

Isotope Effects in Proton-transfer Reactions

IV.* Theoretical Calculations of Isotope Effects in the Racemization of 2-Methyl-3-phenylpropionitrile

NILS-ÅKE BERGMAN, WILLIAM H. SAUNDERS, Jr.** and
LARS MELANDER

Department of Organic Chemistry, University of Göteborg and Chalmers Institute of Technology, Fack, S-402 20 Göteborg 5, Sweden

A computer program is used to calculate the kinetic isotope effect in the proton/deuteron abstraction from 2-methyl-3-phenylpropionitrile by methoxide ion in methanol as well as the equilibrium constant for the protium-deuterium exchange between the nitrile and methanol. A somewhat simplified model for the nitrile is used. Two models for the transition state are used. One of the models is used for reactant-like transition states, the other for product-like transition states. Some of the transition-state force constants are varied in order to take different degrees of transition-state symmetry into consideration. Several types of variation of the transition-state force constants are tested. The effect of these variations is discussed.

In the equilibrium calculation the O-H stretching force constant is varied in order to simulate varying degree of hydrogen bonding.

The results show that very weak kinetic isotope effects can be obtained for highly unsymmetric transition states. In the case of a very reactant-like transition state the isotopic rate ratio approaches the square root of the inverse ratio between the two isotopic reduced masses of the reactant molecules. For a highly product-like transition state the isotopic rate ratio approaches the square root of the inverse ratio between the two isotopic reduced masses of the product molecules multiplied by the ratio of the equilibrium constants of the corresponding isotopic reaction equilibria. For all models tested it is shown that the proton cannot be more than 1 % transferred for a reactant-like transition state or must be more than 99 % transferred for a product-like transition state if the value of the isotopic rate ratio is to deviate from the limiting value by less than 10 %.

The results are compared with the experimental value for the kinetic isotope effect in the racemization of 2-methyl-3-phenylpropionitrile in methanol and the value found experimentally for the isotope exchange equilibrium constant.

* For Part III of this series, see Ref. 20.

** Present address: Department of Chemistry, University of Rochester, Rochester, New York 14627, USA.

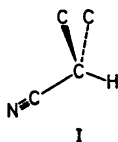
Recently very weak isotope effects have been observed in the racemization of 2-methyl-3-phenylpropionitrile in mixtures of methanol and dimethyl sulfoxide.¹ These weak isotope effects have been interpreted in terms of a very product-like transition state for the proton abstraction, the proton being considered almost completely transferred to the methoxide ion. Theoretical calculations of the isotope effect in this reaction have now been performed to see whether the magnitudes of the observed effects are compatible with a product-like transition state or not. Calculations of isotope effects in related systems are reviewed by Wolfsberg² and are also found in two more recent papers^{3,4}.

METHODS OF CALCULATIONS

The calculations have been made with a computer program originally devised by Schachtschneider⁵ for calculating vibrational frequencies by the **FG**-matrix method.⁶ The program has been modified by Wolfsberg and Stern⁷ to calculate isotope effects and has now been adapted to the IBM 360 Model 65 computer at Göteborgs Datacentral. The required input for the program consists of molecular geometries, atomic masses and force constants for the molecules considered. Kinetic isotope effects are calculated within the framework of the transition-state theory without tunneling correction. The program can be used for calculations of isotope effects on chemical equilibria as well.

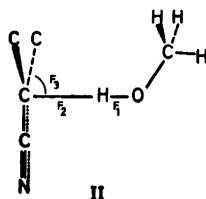
MODELS USED IN THE CALCULATIONS

The model for the ground state (*I*) used in the calculations is a "simplified" molecule obtained from the real one by a cut-off procedure in which the atoms beyond the carbon atoms in the methyl and methylene groups are simply excluded. This procedure is justified by the calculations by Stern and Wolfsberg.⁸ (The procedure should be applied with great caution; one must be

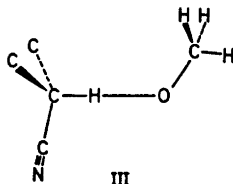


particularly sure that the atoms cut off do not have any appreciable influence on the isotope effect introduced by the moment-of-inertia factor.) The model for the product-like transition state (*II*) consists of a "simplified" planar carbanion attached to a methanol molecule. A tetrahedral nitrile attached to a methoxide ion was chosen as model for the reactant-like transition state (*III*). In the equilibrium calculation the ground state (*I*) was used together with a complete methanol molecule.

