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Model Computations on Transition States in the Proton Abstraction from Carbon Acids. Influence of Coupling of Atomic Motions on the Importance of Tunnelling and on the Reduced Mass along the Reaction Co-ordinate

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When the abstraction of a proton from a carbon acid is accompanied by mesomeric charge delocalization in the carbanion, the latter will attain a conformation which is different from that of the acid, and it seems natural to depict the transition-state force field by a force-constant matrix containing certain off-diagonal elements. The effect of the introduction of such force constants on the imaginary frequency and on the reduced mass along the reaction co-ordinate has been investigated by model computations according to the Schachtschneider-Wolfsberg-Stern method. The results indicate that this kind of coupling of atomic motions will increase the imaginary frequency and hence promote tunnelling in spite of a simultaneous increase of the reduced mass.

Interaction between the proton in flight and a heavy dipole molecule in the solvent has been found to increase the reduced mass along the reaction co-ordinate and to decrease the imaginary frequency. Such a coupling of motions will thus repress tunnelling.

Until recently [1] the tunnelling mass in proton-transfer reactions has been assumed simply to be equal to the mass of the proton. Besides the attractive simplicity of a transition-state model in which the normal mode corresponding to the reaction co-ordinate * consists in a motion of a hydrogen nucleus relative to exclusively heavy, resting atoms, such a model has also the advantage of according with the feeling that the easiest reaction path and hence the fastest reaction should invariably be associated with the smallest conceivable tunnelling mass. Still it is obvious that this kind of model cannot be realistic in general even as a fair approximation. Since atoms other than hydrogen are not infinitely heavy, there must be at least some compensatory motion of these; this is a trivial fact. Also the positions of the heavy atoms relative to each other cannot in general be fixed in the normal mode concerned. This fact is realized in the following way for the simple transfer of a proton between two heavier atoms.

The longitudinal motions in terms of the internal co-ordinates of a linear three-particle system XYZ can be visualized by means of the motions of a mass particle under the influence of gravity on a surface representing the potential energy (vertically) as a function of the two distances X − Y and Y − Z.[2] The two distance co-ordinate axes (which may have to be scaled somewhat differently) should be horizontal and make a certain acute angle to one another in order for the particle to behave properly, and the mass of the particle should bear a certain relation to the masses of the three atoms. (These measures correspond to bringing the kinetic energy into unit matrix form.) From this model, shown in principle in

* In the present paper the term *reaction co-ordinate* will be used in its more precise meaning of the *normal co-ordinate* corresponding to the imaginary normal frequency of the transition state. For the more general concept the term *reaction path* will be used. Thus the reaction co-ordinate coincides with the reaction path in the saddle point corresponding to the transition state.

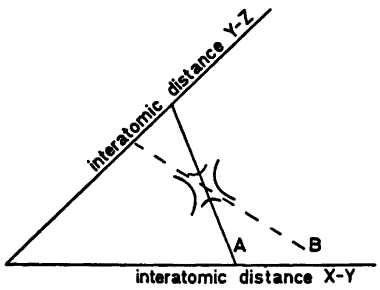

Fig. 1. Simple model used in representing the longitudinal motions of a linear three-atomic system XYZ.[2] The potential energy is represented along an axis perpendicular to the paper. Curved lines join positions of equal potential energy.

Fig. 1, it is obvious that only motions parallel to a certain direction (say A, in case of equal masses for X and Z perpendicular to the bisector of the angle between the distance axes) correspond to a constant sum of the distances X−Y and Y−Z, *i.e.*, to a constant distance between X and Z. This means that the latter distance can be constant in the normal mode corresponding to motion along the reaction co-ordinate only provided that the potential-energy landscape offers the easiest path, the reaction path, with a reaction co-ordinate parallel to A. If there is a lower and/or thinner potential-energy barrier perpendicular to B, the transition state will have its reaction co-ordinate parallel to B, and the corresponding mode will involve a motion of X and Z relative to each other.

If the equation of the potential-energy surface in the immediate vicinity of the saddle point is written

$$2V = F_{11}(\Delta r_{XY})^2 + 2F_{12}\Delta r_{XY}\Delta r_{YZ} + F_{22}(\Delta r_{YZ})^2 \quad (1)$$

where V denotes potential energy, F force constant, and Δr increase in bond length, it is obvious that increased relative importance of the cross term tends to make the angular position of the saddle more and more symmetric with respect to the two displacements Δr_{XY} and Δr_{YZ} and hence to the two co-ordinates r_{XY} and r_{YZ}. Disregarding any possible difference in scaling of the two co-ordinate axes, caused by a difference in mass between X and Z, a large interaction force constant F_{12} may cause the saddle point to take a rather symmetric orientation in Fig. 1 even if F_{11} and F_{22} differ considerably from each other in relative magnitude. Since in proton-transfer reactions the central atom is hydrogen, F_{12} is likely to have a rather large positive value, because hydrogen does not form two stable bonds of covalent character. (The "hydrogen bond" is of low stability, and the ion HF_2^- may be rather exceptional. A positive F_{12} corresponds to a negative contribution to the potential energy when Δr_{XY} and Δr_{YZ} have opposite signs, *i.e.*, for a motion in which one neighbour is approaching and the other leaving the central hydrogen.) This is likely to hold for energetically not too unsymmetric reactions and may be at least part of the explanation why recent experimental estimates of the tunnelling mass [1] have given values so close to the proton mass.

