Faraday Discuss Chem. Soc., 1982, **74**, 229–243

Primary Kinetic HH/HD/DH/DD Isotope Effects and Proton Tunnelling in Double Proton-transfer Reactions

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Received 18*th May*, 1982

Double proton-transfer reactions are characterized by three primary kinetic H/D isotope effects (k.i.e.) involving a set of rate constants k^{HH}, k^{HD}, k^{DH} and k^{DD}. We have succeeded in measuring such sets for well defined symmetrical double proton-transfer reactions where $k^{HD} = k^{DH}$ for the intramolecular hydrogen migration in *meso*-tetraphenylporphine (TPP) and for the intermolecular 1 : 1 proton exchange between acetic acid and methanol dissolved in tetrahydrofuran. In this system we also detected a triple proton transfer involving one methanol and two acetic acid molecules. Rate constants k^{HHH}, k^{HHD}, k^{HDD} and k^{DDD} of this reaction are reported. Additionally, we also observed an intramolecular double proton-transfer reaction in 2,5-dianilino-benzoquinone- 1,4-dianil (azophenine, AP) for which we have measured the HH/HD k.i.e. For the determination of rate constants dynamic n.m.r. spectroscopy was used.

The predictions of the fractionation-factor theory, transition-state theory and different proton-tunnelling theories on the HH/HD/DH/DD k.i.e. of symmetrical double proton-transfer reactions are discussed with special emphasis on the rule of the geometric mean and compared with the experiments. The kinetic and the i.r. results for TPP and AP are well reproduced by the vibrational model of tunnelling as proposed previously by us. TPP is, therefore, the first proton-transfer system with NH-stretching levels not broadened by hydrogen-bond effects. The k.i.e. of the intermolecular proton exchange in the system acetic acid + methanol + tetrahydrofuran are consistent with tunnelling from the OH-stretching ground states. The energy of activation is associated with the enthalpy of formation of the cyclic complex in which the exchange takes place and the excited intermolecular vibrational states within this complex. The tunnelling theories are modified in order to take this enthalpy into account.

The study of kinetic isotope effects (k.i.e.) in non-catalysed double proton-transfer reactions (HH reactions) of the type

$$AH + XH^* = BH^* + YH$$

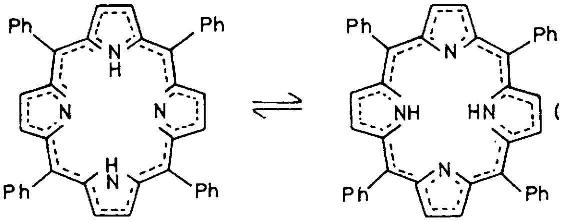
is motivated by the fact that these processes take place between a variety of molecules in protic and aprotic [1-11] media and in the gaseous [12] and the solid [13,14] state. In organic and biochemical systems they are related to bifunctional catalysis [15-20] and biological activity.[21,22] On the other hand, these reactions are an old topic of theoretical chemistry.[12,23-25] In solution, tunnelling probabilities should be higher in the case of neutral HH transfer than in an ionic single H-transfer reaction because there is no need for the solvent molecules to reorientate [1,26] around the reacting molecules.

For aqueous solutions it has long been known [27-30] that more than one proton donor can contribute to the observed k.i.e. arising either because of a different H/D composition in the proton-donor site with respect to the solvent (fractionation) or because a number $n > 1$ of protons are transported in the rate-limiting step. In order to deduce n from the kinetic data the " rule of the geometric mean " [31] (r.g.m.)

has been extensively used in the subsequent " fractionation-factor theory." For $n = 2$ this rule states the following relation between the bimolecular rate constants

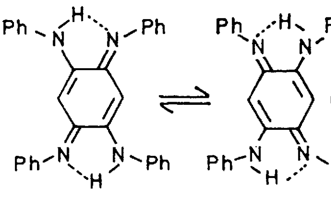
$$k^{\mathrm{HD}} = (k^{\mathrm{HH}}k^{\mathrm{DD}})^{1/2}.$$

This assumption has, however, been proved neither experimentally nor theoretically by studying the k.i.e. of proton-transfer reactions where n is known *a priori*, *i.e.* without using the r.g.m. Though the kinetics of several HH-transfer reactions[4-11,32-37] have been studied in the past by dynamic n.m.r. spectroscopy, full HH/HD/DH/DD k.i.e. have not yet been reported. In continuation of previous work[4-11] we present here for the first time such data sets for several symmetrical HH reactions where $k^{\mathrm{HD}}=k^{\mathrm{DH}}$. The processes studied were the intramolecular HH migration in *meso*-tetraphenylporphine [TPP, reaction (I)], the intramolecular HH migration in 2,5-dianilino-benzoquinone-1,4- dianil or azophenine [AP, reaction (II)] and the intermolecule HH exchange between acetic acid and methanol in tetrahydrofuran [THF, reaction (III)].



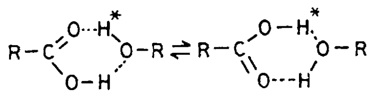
(I)

TPP



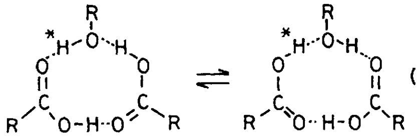
(II)

AP

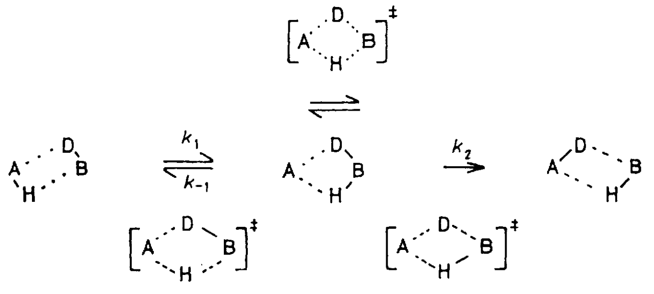


(III)

R=CH₃



(IV)



(V)

In the last system we have, additionally, obtained the full k.i.e. of a triple proton-transfer involving one methanol and two acetic acid molecules [reaction (IV)]. The r.g.m. is found to be realized only in the HHH process. With particular emphasis on this rule the k.i.e. of symmetrical HH reactions are discussed briefly within the framework of the transition-state and different tunnelling theories. After modification the latter are able to accommodate the experimental data which prove, in the case of TPP together with i.r. results, to be a vibrational model of tunnelling previously proposed by us.[6,7]

KINETIC ISOTOPE EFFECTS IN SYMMETRICAL HH-TRANSFER REACTIONS

TRANSITION-STATE THEORY

We will discuss the k.i.e. in the simplest form of transition-state theory (t.s.t.), *i.e.* in terms of the loss of zero-point energies (z.p.e.) of the AL stretching vibrations (L = H,D) in the t.s. We consider two reaction pathways as shown in reaction (V) for the HD process.