Bond angles at the carbon atom in methanol, the "asymmetric" carbon in the ground state and the "asymmetric" carbon in the reactant-like transition state were assumed to be tetrahedral. The C-O-H angle in methanol was



taken as $108^{\circ}52'$ ⁹ and the C-C-C angle in the transition state (II) as $111^{\circ}30'$ (the same as in isobutylene¹⁰) and the C-C-CN angle as $124^{\circ}15'$. The bond lengths used are taken from the literature and are found in Table 1. In some cases they are estimated values from similar bonds in other molecules.



Force constants for the different models are taken from the literature^{6,11-15} or are reasonable estimated values based on similar bonds in other molecules. All force constants used in the calculations are listed in Table 2. Off-diagonal elements in the F-matrix were used only to obtain a zero or imaginary reaction-coordinate frequency (see below). Some force constants are varied in the transition state for the purpose of taking transition states

Table 1. Bond lengths (in Å) used in the isotope-effect calculations.

	r_{C-C}	r_{C-CN}	r_{C-N}	r_{C-H}	r_{O-H}	r_{C-O}	r_{C-H} (MeOH)
Ground state (I)	1.54 ^a	1.46 ^a	1.16 ^a	1.09 ^a			
Transition state (II)	1.54 ^a	1.34 ^b	1.30 ^b	2.00 ^c	0.956 ^d	1.427 ^d	1.096 ^d
Transition state (III)	1.54 ^a	1.46 ^a	1.16 ^a	1.09 ^a	1.87 ^c	1.427 ^d	1.096 ^d
Methanol					0.956 ^d	1.427 ^d	1.096 ^d

^a Ref. 10.

^b The C-C bond length is assumed to have the same value as in isobutylene and the C-N bond length is the same as that found in oximes.

^c The distance between the "asymmetric" carbon atom in the nitrile and the oxygen atom in methanol was chosen as 2.96 Å. From this value then follow the C-H and O-H distances in the product-like (II) and reactant-like (III) transition state, respectively, if normal O-H distance is assumed in (II) and normal C-H distance in (III).

^d Ref. 9.

Table 2. Force constants used in the isotope-effect calculations.

Type of force constant ^a	Value in MeOH ^b	Value in (I)	Value in (II) ^b	Value in (III) ^b
C-C, s		4.35 ^c	4.35 ^c	4.35 ^c
C-CN, s		5.26 ^d	9.5 ^e	5.26 ^d
C-H, s (nitrile)		4.59 ^f	4.59 ^f	4.59 ^f
C-H, s (methanol)	4.80 ^g		4.80 ^g	4.80 ^g
C-N, s		17.5 ^d	10.0 ^e	17.5 ^d
O-H, s	7.53 ^g		7.53 ^g	7.53 ^g
O-C, s	5.27 ^g		5.27 ^g	5.27 ^g
C-C-C, b		1.084 ^f	0.6 ^h	1.084 ^f
C-C-CN, b		1.084 ^f	0.9 ⁱ	1.084 ^f
C-C-H, b		0.657 ^f	0.6 ^f	0.657 ^f
C-H-O, b			0.3 ^h	0.3 ^h
C-O-H, b	0.789 ^g		0.789 ^g	0.789 ^g
C-C-N, b		0.319 ^d	0.3 ^h	0.319 ^d
H-C-H, b	0.56 ^g		0.56 ^g	0.56 ^g
H-C-O, b	0.88 ^g		0.88 ^g	0.88 ^g
HC-OH, t	0.03 ^g		0.03 ^g	0.03 ^g
CC-OC, t			0.03 ^l	0.03 ^l