If eqn. (1) is to represent a saddle point it is required that $F_{12}^2 > F_{11}F_{22}$. That a large F_{12} tends to increase the curvature of the potential-energy surface along the reaction coordinate is easily demonstrated for the case $F_{11} = F_{22} = F$. The transformation $\Delta r_{XY} = (\xi + \eta)/\sqrt{2}$, $\Delta r_{YZ} = (\xi - \eta)/\sqrt{2}$ converts then eqn. (1) into eqn. (2).

$$2V = (F_{12} + F)\xi^2 - (F_{12} - F)\eta^2 \quad (2)$$

The expression of $\partial^2 V/\partial\eta^2 = -(F_{12} - F)$ shows the curvature along η in a right-angled co-ordinate system, and the fact that our model requires skewing does not jeopardize the conclusion that an increasing F_{12} increases the absolute magnitude of the (negative) curvature of the skewed surface along the reaction co-ordinate. The importance of tunnelling depends thus strongly on F_{12}. This must be borne in mind in all model computations in which a more or less arbitrary F_{12} is introduced. It is rather common that F_{12} is dealt with merely as a convenient means of securing an imaginary frequency.

From eqn. (2) it is also obvious that the positive curvature along ξ is increased by an increasing F_{12}. This is rather inconsequential in the present context, however, because if the assumption of symmetry is extended to the atomic masses, the corresponding vibrational mode is non-isotopic with respect to hydrogen, which is at rest. Hence the "classical" kinetic

isotope effect would be independent of F_{12}. However, an estimate of the relative importance of tunnelling and the "classical" contribution to the overall isotope effect would lead to an overestimation of the former for too large values of F_{12}.

For energetically very unsymmetric reactions, on the other hand, the possibility exists that F_{11} and F_{22} are rather different in magnitude and even of different signs.[3] The condition $F_{12}^2 > F_{11}F_{22}$ is upheld even for a vanishing F_{12} provided that F_{11} and F_{12} have opposite signs. This is the reason why also negative carbon-hydrogen and oxygen-hydrogen stretching force constants have been tried in the following together with a vanishing off-diagonal force constant representing the coupling between the carbon-hydrogen and the hydrogen-oxygen stretchings.

A more realistic model of the transition state in proton transfer from carbon acids has to include several atoms and force constants. Since there exists no simple algebraic way to express roots of polynomial equations of high degree in terms of the coefficients of the equation, relations between the imaginary frequency and the force constants have to be revealed by means of numerical solution of the secular equation. For this purpose we have used the Schachtschneider-Wolfsberg-Stern method,[4,5] which also affords the "classical" isotope effect when a model for the reactant is introduced. An approximate correction factor [6a] for the tunnel effect can easily be appended afterwards, if desired. In the present investigation we have been chiefly interested in the effect on the imaginary frequency $\nu^{\ddagger}_{H}$ and on $\nu^{\ddagger}_{H}/\nu^{\ddagger}_{D}$ of different off-diagonal force constants in the transition state and of force constants arising from the interaction between the latter and a solvent molecule.

Off-diagonal force constants have not been commonly used in model calculations of, *e.g.*, isotope effects. However, Yankwich [7] and his collaborators have used off-diagonal force constants in the modelling of transition states in the decomposition of, *e.g.*, oxalic acid for the purpose of creating a reaction co-ordinate with a preselected motion and a preselected imaginary frequency. Our approach is in some respects opposite to that of Yankwich *et al.* While their computations provide off-diagonal force constants which correspond to a preselected reaction co-ordinate behaviour but have no obvious physical interpretation, the purpose of our computations is to find out the consequences for the transition-state behaviour of off-diagonal force constants which may be required by the electronic structure of the transition state.

Saunders *et al.*[8] have used off-diagonal elements in connection with model computations on the mechanism of elimination and regarded them in about the same way as they have been regarded in the present paper, *i.e.*, as chemically required features of the force field of the transition state.

It must be remembered that any force-constant model of the transition state is limited in itself to a description of the shape of the col in the multi-dimensional space in terms of a second-degree hypersurface representing the potential energy in the immediate neighbourhood of the saddle point. This is sufficient for the prediction of the normal vibrational modes and their frequencies, the imaginary as well as the real ones. On the other hand, the treatment does not contain any assumption concerning the height of the potential-energy barrier. Thus only isotopic rate ratios but no absolute rates can be obtained, and the tunnel correction [6a] has to be limited to its first term $\frac{1}{2}u^{\ddagger}/\sin\frac{1}{2}u^{\ddagger}$ with $u^{\ddagger} = h|\nu^{\ddagger}|/\mathbf{k}T$, h and $\mathbf{k}$ being Planck's and Boltzmann's constants, respectively, and T the absolute temperature. This simple expression can only be used with rather moderate values of $u^{\ddagger}$, however, and since the tunnel correction factor increases with $|\nu^{\ddagger}|$, the trend in $|\nu^{\ddagger}_{H}|$ will frequently be used in the following as a simple indicator of the trend in the importance of tunnelling. Quantitative estimates of the force constants are very difficult or impossible, and a direct comparison between values of $|\nu^{\ddagger}|$ computed in this way and those obtained from experimental data is hardly warranted.