The second pathway involves the formation of an ionic intermediate and two transition states which are degenerate in the case of the HH and the DD reaction but non-degenerate in the HD reactions because of the different z.p.e. of the remaining BH and BD stretching vibrations. We treat the simple case where the vibration of the non-transferred H or D remains constant in the intermediate and the first t.s., *i.e.* we neglect secondary k.i.e. The observed rate constant k for the two-step process is given in the usual way by

$$k = \frac{k_1 k_2}{k_{-1} + k_2}.$$

With

$$k_1^{\mathrm{H}}/k_1^{\mathrm{D}} = k_{-1}^{\mathrm{H}}/k_2^{\mathrm{D}} = k_2^{\mathrm{H}}/k_2^{\mathrm{D}} = k^{\mathrm{H}}/k^{\mathrm{D}}$$

one obtains

$$k^{\mathrm{HH}}/k^{\mathrm{DD}} = \varphi \tag{1}$$

and

$$k^{\mathrm{HD}}/k^{\mathrm{DD}} = 2\varphi/(1 + \varphi) \tag{2}$$

where φ is the usual kinetic isotope effect of a single proton-transfer reaction. The same result is obtained when A = B. The r.g.m. is not fulfilled and at low temperatures the energies of activation for the HD and the DD processes are equal.

The k.i.e. of the concerted proton motion with the symmetrical t.s. are more difficult to evaluate because a detailed discussion of all vibrations in the t.s. would be required. Therefore we discuss here only stretching modes of a linear t.s. of the type A · · · H · · · B · · · H · · · A. As was pointed out by Kreevoy[38] and Bell *et al.*,[1,17] such a state contains a non-imaginary symmetric HH stretching frequency $\nu_{+}^{\ddagger}$ which has a z.p.e. If $\nu_{+}^{\ddagger}$ is of the same order as the $\nu_{\mathrm{AH}} = \nu^{\mathrm{H}}$ in the reactant states, the z.p.e. of only one AH stretching vibration is lost in the t.s. and eqn (1) would apply, *i.e.* the difference in the energies of activation, $E_{\mathrm{a}}^{\mathrm{HH}} - E_{\mathrm{a}}^{\mathrm{DD}}$, should not be higher than 1.2 kcal mol^{-1} as in a usual single proton-transfer reaction. For a discussion of the k.i.e. we consider the frequencies of two AH vibrations characterised by equal force constants $f_{11} = f_{22}$ and which are coupled together by the coupling constant f_{12}. For an infinite mass of A we obtain in analogy to equations given by Herzberg[39]

$$\nu_{\pm} = \frac{1}{2\pi}(f_{11}/m_{\mathrm{H}})^{1/2}(1 \pm x)^{1/2} = \nu_{\pm}^{\mathrm{DD}}(2)^{1/2} \tag{3}$$

and

$$\nu_{\pm}^{\mathrm{HD}} = b_{\pm}\, \nu_{\pm}^{\mathrm{HH}};\ b_{\pm} = \tfrac{1}{2}\{[3 \pm (1 + 8x^2)^{1/2}]/(1 + x)\}^{1/2},\ 0 \leqslant x \leqslant 1 \tag{4}$$

where m_{H} is the mass of the proton and $x = f_{12}/f_{11}$, the coupling parameter. Whereas

x is close to 0 in the reactant state, in a totally coupled t.s. $x^{\ddagger} = 1$. The barrier of the reaction is then given by

$$E_{\mathrm{d}}^{\mathrm{LL}} = E_{\mathrm{d}} + 1/2\,\boldsymbol{h}\,\nu_{+}^{\ddagger\,\mathrm{LL}},\ \mathrm{LL} = \mathrm{HH, HD, DD} \tag{5}$$

where E_{d} is the potential barrier. The energies of activation, $E_{\mathrm{a}}^{\mathrm{LL}}$, differ from $E_{\mathrm{d}}^{\mathrm{LL}}$ by the z.p.e. of two AL stretching vibrations of the reactants. One obtains, assuming that the frequency factors $A^{\mathrm{HH}} = A^{\mathrm{HD}} = A^{\mathrm{DD}}$

$$R = \frac{\ln(k^{\mathrm{HH}}/k^{\mathrm{HD}})}{\ln(k^{\mathrm{HD}}/k^{\mathrm{DD}})} = \frac{E_{\mathrm{a}}^{\mathrm{HD}} - E_{\mathrm{a}}^{\mathrm{HH}}}{E_{\mathrm{a}}^{\mathrm{DD}} - E_{\mathrm{a}}^{\mathrm{HD}}} = \frac{\nu_{+}^{\mathrm{H}} - \nu_{+}^{\mathrm{D}} - (\nu_{+}^{\ddagger\,\mathrm{HH}} - \nu_{+}^{\ddagger\,\mathrm{HD}})}{\nu_{+}^{\mathrm{H}} - \nu_{+}^{\mathrm{D}} - (\nu_{+}^{\ddagger\,\mathrm{HD}} - \nu_{+}^{\ddagger\,\mathrm{DD}})}. \tag{6}$$

The r.g.m. is fulfilled, *i.e.* $R = 1$, when

$$\nu_{+}^{\ddagger\,\mathrm{HD}} = 1/2\,(\nu_{+}^{\ddagger\,\mathrm{HH}} + \nu_{+}^{\ddagger\,\mathrm{DD}}). \tag{7}$$

Setting $x^{\ddagger} = f_{12}^{\ddagger}/f_{11}^{\ddagger}$ for the t.s., $y = \nu_{+}^{\ddagger\,\mathrm{HH}}/\nu_{+}^{\mathrm{H}}$ and taking $f_{12} = 0$ in the reactant states one obtains

$$R = \frac{1 - (1/2)^{1/2} - y(1 - b_{+}^{\ddagger}),}{1 - (1/2)^{1/2} - y[b_{+}^{\ddagger} - (1/2)^{1/2}],} \tag{8}$$

and

$$E_{\mathrm{a}}^{\mathrm{DD}} - E_{\mathrm{a}}^{\mathrm{HH}} = 1/2\,\boldsymbol{h}\,(2 - y)(\nu_{+}^{\mathrm{H}} - \nu_{+}^{\ddagger}). \tag{9}$$

We estimate that y does not become greater than 1. The r.g.m. is fulfilled exactly only for $y = 0$. If the experimental values of $E_{\mathrm{a}}^{\mathrm{DD}} - E_{\mathrm{a}}^{\mathrm{HH}}$ exceed 1.2 kcal mol^{-1} and if they are interpreted in terms of eqn (9) with y close to 0 then this interpretation is corroborated by finding a value of $R = 1$.