^a s=stretching force constants in m dyn Å⁻¹, b=bending force constants in m dyn Å rad⁻², t=torsional force constants in m dyn Å rad⁻². ^b Force constants in italics are limiting values for force constants which are varied in the calculations. For the type of variation see Table 3. ^c The value corresponds to the average value of the C-CH₃ and C-CH₂ stretching force constants given in Ref. 11. ^d Ref. 12. ^e Ref. 6. ^f Ref. 11. ^g Ref. 13. In some cases estimated values. ^h Estimated value. Cf. the value given for the allene molecule in Ref. 14. ⁱ Estimated value. Cf. the value given for acrylonitrile in Ref. 15. ^j The value is an approximate value estimated from the C-C-H bending force constant for a tetrahedral case. Cf. Ref. 11. ^k Estimated value for a linear bending constant. ^l Torsion around the C-H-O axis. Estimated value.

with different symmetries (positions along the reaction path) into consideration. As there is no rule which says exactly how this variation should be done several models (1,2,3,4,5) were tested to see the effect of different variations. The models used are listed in Table 3.

The transition-state symmetry was expressed in terms of x ($x=0$ for a completely reactant-like transition state and $x=1$ for a completely product-like transition state. In other words, x is the bond order of the reacting OH-bond). When $x \rightarrow 0$ or $x \rightarrow 1$ the values of the force constants in the transition state go toward their values in reactant and product, respectively. Transition-state model III was used for $0 \leq x \leq 0.3$ and model II for $0.5 \leq x \leq 1$. The main difference between the models in Table 3 is the dependence of the force constants on x . The different models are discussed more thoroughly below.

A zero or imaginary reaction-coordinate frequency was obtained by setting the determinant of the block of the F-matrix containing the stretching force constants of the reacting bonds equal to or less than zero:

$$\begin{vmatrix} F_1 & F_{12} \\ F_{12} & F_2 \end{vmatrix} \leq 0 \quad \text{or} \quad F_{12} = A(F_1 F_2)^{\frac{1}{2}} \quad \text{where} \quad A \geq 1$$

Table 3. Different models used in the variation of the transition-state force constants.

Type of force constant ^a	Model 1	Model 2	Model 3	Model 4	Model 5	MeOH ^b
O-H, s (F_1)	7.53x	7.53x	7.53x	7.53x ²	7.53x	7.53y
C-H, s (F_2)	4.59(1-x)	4.59(1-x)	4.59(1-x)	4.59(1-x) ²	4.59(1-x)	
C-C-H, b (F_3) ^c	$F_3(1-x)$	$F_3(1-x)^2$	$F_3(1-x)^2$	$F_3(1-x)^2$	$F_3(1-x)^{\frac{1}{2}}$	
C-O-H, b	0.789x	0.789x ²	0.789x ²	0.789x ²	0.789x ^{1/2}	
C-H-O, b	0.3[4x(1-x)]	0.3[4x(1-x)] ²	0.3[4x(1-x)] ²	0.3[4x(1-x)] ²	0.3[4x(1-x)] ^{1/2}	
HC-OH, t	0.03x	0.03x ²	0.03x ²	0.03x ²	0.03x ^{1/2}	
CC-OC, t	0.03[4x(1-x)]	0.03[4x(1-x)] ²	0.03[4x(1-x)] ²	0.03[4x(1-x)] ²	0.03[4x(1-x)] ^{1/2}	
F_{12} ^d	[1+x(1-x)] (F_1F_2) ^{1/2}	[1+x(1-x)] (F_1F_2) ^{1/2}	[1+x ² (1-x) ²] (F_1F_2) ^{1/2}	[1+x ² (1-x) ²] (F_1F_2) ^{1/2}	[1+x(1-x)] (F_1F_2) ^{1/2}	

^a s=stretching force constant, b=bending force constant, t=torsional force constant.