The term "mass along the reaction co-ordinate" imparts the feeling that the imaginary frequency is settled by a single physically existing mass and a negative force constant corresponding to the curvature of the potential-energy surface. In a polyatomic entity this is no more true for the imaginary normal frequency than for the ordinary real normal frequencies, which in general result from a com-

plicated interplay of several atomic masses and the force field. It is even true that two isotopic systems will in general not have exactly the same reaction co-ordinate, although they correspond to the same potential-energy surface before it is skewed. In the case of the simple three-atomic system discussed above, the latter fact is reflected by the model of Fig. 1 being somewhat different for different isotopic systems. Thus the skewing angle and the scaling of the axes are dependent on the masses of the real atoms, and isotopic substitution will consequently reshape that kind of potential-energy surface. Nevertheless, for a discussion of the degree of participation of heavy atoms in the normal mode of decomposition, the semi-quantitative concept of a "reduced mass along the reaction co-ordinate" may be useful. This is founded on an assumed similarity between the reaction co-ordinates, in virtue of which $(\nu^{\ddagger}_{H}/\nu^{\ddagger}_{D})^2$ could serve as an approximate measure of the ratio $m^{\ddagger}_{D}/m^{\ddagger}_{H}$ between the two reduced masses. The ratios would be equal if the curvature of the potential-energy surface in the direction of the proper reaction co-ordinate were exactly the same in the two isotopic cases. A proton/deuteron in flight among solely much heavier and thus resting atoms would give $\nu^{\ddagger}_{H}/\nu^{\ddagger}_{D}=\sqrt{2}$, and if additional, nonisotopic masses take part in the motion a value between 1 and $\sqrt{2}$ is to be expected. Owing to the finite mass of carbon, oxygen, *etc.*, the upper limit $\sqrt{2}$ is hardly reached. In spite of the uncertainty caused by the difference in reaction co-ordinates it seems hard to devise a more reliable single gauge of the degree of participation of masses other than that of the central hydrogen in the motion along the reaction co-ordinate.

The chemical constitution of most strong carbon acids and, in particular, of their anions makes it interesting to investigate the effect of certain off-diagonal force constants on the degree of tunnelling. Strong carbon acids are frequently strong because splitting off of the proton allows the remaining carbanion to be stabilized by electron delocalization. This rearrangement of the electronic structure is accompanied by some rearrangement also of the relative position of the atomic nuclei, different hybridization and bond orders requiring different bond angles and bond lengths for the overall molecular energy to be at a minimum. The simple carbon acid nitromethane may be taken as an example. In the acid, carbon has four ligands and is approximately tetrahedral, and the carbon-nitrogen bond is a single bond. In its anion, carbon has only three ligands, the carbon-nitrogen bond has considerable double-bond character, while the nitrogen-oxygen bonds have lost most of the fractional double-bond character they have in the acid. The relative positions of the atoms must change in the proton abstraction in such a way that the remaining part of the molecule becomes flat, that carbon and nitrogen approach each other slightly, and that the nitrogen-oxygen distances increase to some extent. The smoothest transition from acid to anion must consequently involve some motion of all the atoms, *i.e.*, the atomic motions must be coupled to each other. In terms of the common valence-force-field treatment of the transition state this corresponds to the existence of several off-diagonal elements in the **F** matrix. It is rather easy to see, for instance, that a simultaneous increase of the distance between carbon and the proton to be abstracted by a base and decrease of the carbon-nitrogen distance must be energetically more favourable than a simultaneous increase (or decrease) of both distances. Hence the expression for the potential energy ($2V=etc.$) ought to contain a term $2F_{HC,CN}\Delta r_{HC}\Delta r_{CN}$ in which the force constant is positive. The same kind of reasoning can be applied to other combinations of co-ordinate displacements. The question is how many finite off-diagonal elements **F** should contain. From the point of view of atomic structure and binding power, it seems natural to include only those elements which correspond to two internal co-ordinates having one atom in common.

The idea of the coupled motions may give the intuitive feeling that the inertial mass along the reaction co-ordinate increases with the introduction of finite off-diagonal force constants, and that this should result in a decreased tunnelling probability. That this is not exactly so in general will be seen in the following.

Recently another kind of coupling has been discussed in connection with experimental results.[1,9] It is quite natural to expect an ap-

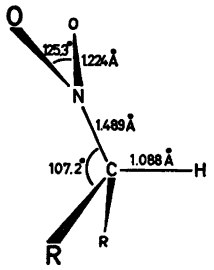

Fig. 2. Bond lengths and bond angles used for nitromethane (R = H).[10] The three atoms H, R and R are assumed to be situated at the corners of an equilateral triangle. One of the NCH planes is assumed to be perpendicular to the plane common to the C, N and both of the O atoms.

preciable interaction with the solvent when the proton is in transit, and this is true about polar solvents in particular. In some of the present computations the transition-state model has been supplemented by the introduction of two atoms, corresponding to a dipole molecule, and the effect of a bending force constant joining it with the proton has been studied. The results seem to corroborate experimental evidence [1] concerning the effect of solvent polarity on tunnelling probability, and this kind of coupling tends to decrease the importance of tunnelling in agreement with intuitive expectation.

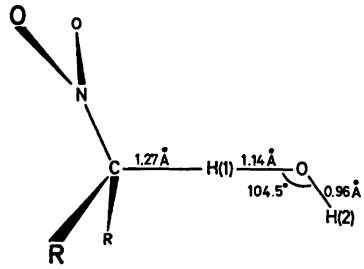

Fig. 3. Bond lengths and bond angles used for the non-planar transition-state model. The C−H(1) and O−H(1) distances are calculated from the corresponding normal bond distances in nitromethane [10] and water,[11] respectively, using Paulings bond number rule [12a] with a bond number equal to 0.5 for the C−H(1) and the O−H(1) bond. The hydroxide O is assumed to be situated on the CH(1) line, and H(2) lies in the NCH(1)O plane. (Angles and bond lengths not given are identical with the corresponding ones in Fig. 2.)