For non-zero values of y eqn (8) predicts $k^{\mathrm{HD}}/k^{\mathrm{HH}}$ to be slightly greater than $k^{\mathrm{HD}}/k^{\mathrm{DD}}$. The deviation from the r.g.m. is, however, small, especially if $x^{\ddagger} = 1$ as is expected for a symmetrical t.s. We obtain $R = 1.19$ for $y = 1$ and $R = 1.06$ for $y = 0.5$. The inclusion of bending modes into the vibrational analysis of a t.s. which shows considerable coupling of the proton motion will probably not change the result that the r.g.m. is fulfilled for this case in crude approximation.

TUNNELLING MODELS

A common feature of all tunnelling models is that the rate constants can be expressed in the form [1,6,7,40-42]

$$k = \sum_{n} k_n p_n \tag{10}$$

where k_n is the tunnelling frequency of the state n and p_n the population of this state. One main difference between the different tunnelling models is the question of whether the summation in eqn (10) has to be carried out over a finite or an infinite number of states, *i.e.* whether the sum must be replaced by an integral. For intramolecular proton transfer between more or less rigid atoms there is an analogy to the NH_3 problem [39] and only a small number of vibrational, generally AH stretching states contribute to k.[6,7,40,43] In intermolecular proton transfer it is necessary according to Bell [1] to sum over an infinite number of states, *i.e.* to replace the sum by an integral, because of the intermolecular flexibility. In a one-dimensional treatment a decision between summation and integration has to be made. The advantage of a multidimensional treatment like the one of Dogonadze *et al.*[41,42] is that a finite number of vibrational states but an infinite number of intermolecular states can be considered.

For the discussion of the HH/HD/DD k.i.e. we restrict ourselves to the one-dimensional case. As has been shown before, [1,7,40] the following relation holds in w.k.b.[1] approximation for a parabolic barrier

$$k_n(l) = (l/\pi^{l-1})\nu D_n(l),\ l = 1,2 \tag{11}$$

$$D_n(l) = \exp[-(2^{3/2}\pi^2/\boldsymbol{h})(E_d - E_n)Q(l)/(E_d)^{1/2}] \tag{12}$$

$$Q(l) = \xi_0(m)^{1/2}/l \tag{13}$$

where ν is the frequency with which the particle strikes the barrier, m the tunnelling mass and ξ_0 the barrier half-width. In the energy-splitting (e.s.) method where $l = 2$ the tunnel rates are related to the resonance tunnel splittings of states in a double-minimum potential.[8,40,43] This resonance tunnel effect is not taken into account in the transmission-function (t.r.) method, where $l = 1$. We have used eqn (11)-(13) successfully [6,7] in connection with

$$p_n = \exp(-E_n(RT)/\sum_n \exp(-E_n/RT) \tag{14}$$

where $\boldsymbol{R}$ is the gas constant and T the temperature in order to explain the HH/DD k.i.e. of the HH reaction in TPP. It was shown that the HH reaction proceeds at high temperatures from the first excited NH stretching state and the DD reaction from the second excited ND stretching state. We assume that the HD reaction can proceed either from excited NH or ND stretching states. The energy levels are given by

$$E_{n,m}{}^{\mathrm{LL}} = (n + 1/2)\boldsymbol{h}\nu_-^{\mathrm{LL}} + (m + 1/2)\boldsymbol{h}\nu_+^{\mathrm{LL}},\ \mathrm{LL} = \mathrm{HH, HD, DD}. \tag{15}$$

In approximation E_d is given by eqn (5), *i.e.* it does not depend on m. The coupling parameter in the reactant states is zero or very small but close to 1 at the top of the barrier. We obtain with $x = 0$, $x^\ddagger = 1$, $y = 1$

$$E_d^{\mathrm{LL}} - E_n^{\mathrm{LL}} = E_d - \boldsymbol{h}n\nu^{\mathrm{L}} - 1/2\boldsymbol{h}\nu^{\mathrm{L}},\ \mathrm{LL} = \mathrm{HH, DD} \tag{16}$$

$$E_d^{\mathrm{HD}} - E_n^{\mathrm{HD}} = E_d - \boldsymbol{h}n\nu^{\mathrm{H,D}} - 1/2\boldsymbol{h}\nu^{\mathrm{H}}[1 + (1/2)^{1/2} - (3/4)^{1/2}]. \tag{17}$$

The energy diagram in fig. 1(*a*) which takes into account the coordinates of the two AL stretching vibrations was constructed according to eqn (5), (16) and (17). By inspection of these equations one can see that by our approximations we have reduced the two-dimensional problem to a one-dimensional one where the HH, HD and DD reactions are described as proceeding along a one-dimensional double-minimum potential with discrete vibrational levels and effective HH/HD/DD z.p.e. given approximately by the r.g.m.