^b Only the O-H stretching force constant is varied in this case $0.8 \leq y \leq 1.0$.

^c $F_3 = 0.6$ for product-like transition state (II) and $F_3 = 0.657$ for reactant-like transition state (III).

^d Stretching-stretching interaction force constant used to get an imaginary or zero reaction-coordinate frequency.

The factor A is related to the curvature of the potential-energy surface along the reaction coordinate in such a way that if $A > 1$ the curvature of the potential energy barrier is negative and if $A = 1$ it is zero. The factor A was varied in two ways (see Table 3).

In the equilibrium calculation the stretching force constant of the O-H bond was allowed to vary in order to simulate the variation of the O-H stretching frequency with hydrogen bonding. This is indicated in Table 3 in the column for MeOH. All force constants not listed in Table 3 were held constant throughout the calculations.

RESULTS AND DISCUSSION

As explained by Melander,¹⁶ extremely reactant-like transition states can be expected to show isotopic rate ratios close to unity. In the limiting case the k_H/k_D ratio approaches the square root of the inverse ratio between the two isotopic reduced masses of the reactant molecules. In the case considered in this calculation, D (Ref. 16) corresponds to the nitrile molecule and E to the methoxide ion giving for the latter ratio with the present simplified models $[(64/63)(94/95)]^{\frac{1}{2}} = 1.003$ (on comparing with experimental data the complete molecular masses should be used). In Fig. 1 the results from runs with different models are compared. For an explanation of the different models reference should be made to Table 3. *Models 1, 2, and 3* show very similar properties. *Models 4 and 5* differ a great deal from the others. In the case of *model 5* this is due to a rapid increase of the isotopically sensitive CCH-bending frequencies and a slow decrease of the COH one when $x \rightarrow 0$. *Model 5* should be compared with *model 1* to see the effect of these bending vibrations. The curve for *model 4* shows that the quadratic variation of the stretching force constants involved causes the isotopic rate ratio to approach its limiting value much faster than

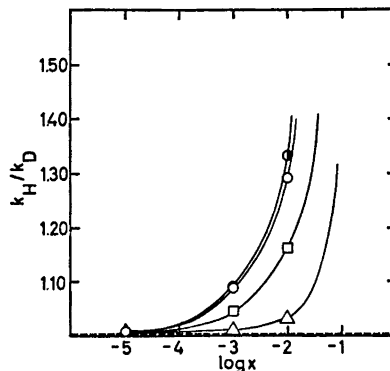


Fig. 1. Variation of the isotope effect with degree of proton transfer (x) for a very reactant-like transition state. \circ Model 1, \bullet Model 2 and Model 3 (the curve for Model 3 coincides with the curve for Model 2), \triangle Model 4, \square Model 5. For an explanation of the models see Table 3. The dashed line corresponds to the limiting value for an extremely reactant-like transition state. Temperature 25°C.

if the variation is linear.* This is due to a more rapid decrease of the O–H stretching force constant when $x \rightarrow 0$. Model 4 should be compared with model 3 since the variation of the stretching force constants is the only difference between these models. For a given small x the ratio F_2/F_1 will be larger for model 4 than for model 3, i.e., model 4 corresponds to a more unsymmetric transition state and hence the isotope effect will be weaker.

In the case of a very product-like transition state the kinetic isotope effect should approach a value close to the equilibrium isotope effect.¹⁶ The force constants used in the calculation (Table 2) correspond to the gaseous state and the calculated $\nu_{\text{OH}} = 3687 \text{ cm}^{-1}$ (observed¹⁹ 3687 cm^{-1}). This frequency is much lower in the liquid state, however, due to hydrogen-bond formation, and a value around 3300 cm^{-1} is more realistic.¹⁹ The magnitude of the equilibrium isotope effect is of course very sensitive to this frequency, and an attempt was made to make allowance for the increased hydrogen bonding in the liquid state. In order to simulate a varying degree of hydrogen bonding, the O–H stretching force constant was changed systematically (see last column in Table 3). Although increased hydrogen bonding influences more than the O–H stretching frequency this is certainly the most drastic change and that which is most important to the magnitude of the isotope effect. The relation between the calculated values of $K_{\text{H}}/K_{\text{D}}$ ** and the O–H frequency can be seen in Fig. 2. In the figure a line representing the ν_{OH} -value found by Falk and Walley¹⁹ has been drawn.