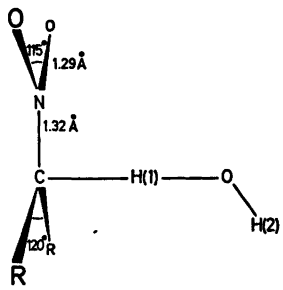

Fig. 4. Bond lengths and bond angles used for the planar transition-state model.[13] The NOO and CRR groups are assumed to be coplanar and perpendicular to the plane of NCH(1)OH(2). The latter plane bisects the ONO and RCR angles. (Angles and other bond lengths not given are identical with the corresponding ones in Fig. 3.)

MODELS AND COMPUTATIONS

The present computations refer to the proton abstraction by hydroxide ion from nitromethane and, in some cases, 2-nitropropane.

Geometry. Bond lengths and bond angles for nitromethane have been taken from Ref. 10 and are shown in Fig. 2.

Bond lengths and bond angles for 2-nitropropane (R = CH_3 in Fig. 2) are assumed to be the same as for nitromethane with the exception that the two methyl groups are treated

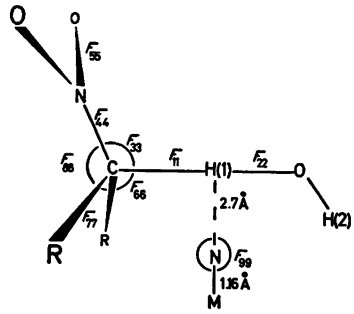

Fig. 5. Transition-state model including a solvent molecule. M and N are situated in the NCH(1)OH(2) plane. M, N and H(1) lie on a straight line, perpendicular to the CH(1)O line. M corresponds to the CCH_3 part of acetonitrile. The H(1)−N distance is equal to the sum of the van der Waals radii [12b] of N and H. The M−N distance is equal to the C≡N distance in CH_3CN.[14] *F* is symbol for (diagonal) force constant. (Distances and angles not given are the same as the corresponding ones in Fig. 3.)

Table 1. Diagonal force constants used in the calculations unless otherwise indicated.

Type of force constant [a]	Value in nitromethane and 2-nitropropane [b]	Value in the transition state [c] and symbol in Fig. 5
C–R, s	5	5
C–H(1), s	5	2.5[d] F_{11}
C–N, s	5.5	5.5, (10) F_{44}
N–O, s	8	8, (6) F_{55}
H(1)–O, s		3.3[e] F_{22}
O–H(2), s		7.2[f]
R–C–R, b	0.5	0.5, (0.35) F_{77}
R–C–H(1), b	0.5	0.25 F_{66}
R–C–N, b	0.7	0.7, (0.5) F_{88}
H(1)–C–N, b	0.7	0.35 F_{33}
C–N–O, b	0.8	0.8
O–N–O, b	0.9	0.9
N–O, b (out of plane)	0.4	0.4
H(1)–O–H(2), b		0.33[e]
C–H(1)–O, b (degenerate linear bending)		0.1[g]
H(1)–N–M, b (degenerate linear bending)		0–0.3[h] F_{99}
ON–CR, t	0.01[f]	0.01[g]
NC–OH(2), t		0.01[g]

[a] s = stretching force constants in mdyn Å^{-1}, b = bending force constants in mdyn Å rad^{-2}, t = torsional force constants in mdyn Å rad^{-2}. [b] Calculated from Ref. 15 with some changes to achieve better consistency with frequency data[16] without using the interactions between non-bonded atoms in Ref. 15. [c] Number in parenthesis indicates value of the force constant used in some computations on the planar transition-state model (Fig. 4). [d] Calculated as half the value in nitromethane. [e] Calculated as half the value in Ref. 17. [f] Calculated as the arithmetic mean of the values for H_2O [17] and OH^-.[18] [g] Estimated value. [h] This force constant is used only in the transition-state model with a solvent molecule included (Fig. 5).

as two mass points with the mass 15 at a distance of 1.54 Å from the central carbon atom.

The geometry of the "carbon acid part" of the transition state is assumed to be the same as for the initial state (nitromethane or 2-nitropropane) in most of the computations, but the hydrogen in transit is moved somewhat towards the hydroxy oxygen. The geometry of the "water part" of the transition state is taken from Ref. 11. The geometry of the transition state has thus been assumed to be the one shown in Fig. 3 with only the exceptions explicitly stated below.

To illustrate the effect of an assumed planarity of the carbanion part of the transition state, the model shown in Fig. 4 was used in some of the computations.

The transition-state model used in the calculations illustrating the coupling between the hydrogen in transit and a solvent molecule is shown in Fig. 5. The solvent interacting with the hydrogen in transit is assumed to be acetonitrile. Thus, M in Fig. 5 corresponds to the CCH_3 part of acetonitrile and is treated as a mass point with the mass 27.

Force constants. The diagonal force constants used in the calculations are given in Table 1. For nitromethane they are based on literature data which have been modified to achieve reasonable agreement with the experimental vibration frequencies when using a simpler force field without non-bonded interactions. The pertinent force constants for 2-nitropropane have been assumed to be the same as for nitromethane. For the transition state the diagonal force constants have been obtained from reactant data using simple assumptions concerning the fractional bonds. In the planar transition-state model (Fig. 4) some of the force constants were varied to account for the change in hybridization. The modified force constants are given in parentheses in Table 1.