The quantity Q in eqn (17) can be evaluated by means of a mass-weighted coordinate system. We obtain in a similar way as before [7] for a synchronous and a completely asynchronous pathway

$$2Q_{\mathrm{syn}} = (\sum_i \Delta r_i^2 m_i)^{1/2}/l, \tag{18}$$

$$2Q_{\mathrm{asyn}} = \sum_i \Delta r_i (m_i)^{1/2}/l \tag{19}$$

where r_i is the distance over which the particle i is transported when the reaction coordinate changes from $-\xi_0$ to $+\xi_0$. We are aware that neither a completely synchronous nor asynchronous pathway is realized in practice. However, as we have discussed previously and as can be seen immediately by introducing eqn (18) and (19)

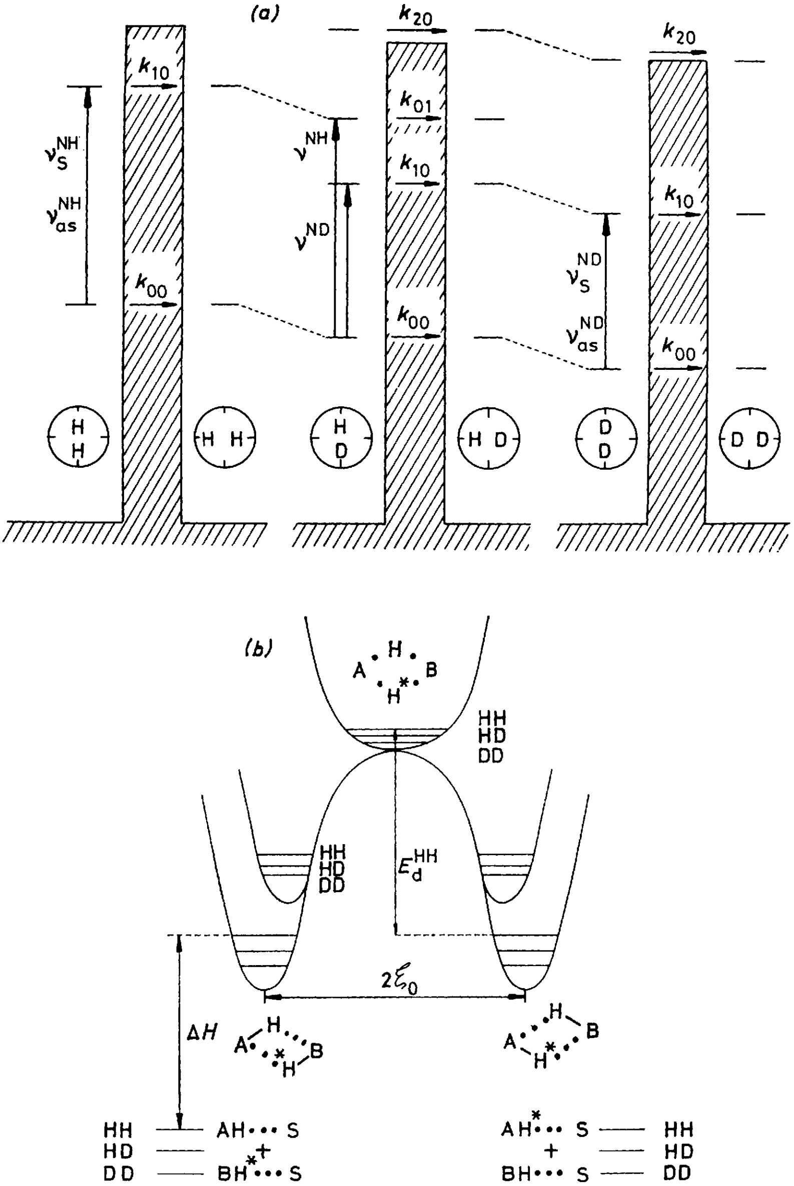


FIG. 1.—Energy diagrams for HH migrations. (*a*) Intramolecular case with fixed heavy atoms, (*b*) intermolecular case with different potential curves for the HH motion as a function of the intermolecular distance R_{AB}, *i.e.* the intermolecular potential energy.

into eqn (13), the tunnelling probability is much higher along the synchronous than along the asynchronous pathway because in very good approximation

$$Q_{\mathrm{asyn}} = (N)^{1/2}Q_{\mathrm{syn}}. \tag{20}$$

In order to treat the intermolecular HH reaction in the system AA + M + THF we have to bear in mind that the cyclic complex in which the exchange takes place has to be formed before tunnelling can take place. Outside the complex the tunnelling probability is zero. The observed rate constants are given by:[8]

$$k_{\mathrm{obs}} = Kk_{\mathrm{ex}} \tag{21}$$

where $K = \exp(-\Delta H/RT + \Delta S/R)$ is the equilibrium constant for the formation of the complex and k_{ex} the exchange rate constant within the complex. In principle, there is an equilibrium isotope effect on the complex formation which will be neglected, however, in the system AA + M + THF. In contrast to the intramolecular exchange we have to take into account that there is a continuous distribution of intermolecular vibrational states within the complex which differ by the mean distance R_{AB} between the exchanging molecules AH and BH. As shown in fig. 1(*b*) the barrier for proton transfer between AH and BH decreases as R_{AB} decreases, *i.e.* as intermolecular excited states are populated. At high energies, *i.e.* very short R_{AB}, there is no longer any barrier for the proton transfer. This behaviour of H-bonded systems has been known, at least in principle, for a long time.[12,44] However, we have no experimental knowledge of this dependence and are, therefore, obliged to set $E_{\mathrm{d}} = E_{\mathrm{d}}(R_{\mathrm{AB}}) =$ constant. As a consequence, we cannot apply eqn (5), (16) and (17) any more and have therefore in the intermolecular case

$$E_{\mathrm{d}}^{\mathrm{DD}} = E_{\mathrm{d}}^{\mathrm{HH}} + \Delta\varepsilon = E_{\mathrm{d}}^{\mathrm{HD}} = \Delta\varepsilon/2 \tag{22}$$

where $\Delta\varepsilon$ contains all changes in the z.p.e. from the reactant states to the barrier saddle point. As shown in fig. 1(*b*) a tight cyclic complex $\mathrm{AH_2B}$ may contain an appreciable amount of z.p.e. so that $\Delta\varepsilon$ may be small. As in the early work of Dogonadze *et al.*[41,42] we consider here only tunnelling between the vibrational ground states on both sides of the barrier, *i.e.* at higher energies the reaction takes place at shorter R_{AB}. Dropping the subscript *n* we obtain

$$k = A\exp(-\Delta H/RT)\int_0^{\infty} D(l)\exp(-E/RT)\mathrm{d}E,\ D = 1 \text{ for } E > E_{\mathrm{d}}. \tag{23}$$