Let us for the present discuss the theoretical cases where $\nu_{\text{OH}} = 3687 \text{ cm}^{-1}$. In this case the limiting value for the isotopic rate ratio for an extremely unsymmetric product-like transition state should be $[(33/32)(94/95)]^{\frac{1}{2}} K_{\text{H}}/K_{\text{D}} = 0.919$ at 25°C (on comparing with experimental data the complete molecular masses should be used).

* Model 4 is perhaps a little artificial. From Pauling's bond-order rule¹⁷ and Badger's rule¹⁸ it can be seen that a linear variation of the stretching force constants is the most likely one.

** K_{H} and K_{D} denote the equilibrium constants for the proton and deuteron transfer reactions, respectively, and $K_{\text{H}}/K_{\text{D}}$ is also the equilibrium constant of the protium-deuterium exchange reaction between nitrile and methanol.²⁰

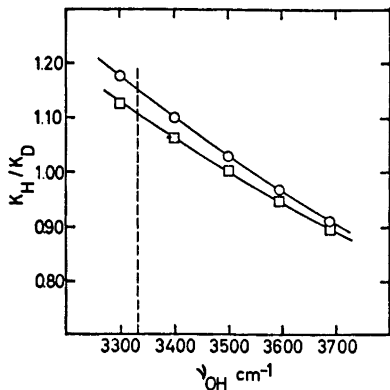


Fig. 2. Variation of K_H/K_D with ν_{OH} . Vertical dashed line corresponds¹⁹ to $\nu_{OH} = 3337 \text{ cm}^{-1}$. \circ Temperature 25°C . \square Temperature 60°C .

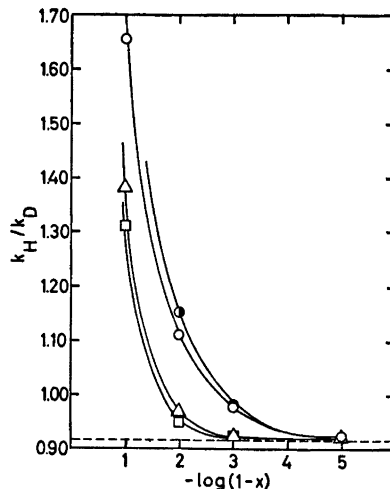


Fig. 3. Variation of the isotope effect with degree of proton transfer (x) for a very product-like transition state. \circ Model 1, \bullet Model 2 and Model 3 (the curve for Model 3 coincides with the curve for Model 2), \triangle Model 4, \square Model 5. For an explanation of the models see Table 3. The dashed line corresponds to the limiting value for an extremely product-like transition state. Temperature 25°C .

In Fig. 3 the different models for a product-like transition state are compared with respect to how fast the isotopic rate ratio approaches the limiting value. As in the case of a reactant-like transition state it is obvious that the largest difference is introduced when the variation of the stretching force constants involving breaking and forming bonds are allowed to vary quadratically with x or $1-x$ (model 4) or when the bending force constants are allowed to vary with the power $\frac{1}{2}$ (model 5) (cf. reactant-like case above). From Fig. 1 and Fig. 3 can be seen how the isotope effect becomes very weak when the transition state is either very close to reactant or very close to product and in the latter case even inverse.