The important off-diagonal force constant F_{12} has been so chosen as to afford an imaginary frequency in the same region as obtained from experimental results [1] (order of magnitude

Table 2. Effect of introduction of off-diagonal force constants into the transition state. Transition-state model: non planar (Fig. 3). $F_{12}=3$ mdyn Å^{-1}. Temperature: 25 °C. The nature of the off-diagonal force constants is evident from their indices, related to those in Fig. 5 and indicating their position in the **F** matrix.

Computation number	F_{13}[a]	F_{14}[b]	F_{16}[a]	F_{17}[a]	F_{18}[a]	F_{34}[a]	F_{45}[b]	$\lvert\nu\mp_H\rvert$/cm^{-1}[c] A	B	$\nu\mp_H/\nu\mp_D$[c] A	B	k_H/k_D[c] A	B
1								668.7	664.3	1.377	1.386	7.088	7.516
2	0.2							727.4	720.9	1.359	1.370	6.856	7.283
3	0.2	1.0						853.7	852.2	1.332	1.340	6.410	6.773
4	0.2	1.0	0.2					928.3	896.7	1.320	1.311	6.173	6.553
5	0.2	1.0	0.2	−0.2				1025.5	918.6	1.300	1.294	5.853	6.443
6	0.2	1.0	0.2	−0.2	−0.2			1119.0	989.4	1.283	1.276	5.569	6.196
7	0.2	1.0	0.2	−0.2	−0.2	−0.2		1121.4	992.0	1.281	1.274	5.569	6.195
8	0.2	1.0	0.2	−0.2	−0.2	−0.2	1.0	1123.2	994.3	1.281	1.274	5.563	6.187

[a] Stretching-bending interaction force constant in mdyn rad^{-1}. [b] Stretching-stretching interaction force constant in mdyn Å^{-1}. [c] A: carbon acid: nitromethane, B: carbon acid: 2-nitropropane.

for $\lvert\nu\mp_H\rvert$ 1000 cm^{-1}). The values of F_{12} and of such force constants which are represented in Table 1 but occasionally assigned different values are explicitly stated in connection with each of the Tables 2 – 6.

The other off-diagonal force constants to be used in the following are given below in connection with each table of results. They are always of a rather moderate magnitude, and the condition $F_{ij}^2 < F_{ii}F_{jj}$ is fulfilled in all cases except in the computations 15 and 16 (Table 4) in which F_{11} has been assumed to be equal to or less than zero.

Computations. The computations have been made with a computer program originally devised by Schachtschneider [4] for calculating vibrational frequencies by the **FG** matrix method.[19] The program has been modified by Wolfsberg and Stern [5] to calculate isotope effects. The computations were performed on an IBM 360/65 or an IBM 370/145 computer at Gothenburg Universities Computing Centre.

RESULTS AND DISCUSSION

For our studies we have chosen the simple carbon acid nitromethane in its reaction with hydroxide ion. When considered necessary, the computations have been supplemented by a similar study of 2-nitropropane in order to avoid unexpected consequences of the low masses of the non-reacting hydrogen atoms in the former molecule. As shown below, the behaviour of the two carbon acids is qualitatively the same, although there are differences in the quantitative outcome of the computations.

Effect of introducing off-diagonal force constants. Table 2 shows the effect of introducing non-vanishing off-diagonal force constants other than F_{12} into the transition-state models for nitromethane (A) and 2-nitropropane (B). The magnitudes of all these constants are open to discussion, of course, but their signs are given by the rule that an adjustment towards the final equilibrium conformation of the carbanion should result in a lower potential energy than a motion opposing the rules governing hybridization and the relation between bond order and bond length (*cf.* above).

The successive introduction of these constants is found to invariably raise the imaginary frequency and the apparent mass along the reaction co-ordinate.* The "classical" isotope effect is weakened, probably because of an increase also in the real frequencies of the transition state. The difference between the two carbon acids is quantitative rather than qualitative.

As could perhaps be anticipated, the importance of the off-diagonal force constants decreases with increasing distance from the

* If, however, $F_{12}=A(F_{11}F_{22})^{\frac{1}{2}}$ and A is given a value between 1 and 1.01, $\nu\mp_H/\nu\mp_D$ has been found in a separate set of computations to pass through a minimum when F_{13} is increased. For larger values of A no such behaviour is observed.

reaction centre. Thus it is obvious that the introduction of F_{34} and F_{45}, not directly related to the stretching of the breaking bond, is rather inconsequential. These constants will therefore be dropped in the following.

The effect of introducing separately several of the off-diagonal force constants has also been tested. The results are not given here, since they show the same general pattern.*

In comparing the results it is of some importance to keep in mind that, owing to the symmetry of the model, the symbols "6" and "8" define two angles each, while "7" denotes a single angle.

Influence of conformation of transition state. In the proton-transfer reaction the spatial arrangement around the carbon atom originally carrying the proton undergoes a gradual change from an approximately tetrahedral to a planar one. The transition state is therefore likely to have some intermediate conformation. The exact geometry is not likely to be critical, and in most of the present computations it has been simply assumed that the transition state has the same angular geometry as the reactant. On the other hand, it seemed advisable to make a few computations also on the other limiting conformation (Fig. 4).

Since the sum of the angle symbolized by "7" and the two angles symbolized "8" (Fig. 5) has the value of 360° in the planar conformation, F_{17} and F_{18} cannot both have negative values, because when the proton in transit moves further away from the carbon atom, these angles cannot all increase, nor does any single angle do so at the expense of any other in the conformation of lowest potential energy. Irrespective of its direction, a deviation from planarity of the carbanion will imply a decrease of the angles concerned. Hence there is no longer any natural coupling between the changes in these internal co-ordinates and the change in the internal co-ordinate symbolized "1", and the off-diagonal force constants F_{17} and F_{18} have to vanish.