For the case $\Delta H = 0$ and $l = 1$ eqn (28) is equivalent to the Bell [1] model of tunnelling at temperatures which are not too high because the permeability $G(E)$ of a parabolic barrier given by Bell [1] is related to D by $G(E) = (1 + D^{-1})^{-1}$. The w.k.b. approximation used in eqn (12) is no longer valid in the region where E approaches E_{d}. For $E > E_{\mathrm{d}}$ we have to set arbitrarily $D = 1$. A in eqn (23) is an effective frequency factor given by

$$A = (l/\pi^{l-1})\nu\exp(\Delta S/R)/\int_0^{\infty}\exp(-E/RT)\mathrm{d}E = (l/RT\pi^{l-1})\nu\exp(\Delta S/R). \tag{24}$$

The quantities Q were taken as in eqn (18) and (19). A computer program was written in order to calculate the integrals in eqn (24) numerically. At low temperatures the reaction proceeds by ground-state tunnelling in the cyclic complex. One expects parallel Arrhenius curves with $E_{\mathrm{a}} = \Delta H$. The k.i.e. depend only on $D_{E\to 0}(l)$. One can easily show that the asymmetry factor R defined in eqn (6) lies between 1.19 and 1, which implies that the r.g.m. is very well fulfilled in this temperature range. This statement applies also for the intramolecular vibrational tunnelling case. At higher temperatures the r.g.m. is no longer fulfilled and R increases. The usual criteria of Bell[1] for tunnelling then apply. In the intermolecular case R changes only slightly with temperature by contrast to the intramolecular case where the rate constants depend not only on tunnelling probabilities but much more on the availability of states from which tunnelling may occur. The complete Arrhenius curve is composed only of a few single Arrhenius curves with very different slopes.

meso-TETRAPHENYLPORPHINE

We have determined the rate constants k^{HD} for TPP by line shape analysis of the very weak signal of the inner hydrogen atom at $\delta = -3$ ppm upfield from tetramethylsilane (TMS) which we found by measuring sealed samples of deuterated ($^{15}N_4$)TPP in $CDCl_3$ and [$^2H_5$]THF. Fig. 2(*a*) shows a superposition of some typical experimental and calculated spectra. The dominant species ($^2H_2{}^{15}N_4$)TPP does not contribute to this signal but only ($^1H^2H^{15}N_4$) TPP, and to a lesser extent ($^1H^2H^{14}N$-$^{15}N_3$)TPP and ($^1H_2{}^{14}N_4$) TPP which contribute 5% and 2 ± 1% of the signal intensity. The spectral pattern of this signal, a doublet at low and a quintet at high temperatures, arises from coupling with the ^{15}N atoms[6,33] and proves the intramolecular character of the reaction. The formalism for the calculation of the lineshape was the same as described previously[6] for the HH problem. The static line width W_0(NH) in the absence of exchange and the signal spacing of the coalesced lines, here the coupling constant $J_{^{15}\mathrm{NH}}$, were determined by simulation of the outer lines of the quintet. A constant difference $W_0(\mathrm{NH}) - W(\mathrm{TMS})$ was found and used to calculate W_0(NH) at lower temperatures where the doublet is observed. Because of the low concentration of ($^1H^2H^{15}N_4$)TPP a 10 mm probe head for 90 MHz ^{1}H n.m.r. was used. The rate constants are listed in table 1. The Arrhenius diagram in fig. 3(A) also contains the k^{HH} and k^{DD} values reported previously by us.[6] We had already obtained evidence for tunnelling in TPP from the experimental values of $A^{\mathrm{DD}}/A^{\mathrm{HH}} = 25$ and

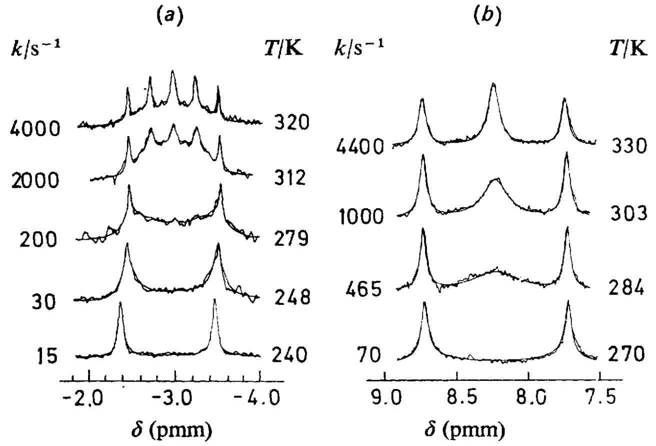


FIG. 2.—90 MHz ^{1}H n.m.r. Line shape analysis of ^{15}NH signals. (*a*) ($^1H^2H^{15}N_4$)-*meso*-tetraphenylporphine in $CDCl_3$, 90° pulses, 6000 scans, 5 s repetition time, 10 mm probe head, saturated solution. (*b*) Saturated solution of ($^1H_2{}^{15}N_4$) azophenine in $CDCl_3$, 45° pulses‘ 200 scans, 7 s repetition time 5 mm probe head. Additional rate constants are 3000, 2300, 800, 200, 150 at 323, 318, 301, 276, 271 K.

$E_a^{DD} - E_a^{HH} = 14$ kJ mol^{-1} which fulfil Bell's criteria of tunnelling, as well as from finding at low temperatures for the HH case temperature-independent values of $\Delta R = 1/T_{1\rho} - 1/T_1 = 5$ s^{-1} for the β-pyrrol proton signals, where $T_{1\rho}$ and T_1 are the longitudinal relaxation times in the rotating and the laboratory frame, measured by pulsed Fourier-transform n.m.r. We interpreted the values of ΔR in terms of k^{HH} as done by Meiboom[46] in his continuous wave experiments. Recently Stilbs *et al.*[35] have found evidence for k^{HH} values lower than the ΔR values reported by us.[6] Since we could