Bell²¹ has argued that a simple three-center transition state can hardly account for the weak isotope effects found in some experiments because the underlying assumption²² of a zero reaction-coordinate frequency is an artificial one which corresponds to an activation energy of zero. This is of course true for a transition state in which the proton is not transferred at all. In the limiting case of a very product-like or a very reactant-like transition state a very small curvature would be expected. In these calculations an attempt has been made to take this into consideration by a variation of the curvature with the degree of proton transfer. Two types of variation of the curvature have been tried and the results can be compared in Table 4. Model 2 corre-

Table 4. Reaction-coordinate frequencies ν_{HL}^\ddagger for different models.

x	ν_{HL}^\ddagger	
	Model 2	Model 3
0.01	16 <i>i</i>	1 <i>i</i>
0.1	263 <i>i</i>	63 <i>i</i>
0.3	1366 <i>i</i>	595 <i>i</i>
0.5	1535 <i>i</i>	725 <i>i</i>
0.7	891 <i>i</i>	367 <i>i</i>
0.9	180 <i>i</i>	44 <i>i</i>
0.99	14 <i>i</i>	1 <i>i</i>

sponds to a variation $A = 1 + x(1 - x)$ and *model 3* to $A = 1 + x^2(1 - x)^2$. In this way *model 2* corresponds to a somewhat larger (more negative) curvature of the potential-energy barrier than *model 3*. A comparison between *model 2* and *model 3* in Fig. 1 and Fig. 3 shows that this variation is of very little importance for a highly unsymmetric transition state.

From the results represented by the curves in Fig. 1 and Fig. 3 it is obvious that a highly unsymmetric transition state is required for the isotope effect to be close to the limiting value for either a reactant-like or a product-like transition state. This is the case for all models tested, and, as the models are rather different, this phenomenon is obviously not the result of the assumed model used in the calculation. If the product-like transition state is considered (Fig. 3), it can be seen that even if $x = 0.9$ an isotopic rate ratio $k_{\text{H}}/k_{\text{D}} = 1.3$ or more can be expected. Not until $1 - x$ is around 0.01 or less is a value of $k_{\text{H}}/k_{\text{D}}$ deviating by less than 10 % from the limiting value obtained. The magnitude of the isotope effect in the product-like case is dependent on the magnitude of the equilibrium isotope effect, and an "inverse" equilibrium isotope effect ($K_{\text{H}}/K_{\text{D}} < 1$) results in a smaller value of $k_{\text{H}}/k_{\text{D}}$ for a given degree of proton transfer than if $K_{\text{H}}/K_{\text{D}} > 1$. In the case of a reactant-like transition state (Fig. 1) the $k_{\text{H}}/k_{\text{D}}$ value similarly departs from the limiting value (near unity) a great deal even when $x = 0.01$.

If the results from this calculation are to be applied with confidence to the experimental data found in the racemization of 2-methyl-3-phenylpropionitrile, the equilibrium constant of the protium-deuterium exchange between the nitrile and methanol has to be known. The value of this equilibrium constant at 60°C ($K_{\text{H}}/K_{\text{D}} \approx 1.2$)²⁰ has about the same magnitude as the isotopic rate ratio ($k_{\text{H}}/k_{\text{D}} = 1.16 \pm 0.05$)¹ within the experimental errors. This corresponds to an isotopic rate ratio in the reverse reaction close to unity. The experimental equilibrium constant is also in fairly good agreement with the value obtained in the equilibrium calculation using the O-H frequency for liquid methanol.¹⁹ If $y = 0.817$ is used, the frequency obtained is 3333 cm^{-1} and the equilibrium constant is $K_{\text{H}}/K_{\text{D}} = 1.11$ at 60°C. When the transition-state *models 3* and *5* are applied to this case the kinetic isotope effects shown in Fig. 4 are predicted. From this figure it is obvious that the best picture of the transition state is one in which the proton is almost completely transferred

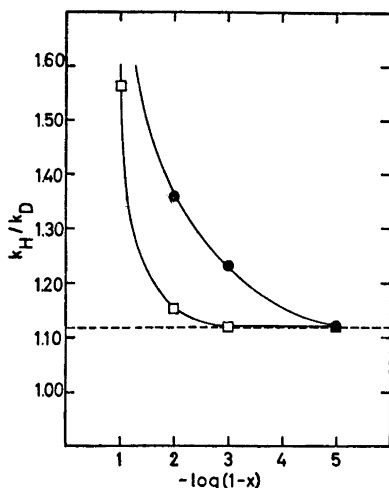


Fig. 4. Variation of the kinetic isotope effect with degree of proton transfer (x) when the O-H stretching force constant is chosen such as to reproduce the observed O-H stretching frequency in liquid methanol. ● Model 3, □ Model 5. The dashed line corresponds to the limiting value for $k_{\text{H}}/k_{\text{D}}$ for an extremely product-like transition state. Temperature 60°C.

