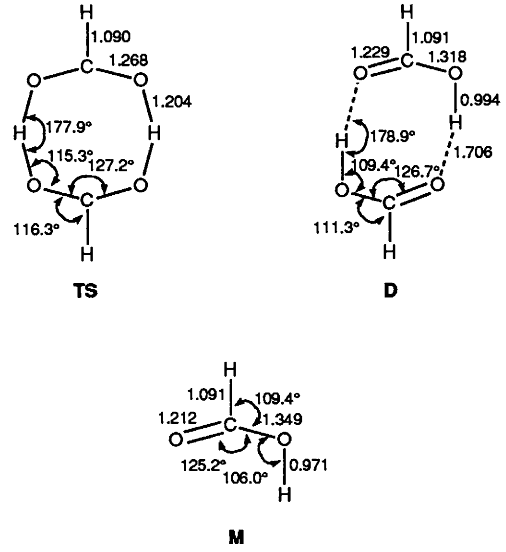

Figure 1. Geometries (distances in Å) calculated at RMP2/6-31G** level of theory for the transition state (TS), the dimer (D), and the monomer (M).

Table 2. Kinetic isotope effects for the two-hydron transfers and difference (Δ) in isotopic sensitivity between IS and TS for different types of X ··· H ··· X motions. Initial state D.

Computational level	k_{HH}/k_{DD}[a]	$\nu_L^{\ddagger}$ (HH) /cm^{-1}	$\Delta_{stretch}$[b]	$\Delta_{ip\text{-}bend}$[b]	$\Delta_{op\text{-}bend}$[b]
RHF/STO-3G	5.2	i1098	1078	−130	−275
RHF/6-31G	21.0	i1743	1700	−205	−288
RHF/6-31 + G**	25.4	i1760	1843	−217	−343
RMP2/6-31G**	11.4	i1347	1356	−146	−238

[a] T = 25.0 °C. [b] $\Delta_{type} = \Sigma(\nu_{HH}^{type} - \nu_{DD}^{type})_{IS} - \Sigma(\nu_{HH}^{type} - \nu_{DD}^{type})_{TS}$.

great (but in the other direction) as going from minimal basis set to VDZ. The fact that the minimal basis calculation gives fairly reasonable relative energies in good agreement with the MP2/6-31G** calculations is probably due to cancellation of errors.

A summary of the calculated isotope effects (with the dimer as initial state) is given in Table 2. All values refer to 25 °C. It was in all cases shown that $k_{HH}/k_{HD} \approx k_{HD}/k_{DD}$ which is expected from the rule of the geometric mean.

The isotope effect values in Table 2 are not that easily interpreted. We have therefore made an analysis of the different normal modes of vibration for both TS and IS (dimer).[4]

The modes were classified as stretches, or in plane or out of plane bendings with respect to the motion of the bridged hydrogens. From these classifications of the motions it was possible to sum the frequency differences between the isotopic species for each group of modes for IS and TS, respectively. These sums are referred to as the isotopic sensitivity for each type of motion. Only vibrations with an isotopic shift greater than 10 cm^{-1} were considered.

It is clear that the stretching vibrations should give rise to a great zero-point-energy effect and a strong kinetic isotope effect. However, this difference in frequencies for the stretching vibrations is counterbalanced by an increase in the isotopic sensitivity of the bending vibrations in the TS which drastically reduces the magnitude of the isotope effect.

This increase in isotopic sensitivity of the bending vibrations in the TS has been found at all computational levels and is not particularly dependent on basis set and not easily predicted from simple models. It makes, however, a substantial contribution to the final value of the isotope effect. The same was found for two-hydron transfer within the formamidine dimer.[4]

A basis set-dependence of the stretching vibrations as well as of the imaginary frequencies can also be seen in Table 2. It is known that frequencies are in general overestimated within the Hartree–Fock approximation and that electron correlation has to be taken into account if accurate frequencies within the harmonic approximation are required.[11] The present calculation on the dimer shows that the differences between calculated (MP2) and experimental[6] vibrational frequencies are approximately half as large as the corresponding differences[6] at the HF/DZ + P level of theory. The similarity between the results with the minimal basis set and the MP2 calculation must therefore be regarded as completely fortuitous.

In any case the results show that the bending vibrations of the transition state play an important role in determining the magnitude of the kinetic isotope effect. It seems that at the present stage an interpretation of an isotope effect for a two-hydron transfer reaction must be accompanied by a thorough theoretical analysis.

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