TABLE 1.—RATE CONSTANTS k OF THE TAUTOMERISM IN TPP

	T/K	solvent	$J_{^{15}NH}$/Hz	W_0(NH) /NH	k/s^{-1}
(*a*) ($^1H^2H^{15}N_4$)TPP					
	320	A	96.4	5.0	4000
	319	B	96.4	5.0	3980
	312	A	96.4	5.0	2000
	311	B	96.8	5.0	1995
	309	B	96.8	5.0	1000
	306	C	97.0	4.0	1500
	305	B	96.9	2.5	600
	302	B	97.1	3.0	1200
	290	B	97.3	3.2	290
	288	A	97.2	3.0	480
	288	B	97.6	3.2	290
	286	B	97.6	3.0	300
	284	B	97.8	3.0	100
	282	B	97.6	3.0	90
	280	A	97.7	3.0	200
	279	A	97.5	3.0	200
	273	B	98.2	3.0	80
	270	A	97.6	3.0	90
	265	A	98.6	5.3	50
	264	B	98.7	3.8	40
	255	A	99.0	4.0	47
	248	A	99.2	5.0	30
	247	A	99.2	3.8	25
	246	B	99.6	3.8	20
	240	A	99.6	4.0	15
	238	A	99.6	4.5	15
(*b*) ($^1H_2$)TPP					
	203	B			2.9
	198	B			2.3
(*c*) ($^2H_2$)TPP					
	236	B			2.1

(*a*) Line shape analysis; (*b*) and (*c*) magnetization transfer experiments in the rotating frame according to ref. (47); A = $CDCl_3$, B = [$^2H_8$]THF.

reproduce our values we examined, therefore, in more detail the conditions under which the identification of ΔR with k is allowed in pulsed n.m.r. We have shown that this identification is valid in special cases and improved the experimental technique in a way to allow the determination of rate constants for the general case without any ambiguity.[47] The rate constants obtained with this improved method[47] are listed in table 1. At temperatures below −80 °C k^{HH} can no longer be determined precisely as it becomes only a small part of the total relaxation rate. For the same reason the statement of Stilbs *et al.*[35] is not conclusive, *i.e.* that k^{HH} obtained by ^{13}C n.m.r. can not exceed the value of $0.05\ s^{-1}$ at −94 °C, which is a very small fraction of the relaxation rate of $1.1 \pm 0.1\ s^{-1}$. Therefore, it is not possible to say at present how much the Arrhenius curve is affected by ground-state tunnelling.

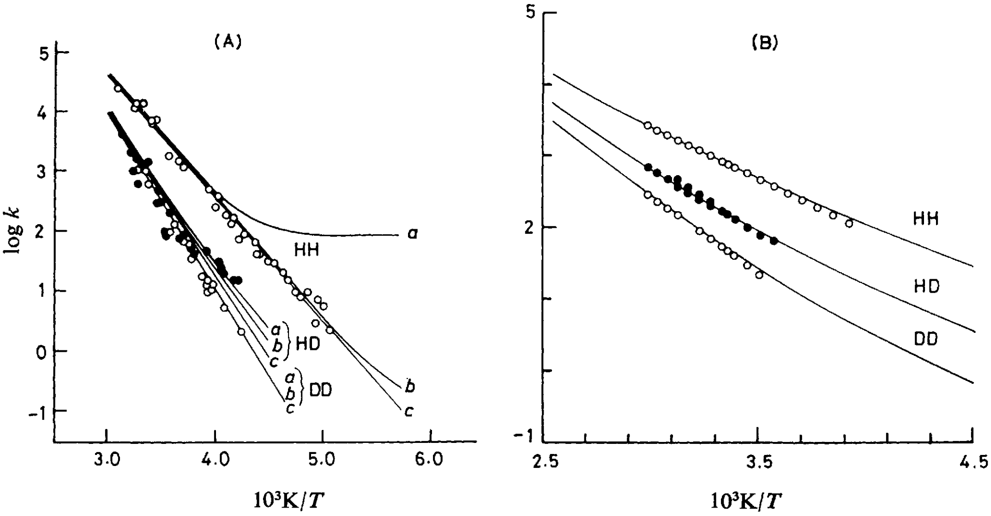


FIG. 3.—Arrhenius diagrams of HH reactions in (A) *meso*-tetraphenylporphine [curve (*a*) $E_a = 74$ kJ mol^{-1}, $\Delta r = 1.54$ Å; curve (*b*) $E_a = 70$ kJ mol^{-1}, $\Delta r = 1.96$ Å; curve (*c*) $E_a = 67$ kJ mol^{-1}, $\Delta r = 2.76$ Å], (B) in the system acetic acid + methanol + tetrahydrofuran. For further explanation see text.

For a discussion of the Arrhenius diagram we summarize some results of our i.r. study of TPP[48] dissolved in CCl_4. We found a very small line width for all NL stretching bands, for example 23 cm^{-1} = 0.28 kJ mol^{-1} for the NH stretching band in ($^1H_2$)TPP. The TPP system is, in fact, owing to its extreme rigidity, the first proton-transfer system with such sharply quantized NH stretching states unbroadened by intermolecular H-bond vibrations. We were able to localize for the first time the NH and the ND stretching vibrations of ($^1H^2H$) TPP at 3335 and 2493 cm^{-1}. The corresponding values for ($^1H_2$)TPP and ($^2H_2$)TPP were different, namely 3318 and 2482 cm^{-1}, which is in good agreement with the literature.[45] These bands are characterized as asymmetric stretching vibrations, the symmetric vibration being forbidden in the i.r. spectrum. In another way, the motions of the two hydrogen atoms are already coupled in the potential wells where the hydrogen atoms have the largest possible interatomic distance. If t.s.t. applied, this distance would decrease in the t.s. and the motion would become even more coupled. The r.g.m. should then be fulfilled in contradiction to the experiment, as shown in the Arrhenius diagram in fig. 3(A). Though the k^{HD} values show much scattering because of the poor signal-to-noise ratio of the ^1H n.m.r. spectra there is no doubt that in the high-temperature region $k^{HD} \approx k^{DD}$. At 298 K we find $k^{HH}/k^{HD} = 10$. At low temperatures k^{HD} seems to be slightly greater than k^{DD}. The large value of $E_a^{DD} - E_a^{HH}$ cannot, therefore, be explained by the loss of the z.p.e. of the two NH stretching vibrations in the t.s.[32] because the r.g.m. should then be fulfilled exactly as mentioned above. This result and the i.r. results prove, therefore, that t.s.t. cannot be applied to the TPP problem. The Arrhenius curves in fig. 3(A) were calculated according to

$$k^{\mathrm{HH}} = k^{\mathrm{HH}}_{00} + k^{\mathrm{HH}}_{10}\exp(-hc\tilde{\nu}_{\mathrm{NH}}/RT) \tag{25}$$