The same purely geometrical restriction does not apply to the angles "3" and "6", although there seems to be little reason why their equilibrium values should decrease past 90°. The latter kind of reasoning applies also to the distance "4". Since the planar model is used mainly as a representative of "almost planar" transition states, however, the off-diagonal elements F_{13}, F_{16} and F_{14} have still been introduced, and the results for nitromethane are shown in Table 3. Column D and E correspond to the planar model with two different sets of diagonal force constants. Column C corresponds to the previous non-planar transition state and contains results already presented in Table 2 and now reproduced in order to facilitate comparison with column D, which results from the same set of force constants.

It is obvious that the introduction of off-diagonal force constants has a similar effect in the planar transition state as in the non-

* See footnote on the preceding page.

Table 3. Comparison between results from computations using non-planar (Fig. 3) and planar (Fig. 4) transition-state models. Carbon acid: nitromethane. $F_{12}=3$ mdyn Å^{-1}. Temperature: 25 °C.

Computation number	F_{13}[a]	F_{14}[b]	F_{16}[a]	$\lvert\nu^{\ddagger}_{H}\rvert$/cm^{-1} [c]			$\nu^{\ddagger}_{H}/\nu^{\ddagger}_{D}$ [c]			k_H/k_D [c]		
				C	D	E	C	D	E	C	D	E
9				668.7	671.4	671.4	1.377	1.376	1.376	7.088	7.068	7.066
10	0.2			727.4	734.6	734.5	1.359	1.357	1.357	6.856	6.816	6.815
11	0.2	1.0		853.7	843.5	810.8	1.332	1.330	1.346	6.410	6.418	6.581
12	0.2	1.0	0.2	928.3	965.9	941.8	1.320	1.279	1.286	6.173	5.925	6.020

[a] Stretching-bending interaction force constant in mdyn rad^{-1}. [b] Stretching-stretching interaction force constant in mdyn Å^{-1}. [c] C: non-planar transition-state model. This column is identical with column A in computations 1–4. D: planar transition-state model using the same diagonal force constants as for the non-planar transition-state model. E: planar transition-state model using the diagonal force constants in parentheses in Table 1.

Table 4. Effect of strong energetic unsymmetry in the reaction, F_{11} and F_{22} strongly dissimilar. Carbon acid: nitromethane. Transition-state model: non-planar (Fig. 3). Temperature: 25 °C.

Computation number	F_{11}[a]	F_{22}[a]	F_{12}[b]	$\lvert\nu^{\ddagger}_{H}\rvert$/cm^{-1} [c]		$\nu^{\ddagger}_{H}/\nu^{\ddagger}_{D}$ [c]		k_H/k_D [c]	
				F	G	F	G	F	G
13	5	0	2	732.3	766.6	1.131	1.128	3.419	3.374
14	4	−1	0	503.0	494.6	1.033	1.031	1.662	1.641
15	−1	6	0	481.4	721.5	1.025	1.032	1.042	1.063
16	0	6.6	2	518.2	865.4	1.067	1.084	1.956	1.992

[a] Stretching force constant in mdyn Å^{-1}. [b] Stretching-stretching interaction force constant in mdyn Å^{-1}. [c] F: no interaction force constants except F_{12}. G: $F_{13}=0.2$ mdyn rad^{-1}, $F_{14}=1.0$ mdyn Å^{-1}, $F_{16}=0.2$ mdyn rad^{-1}, $F_{17}=F_{18}=-0.2$ mdyn rad^{-1}.

planar one. It seems safe to conclude that the geometry is not critical, nor does the choice of diagonal force constants more appropriate for a carbanion (E) cause any major change in comparison with the outcome from the use of more reactant-like ones (D).

Effect of energetic unsymmetry in the reaction. It seems possible that strongly exo- and endothermic reactions may have so distorted potential-energy surfaces that one of the force constants F_{11} and F_{22} approaches and even passes zero.[3] Some computations have been carried through in order to elucidate the effect of the introduction of off-diagonal force constants in such cases.

In Table 4 sets of F_{11}, F_{22}, and F_{12} have been used which have one of these three constants equal to zero. Computations 13 and 14 correspond to very reactant-like transition states, and 15 and 16 to very product-like ones. In the former case the isotope effect should almost vanish.[20] That there is still a considerable deviation of k_H/k_D from unity is due to the fact that there is no exact matching between the assumed force constants for the transition state and those for the reactant. The assumption [20] of a vanishing interaction between the two fragments is thus not valid in the present case.

The effect of the introduction of the interaction force constants F_{13}, F_{14}, F_{16}, F_{17}, and F_{18} is seen from a comparison between columns F and G in Table 4. With the reactant-like transition state (computations 13 and 14) the effect on $\lvert\nu^{\ddagger}_{H}\rvert$ is small and even uncertain as to its direction. In such a reactant-like transition state the motion along the reaction co-ordinate consists mainly in a relative motion between the carbon acid and the hydroxide ion, and the hydrogen-oxygen distance dominates the reaction co-ordinate. Hence neither the carbon-hydrogen distance "1" nor the other internal co-ordinates of the carbon acid have much to do with this motion.