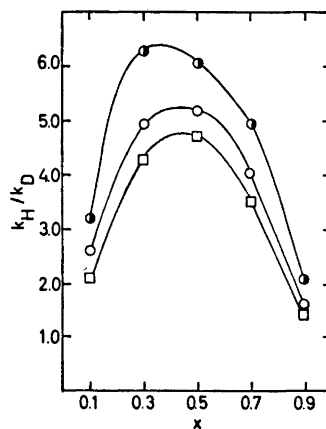


Fig. 5. Variation of $k_{\text{H}}/k_{\text{D}}$ with degree of proton transfer (x) in the transition state. ○ Model 1, ● Model 2, □ Model 5. For an explanation of the models see Table 3. Temperature 25°C.

to the methoxide ion, because $(1-x) \leq 0.01$ is needed to reproduce the observed value of about $k_{\text{H}}/k_{\text{D}} = 1.16$.¹

The reaction coordinate will hence probably be almost identical with the C-H distance. The movement along the reaction coordinate will then simply be an increase in the C-H distance and a very small decrease in the O-H distance, *i.e.*, mainly a separation of the carbanion from the methanol molecule.

It is also of general interest to see how the $k_{\text{H}}/k_{\text{D}}$ ratio varies with x between the values 0.1 and 0.9. In Fig. 5 the results from the calculations using models 1, 2, and 5 are gathered. In model 1, a linear variation of the bending and torsional force constants is used. It gives rise to higher bending frequencies in the transition state than obtained in model 2, and since these bendings are isotopically sensitive a decrease in the isotope effect results. This is even more striking when model 5 is used in which the bending force constants vary more slowly. A maximum in the strength of the isotope effect is observed when $F_1 \approx F_2$, *i.e.*, $x \approx 0.4$. This phenomenon which was explained in terms of force constants by Westheimer²² and in terms of the shape of the potential-energy surface by Melander²³ has recently been confirmed by many authors.²⁻⁴

In Fig. 6 the effect of the curvature of the potential-energy barrier on the shape of the $k_{\text{H}}/k_{\text{D}}$ vs. degree of proton transfer curve can be seen. As explained above model 2 corresponds to a somewhat larger curvature of the potential-energy barrier than model 3. The result found here that this causes a

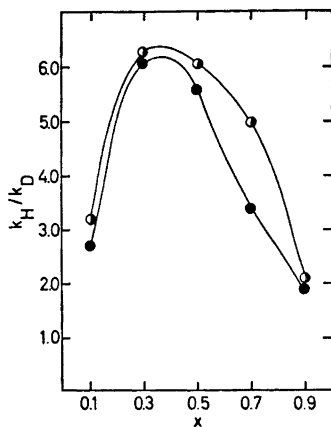


Fig. 6. Variation of k_H/k_D with degree of proton transfer (x) for different curvatures of the potential energy barrier. ○ Model 2, ● Model 3. For an explanation of the models see Table 3. Temperature 25°C.