$$k^{\mathrm{DH}} = k^{\mathrm{HD}} = k^{\mathrm{DH}}_{00} + k^{\mathrm{DH}}_{10}\exp(-hc\tilde{\nu}_{\mathrm{ND}}/RT) + k^{\mathrm{DH}}_{01}\exp(-hc\tilde{\nu}_{\mathrm{NH}}/RT) + k^{\mathrm{DH}}_{20}\exp(-2hc\tilde{\nu}_{\mathrm{ND}}/RT) \tag{26}$$

$$k^{\mathrm{DD}} = k^{\mathrm{DD}}_{00} + k^{\mathrm{DD}}_{10}\exp(-hc\tilde{\nu}_{\mathrm{ND}}/RT) + k^{\mathrm{DD}}_{20}\exp(-2hc\tilde{\nu}_{\mathrm{ND}}/RT) \tag{27}$$

where c is the velocity of light. The tunnelling rates k^{LL}_{nm} are defined in fig. 1(*a*) and eqn (11). The HH and the DD curves were very well described by

$$k^{\mathrm{HH}} = 10^{10.9}\exp(-hc\tilde{\nu}_{\mathrm{NH}}/RT) \tag{28}$$

$$k^{\mathrm{DD}} = 10^{12.8}\exp(-2hc\tilde{\nu}_{\mathrm{ND}}/RT) \tag{29}$$

where $\nu_{\mathrm{NH}} \approx \nu^{\mathrm{HH}}_{\mathrm{s}} \approx \nu^{\mathrm{HH}}_{\mathrm{as}} \approx 3330\ \mathrm{cm}^{-1} \approx (2)^{1/2}\nu_{\mathrm{ND}}$. The k_{nm} values were calculated according to eqn (12) and (13) with the exception of k^{DH}_{20} and k^{DD}_{20} which were determined experimentally because the w.k.b. approximation is not valid at the top of the barrier. Since we expect that k^{DH}_{20} is slightly greater than k^{DD}_{20} because of the dependence on ν, we adopted a value of $7 \times 10^{12}\ \mathrm{s}^{-1}$ for the former. The masses for the synchronous tunnelling process were calculated according to eqn (21), *i.e.* $m^{\mathrm{HH}} = 2$, $m^{\mathrm{HD}} = 3$ and $m^{\mathrm{DD}} = 4$. As previously[7] eqn (11) was multiplied by a factor of 2 because each H can migrate either to the N on its right or on its left. Additional parameters were only E_{d} and Q, from which we calculated for $l = 2$ and a synchronous pathway the ground-state proton transport distances Δr given in fig. 3(A). From the crystallographic data we calculated[7] a Δr value of *ca.* 2 Å which is in good agreement with curve (*b*) in fig. 3(A). The experimental data are well described by curves (*b*) and (*c*) whereas in curve (*a*) the ground-state tunnelling rate k^{HH}_{00} is overestimated. The main success of the model is that all energies of activation can be explained by one experimental NH stretching frequency. The HH reaction proceeds by tunnelling from the first excited $\mathrm{NH_s}$ or $\mathrm{NH_{as}}$ stretching state, whereas the HD and the DD reactions proceed predominantly from the second excited ND stretching states which lie at the top of the barrier, as indicated in fig. 1(*a*). There is no evidence for additional vibrational levels from which the HH reaction could equally take place. k^{DH}_{20} and k^{DD}_{20} are slightly smaller than $\nu^{\mathrm{DD}}_{\mathrm{as}}$, probably because of an incomplete barrier permeability even at the top of the barrier.[1] The model can also explain why k^{HD} is probably greater than k^{DD} at lower temperatures by the prediction that HD tunnelling from the first excited NH stretching level should no longer be negligible. The scattering of the k^{HD} values does, however, not permit us to affirm this point definitively. In summary, neither t.s.t. nor an intermolecular tunnelling model are able to explain the k.i.e. and the i.r. data of TPP but only the vibrational model of tunnelling. We are aware that the one-dimensional treatment of the HD reaction involves severe assumptions but we hope that a better description will be possible within the framework of this model in the future.

AZOPHENINE

We report for the first time ^{1}H n.m.r. spectra of $(^1\mathrm{H}_2{}^{14}\mathrm{N}_4)$AP [reaction (II)] in fig. 2(*b*), as well as k^{HH} and k^{HD} values for the intramolecular hydrogen migration. For the corresponding reaction in the oxygen analogue 2,6-dihydroxybenzoquinone Graf[37] and Bren *et al.*[34] reported rate constants which did depend considerably on the type of the solvent. An HH/DD k.i.e. of 2 at −50 °C was observed.[34] The data indicated an intermolecular contribution to the observed rate constants. In the case of ($^{15}N_4$)AP the observation of a doublet at low and a triplet at high temperatures arising from coupling between the H and the ^{15}N atoms proves a fast purely intramolecular HH reaction. A very similar computer program as in the TPP case [6] was used for the calculation of the NH signal. W_0 and the coupling constant of $J_{^{15}\mathrm{NH}} =$ 90 Hz was obtained at each temperature from the outer lines of the signal. The frequency of the NH stretching vibration was given by Musso *et al.*[49] as 3290 cm^{-1}, which is within error limits equal to the energy of activation. The rate constants k^{HH} are, thus, very well described by the equation

$$k^{\mathrm{HH}} = 10^{9.8}\exp(-hc\tilde{\nu}_{\mathrm{NH}}/RT) \qquad (30)$$

and differ from the corresponding values for TPP only by the frequency factor which is *ca.* 10 times smaller in AP. We conclude tentatively that the HH reaction in AP proceeds also by tunnelling between the first excited NH stretching levels as in TPP. Because of experimental limitations we did not succeed in measuring k^{HD} values of AP in the same solvent but only in 1,2-$C_2D_4Cl_2$ and obtained a value of $(k^{\mathrm{HH}}/k^{\mathrm{HD}})_{298\ \mathrm{K}} = 4$. This k.i.e. is lower than the value for TPP. We speculate that the lower frequency factor and the lower k.i.e. in AP arises from the fact that the HH reaction is accompanied by a motion of C and N atoms because double bonds are converted to single bonds in contrast to the aromatic TPP. We hope to report in the future the full HH/HD/DD k.i.e. for AP which will throw more light on this interesting reaction and the vibrational model of intramolecular tunnelling as a whole.