In the product-like transition state, corresponding to computations 15 and 16, on the other hand, the carbon-hydrogen distance "1" dominates the reaction co-ordinate, and the off-diagonal force constants associated with that co-ordinate have an effect on $\lvert\nu^{\ddagger}_{H}\rvert$ similar to that in the more symmetric transition state treated above.

The influence of the off-diagonal force constants on the reduced mass along the reaction co-ordinate is very weak. This could be expected in view of the large reduced mass which results from a relative motion of two heavy fragments. In the product-like transition state, in which the distance "1" is heavily involved in this motion, the direction of the small effect is opposite to that in the more symmetric case, and the reduced mass seems to decrease slightly. It is impossible to decide whether this is to be considered a "mass" or a "barrier-shape" effect.

Effect of steric hindrance. It is a well-established experimental fact that steric hindrance tends to increase the importance of tunnelling. It is consequently of interest to modify the force field in a direction that would correspond to steric interaction between the reactants. Except for an increase F_{12},[21] corresponding to an augmented potential-energy increase on simultaneous decrease of the carbon-hydrogen

Table 5. Effect of increase in the bending force constants, illustrating possible effect of steric hindrance. Carbon acid: 2-nitropropane. Transition-state model: non-planar (Fig. 3). $F_{12} = 3$ mdyn Å^{-1}.

Computation number	F_{33}[a]	F_{66}[a]	$\|\nu^{\ddagger}_{H}\|$/cm^{-1} [b]		$\nu^{\ddagger}_{H}/\nu^{\ddagger}_{D}$ [b]		k_H/k_D [b]	
			F	G	F	G	F	G
17(=1B, 6B)	0.35	0.25	664.3	989.4	1.386	1.276	7.516	6.196
18	0.50	0.35	663.8	986.7	1.387	1.278	6.769	5.588

[a] Bending force constant in mdyn Å rad^{-2}. [b] F: no interaction force constants except F_{12}. G: $F_{13} = 0.2$ mdyn rad^{-1}, $F_{14} = 1.0$ mdyn Å^{-1}, $F_{16} = 0.2$ mdyn rad^{-1}, $F_{17} = F_{18} = -0.2$ mdyn rad^{-1}.

and hydrogen-oxygen distances, an increase in the forces opposing flattening of the carbanionic part is likely. The former modification is known to increase $|\nu^{\ddagger}_{H}|$.[21] The effect of the latter on the transition state of 2-nitropropane has been investigated in computation 18, the results of which are shown in Table 5 together with those previously obtained in computations 1B and 6B.

The increase in the bending force constants F_{33} and F_{66} is found to have negligible effects on $|\nu^{\ddagger}_{H}|$ and $\nu^{\ddagger}_{H}/\nu^{\ddagger}_{D}$, the former actually decreasing slightly. The importance of tunnelling is thus at least not increased for that reason.

The only obvious effect of increasing F_{33} and F_{66} is a weakening of the classical isotope effect. This was to be expected because of an increase in the transition state of zero-point energy sensitive to the isotopic mass of the proton in flight.

Effect of introduction of a dipole solvent molecule. Tunnelling has been found to be more important in less polar solvents than in more polar ones, and this has been ascribed to a coupling between the motions of the proton in flight and solvent molecules in the latter.[1,9] Such a coupling will increase the reduced mass along the reaction co-ordinate. It seems to be of interest to introduce this kind of coupling in the present study of the vibrational behaviour of a transition state.

A dipole molecule M−N, thought of as a simplified model of acetonitrile, $CH_3C{\equiv}N$, with its negative pole at N, has been introduced into the ordinary transition-state model (Fig. 5). The dipole points with its negative end at the proton in flight, and its direction is assumed to be perpendicular to the line defined by the three reaction centres. The N−H distance is assumed to be the sum of the van der Waals radii of N and H.

Computation 19 (Table 6) was carried through without any force constants pertaining to the atoms M and N and gives the same results as computations 1A and 6A. In computations 20 and 21 the dipole molecule is assumed to exert its action *via* a bending force constant F_{99}, which has the same value in the plane of the paper and in a plane perpendicular to it. The effect is a decrease in $|\nu^{\ddagger}_{H}|$, accompanied by an increase in the reduced mass.

Table 6. Effect of introduction of a dipole solvent molecule into the transition state. Carbon acid: nitromethane. Transition-state model: non-planar (Fig. 5). $F_{12} = 3$ mdyn Å^{-1}.

Computation number	F_{99}[a]	F_{NM}[b]	$F_{H(1)N}$[b]	$\|\nu^{\ddagger}_{H}\|$/cm^{-1} [c]		$\nu^{\ddagger}_{H}/\nu^{\ddagger}_{D}$ [c]	
				F	G	F	G
19				668.7	1119.0	1.377	1.283
20	0.1			653.2	1111.7	1.373	1.281
21	0.3			626.4	1098.0	1.361	1.278
22	0.1	16		653.2	1111.7	1.373	1.281
23	0.1	16	0.5	653.2	1111.2	1.374	1.281

[a] Bending force constant in mdyn Å rad^{-2}. [b] Stretching force constant in mdyn Å^{-1}. [c] F: no interaction force constants except F_{12}. G: $F_{13} = 0.2$ mdyn rad^{-1}, $F_{14} = 1.0$ mdyn Å^{-1}, $F_{16} = 0.2$ mdyn rad^{-1}, $F_{17} = F_{18} = -0.2$ mdyn rad^{-1}.