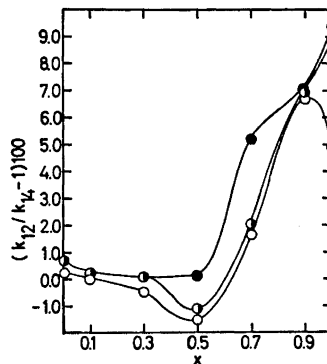


Fig. 7. Variation of the C-14 isotope effect with degree of proton transfer (x). ○ Model 1, ● Model 2, ● Model 3. Initial points and final points correspond to $x=0.01$ and $x=0.99$, respectively. For an explanation of the models see Table 3. Temperature 25°C.

broadening of the k_H/k_D maximum is in agreement with the result of Willi and Wolfsberg.²⁴

One further interesting point which was investigated in these calculations was the effect of a carbon-14 atom in the asymmetric position of the nitrile. As found earlier²⁵ a strong carbon isotope effect results only when the proton is more than half transferred (Fig. 7). A comparison between *models 2* and *3* shows that this holds in spite of a somewhat larger curvature of the potential-energy barrier for *model 2*. A measured carbon isotope effect of 5 % or more should then represent a transition state where the proton is almost completely transferred.

Acknowledgements. Financial support from the *Swedish Natural Science Research Council* and a grant from *Anslaget för kostnader för datamaskintid* are gratefully acknowledged. One of us (W. H. S.) thanks the *U.S. National Science Foundation* for a Senior Postdoctoral Fellowship, 1970–1971.

REFERENCES

1. Melander, L. and Bergman, N.-Å. *Acta Chem. Scand.* **25** (1971) 2264.
2. Wolfsberg, M. *Ann. Rev. Phys. Chem.* **20** (1969) 449.
3. Katz, A. M. and Saunders, W. H., Jr. *J. Am. Chem. Soc.* **91** (1969) 4469.
4. More O'Ferrall, R. A. *J. Chem. Soc. B* **1970** 785.
5. Schachtneider, J. H. and Snyder, R. G. *Spectrochim. Acta* **19** (1963) 117.
6. Wilson, E. B., Jr., Decius, J. C. and Cross, P. C. *Molecular Vibrations*, McGraw, New York 1955.
7. Wolfsberg, M. and Stern, M. J. *Pure Appl. Chem.* **8** (1964) 225.

8. Stern, M. J. and Wolfsberg, M. *J. Chem. Phys.* **45** (1966) 4105.
9. Venkateswarlu, P. and Gordy, W. *J. Chem. Phys.* **23** (1955) 1200.
10. Wheland, G. W. *Resonance in Organic Chemistry*, Wiley, New York 1955, p. 729.
11. Snyder, R. G. and Schachtschneider, J. H. *Spectrochim. Acta* **21** (1965) 169.
12. Yamadera, R. and Krimm, S. *Spectrochim. Acta A* **24** (1968) 1677.
13. Margottin-Maclou, M. *J. Chim. Phys.* **63** (1966) 215.
14. Venkateswarlu, K. and Krishna Pillai, M. G. *Z. physik. Chem. (Frankfurt)* **18** (1958) 396.
15. Bernas, A., Bensasson, R., Rossi, I. and Barchewitz, P. *J. Chim. Phys.* **59** (1962) 442.
16. Melander, L. *Acta Chem. Scand.* **25** (1971) 3821.
17. Pauling, L. *The Nature of the Chemical Bond* 3rd Ed., Cornell University Press, Ithaca 1960, p. 239.
18. Badger, R. M. *J. Chem. Phys.* **2** (1934) 128; **3** (1935) 710; see also Herschbach, D. R. and Laurie, V. W. *Ibid.* **35** (1961) 458.
19. Falk, M. and Walley, E. *J. Chem. Phys.* **34** (1961) 1554.
20. Bergman, N.-Å. *Acta Chem. Scand.* **25** (1971) 1517.
21. Bell, R. P. *Discussions Faraday Soc.* **39** (1965) 16.
22. Westheimer, F. H. *Chem. Rev.* **61** (1961) 265.
23. Melander, L. *Isotope Effects on Reaction Rates*, Ronald Press, New York 1960, pp. 24-32; cf. also pp. 74-75.
24. Willi, A. V. and Wolfsberg, M. *Chem. Ind. (London)* **1966** 2097.
25. Saunders, W. H., Jr. *Chem. Ind. (London)* **1966** 663.

Received June 5, 1971.