ACETIC ACID + METHANOL + TETRAHYDROFURAN

In continution of previous work [8,9,11] we have succeeded in measuring all the k.i.e. of proton exchange in the system AA + M + THF using a combination of ^{1}H and ^{2}H dynamic n.m.r. spectroscopy. The rate law of the exchange is given by

$$v = k^{\mathrm{LL}}C_{\mathrm{AA}}C_{\mathrm{M}} + k^{\mathrm{LLL}}C^2_{\mathrm{AA}}C_{\mathrm{M}}. \qquad (31)$$

In our previous experiments the second triple proton-transfer term involving two AA and one M molecule was not found because the C_{AA} could not be varied over a wide range because of experimental limitations. The bimolecular rate constants at $C_{\mathrm{AA}}\rightarrow 0$ obtained by ^{1}H n.m.r. at high deuterium fractions and by ^{2}H n.m.r. for low deuterium fractions were equal and could, therefore, unambiguously be identified with k^{HD} for the double proton-transfer process. A detailed description of the experiments will be given elsewhere. Table 2 contains all the kinetic data. The r.g.m. is fulfilled for the HHH and in approximation also for the HH reaction. Therefore, no solvated ion pair is formed as an intermediate, which was already postulated [8] in view of the large frequency factors. We obtain the interesting result that the frequency factor for the HH motion is much smaller than for the DD motion while the frequency factor for the HHH motion is much higher than for the DDD motion. These results cannot be explained by the t.s.t. but only by tunnelling. Fig. 3(B) shows the Arrhenius diagram for HH/HD/DD reactions from which three energies of activation and three frequency factors can be obtained. The Arrhenius curves were, however, calculated using eqn (22)-(24) by adapting only 4 parameters, $E_{\mathrm{d}} = 31.0$ kJ mol^{-1}, $\Delta H = 19.7$ kJ mol^{-1} for the enthalpy of formation of the cyclic complex from the solvated reactant states, an effective frequency factor log $A = 10.4$ for all reactions, and the parameter Q derived from eqn (18)-(20)

$$Q^{\mathrm{HH}} = 2^{s-1}\Delta r 2^{1/2}/l = (2/3)^{1/2}Q^{\mathrm{HD}} = 2Q^{\mathrm{DD}} = 0.25\ \text{Å} \qquad (32)$$

TABLE 2.—KINETIC PARAMETERS OF PROTON EXCHANGE IN THE SYSTEM ACETIC ACID + METHANOL + TETRAHYDROFURAN

	E_a/kJ mol^{-1}	log A	k_{298K}/dm^3 mol^{-n} s^{-n}
HH	27.9 ± 1	7.77 ± 0.2	746 ± 198
HD	34.8 ± 2	8.27 ± 0.2	144 ± 11
DD	40.5 ± 2	8.78 ± 0.2	48 ± 19
HHH	30.7 ± 2	8.89 ± 0.2	3235 ± 782
HHD	31.6 ± 2	8.7 ± 0.1	1457 ± 40
HDD	30.2 ± 2	8.06 ± 0.2	584 ± 141
DDD	27.7 ± 3	7.31 ± 0.2	281 ± 7

k.i.e. at 298 K: $k^{HH}/k^{DD} = 15.5 \pm 4.4$, $k^{HH}/k^{HD} = 5.1 \pm 1.4$, $k^{HD}/k^{DD} = 3.1 \pm 0.9$, $k^{HHH}/k^{DDD} = 11.5 \pm 2.7$, $k^{HHH}/k^{HHD} = 2.2 \pm 0.5$, $k^{HHD}/k^{HDD} = 2.5 \pm 0.5$, $k^{HDD}/k^{DDD} = 2.1 \pm 0.5$

where $s = 0$ for a synchronous and $s = 1/2$ for an asynchronous pathway. A fifth parameter, $\Delta\varepsilon$ in eqn (22), which describes the differences in the z.p.e. between the reactant states and the state at the top of the barrier, *i.e.* the differences in the energies of activation of the different curves at high temperatures, was found to affect the curves only very little as long as it was kept small, *i.e.* not greater than *ca.* 2-3 kJ mol^{-1}. For the curves in fig. 3(*b*) a value of $\Delta\varepsilon = 1.75$ kJ mol^{-1} was used. Note that the behaviour of the k.i.e. as a function of the temperature depends only on the value of Q but not on the tunnel model used. The difference between the models is only the value of Δr calculated from Q according to eqn (30). For the synchronous pathway we obtain $\Delta r = 0.71$ Å for the e.s. model which should apply in this symmetrical case and $\Delta r = 0.38$ Å for the t.r. model. Within error limits the Bell equation and eqn (23) with $l = 1$ describe the curves with the same parameters as long as eqn (21) is applied. Half of these distances is obtained if one assumes an asynchronous proton motion. A special success of the intermolecular tunnelling model proposed here is that it also explains the parallel Arrhenius curves of the triple proton transfer with reasonable parameters. We are convinced that the description given here applies not only for proton exchange in an hydrogen-bond-acceptor solvent S like THF, where the AH ··· S and BH ··· S dominate,[9] but also for aprotic solvents where at low temperatures the AH and BH molecules form a number of different H-bond associates in which no proton exchange can take place. Also in this case a minimal energy ΔH is required for the formation of the active complex in which tunnelling can occur.

CONCLUSIONS

Experimental and theoretical evidence has been accumulated that neutral double proton transfer in rigid molecules takes place between quantized vibrational states by tunnelling. The k.i.e. depend not only on the tunnelling probability but also on the availability of vibrational states. In intermolecular HH reactions tunnelling occurs from excited intermolecular states. The enthalpy of formation of the active complex in which the exchange takes place has to be taken into account when calculating Arrehenius curves. The r.g.m. for double and poly proton-transfer reactions is fulfilled only at low temperatures where it is linked with frequency factor ratios of $A^H/A^D \gg 1$. At high temperatures Bell's criteria of tunnelling, *i.e.* $A^H/A^D \ll 1$ and $E_a^{HH} - E_a^D$ greater than the differences in the z.p.e., are linked with the breakdown of the r.g.m.

We thank Prof. R. P. Bell, H. Zimmermann, R. L. Schowen and M. M. Kreevoy for helpful suggestions and Dr K. B. Schowen for reading the draft of this paper. We also thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support. The calculations were done on the Univac 1108 computer of the Rechenzentrum der Universität Freiburg.

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