A comparison between computations 20 and 22 (Table 6) shows that the introduction of a large stretching force constant between M and N has no effect on the magnitudes studied, and the same holds, at least approximately, for the subsequent introduction of a small stretching force constant between the proton in flight and the atom N (computation 23). That the latter force constants should have little or no effect on the imaginary frequency was to be expected, of course, since they act in a direction which is perpendicular to the main component of the reaction co-ordinate.

CONCLUSIONS

Intuitively it seems likely that extra coupling pertaining to the proton in flight, transmitted *via* additional off-diagonal force constants should result in an increased reduced mass along the reaction co-ordinate of the transition state and therefore in a decreased amount of tunnelling. The present results are in some respects at variance with such naive expectations. The introduction of off-diagonal force constants in a fairly symmetric transition state (Table 2) does decrease $\nu^{\ddagger}_{H}/\nu^{\ddagger}_{D}$ but increase $|\nu^{\ddagger}_{H}|$, which means that tunnelling should increase in importance in spite of an increase in the reduced mass. The reason for the fallacy of at least our intuitive thinking is probably that our interest has been concentrated on the reduced mass along the reaction co-ordinate and that the remodelling of the barrier on the hypersurface escapes attention, simply because it is more difficult to imagine. Additional off-diagonal force constants do obviously increase the curvature along the reaction co-ordinate to such an extent that this change overcompensates the increase in reduced mass.

As is evident from Table 4, the results for extremely reactant-like or product-like transition states are exceptional. There are several reasons why tunnelling should be relatively unimportant in such cases. It seems natural to suppose that the curvature of the potential-energy surface along the reaction co-ordinate is smaller than for energetically more symmetric reactions. This together with the large reduced mass and the small energy region available for tunnelling will tend to decrease its importance in such reactions. Nevertheless it should be observed that the contribution from tunnelling to the observable isotope effect must be small also because of the similarity of $\nu^{\ddagger}_{H}$ and $\nu^{\ddagger}_{D}$ (*cf.* Table 4). The reduced mass along the reaction co-ordinate is so large that the difference in isotopic composition is of minor importance.

The result concerning the role of a polar solvent (Table 6) seems to be in accordance with already existing experimental evidence that tunnelling is favoured by low polarity of the solvent or by steric hindrance to solvation in the transition state.

The idea that steric hindrance could possibly promote tunnelling by its resistance to rehybridization and hence prevention of some of the coupled motion is not supported by the present results. Such a steric hindrance would correspond primarily to an increase in the bending force constants concerned, but increments of that kind have turned out to have little effect on $\nu^{\ddagger}_{H}$ also in the presence of several off-diagonal force constants (Table 5).

The inclusion of several off-diagonal force constants corresponds primarily to an attempt at reproducing probable effects of incipient mesomerism in the carbanionic part of the transition state. The question arises how to compare two cases, one with and the other without disposition towards mesomerism. There may be other differences of importance for the shape of the barrier than the existence of off-diagonal force constants. Possible differences in barrier height must be left out of the present discussion, effects from purely conformational differences have been shown above to be inconsequential (Table 3), and thus effects on the diagonal force constants remain to be discussed. Carbanions with localized charge are likely to be pyramidal, while those of the nitronate anion type would be expected to be planar around the central carbon atom. It is not obvious how this difference should affect all the force constants. Stretching force constants should be increased or decreased according to the changes in bond order which have taken place as a consequence of the incipient mesomerism. The bending force constants F_{77} and F_{88} are likely to undergo some reduction when the corresponding angles increase. The combined effect of these force-constant changes has been tested on the planar transition-state

model, Table 3. A comparison of columns D and E indicates that the influence is rather weak, the more carbanion-like force constants giving somewhat lower values of $|\nu^{\ddagger}_{H}|$ but higher values of $\nu^{\ddagger}_{H}/\nu^{\ddagger}_{D}$ in the presence of certain off-diagonal force constants. F_{14} seems to be responsible for this. The direction of a possible change in F_{33} and F_{66}, caused by incipient mesomerism, is uncertain, but a comparison between computations 17 and 18 (Table 5) shows that the magnitude of these force constants is critical neither for $|\nu^{\ddagger}_{H}|$ nor for $\nu^{\ddagger}_{H}/\nu^{\ddagger}_{D}$. In conclusion, differences in diagonal force constants caused by differences in disposition towards mesomerism have little influence on the importance of tunnelling, and they will hardly be able to mask the action of off-diagonal force constants of moderate magnitude.

The conclusion which could possibly be drawn concerning a relation between the disposition towards tunnelling and the degree of incipient mesomerism in the transition state seems to be that mesomerism is likely to promote tunnelling in spite of a probable increase in the reduced mass along the reaction coordinate. From the experimental point of view, tunnelling has been shown, indeed, to take place with some carbon acids the carbanions of which are typically mesomeric. Unfortunately, however, it is hardly possible to make a comparison with carbon acids of the opposite kind. Since the possibility of mesomerism in the anion is the most important structural feature making carbon acids strong, it is difficult to find a carbon acid with little mesomerism in its anion but still strong enough for a meaningful comparison or even amenable to tests concerning the importance of tunnelling. Sulfone and cyano groups seem to acidify neighbouring CH without extensive charge delocalization in the carbanion, but it is questionable whether there actually exists a two-sided barrier of appreciable height with these carbon acids.[6b] Any comparison should perhaps be limited to nitro and carbonyl compounds with carbanions "more or less disposed" to mesomeric charge delocalization.

The main value of the results obtained in the present investigation lies probably in the demonstration that coupling between the motion of the hydrogen in flight and heavy atoms need not invariably lead to decreased importance of tunnelling but may have the opposite effect.

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