The Effect of Anharmonic Vibrational Coupling on Deuterium Isotope Exchange Equilibria Involving Ring Dimers of Carboxylic Acids

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The observed isotope fractionation factor, α, for deuterium isotope exchange between liquid acetic acid and hydrogen gas is compared with a value of α calculated on the basis of a harmonic force field for the dimer. The calculated value of α is found to be about 30 % higher than the observed value. The discrepancy is considered to be due to the neglect of anharmonic coupling between the hydroxyl bond stretching- and the hydrogen bond stretching vibrations of the dimer.

According to the statistical mechanical theory of isotope effects, equilibrium constants for isotope exchange depend primarily on the vibrational parameters of the exchanging isotopic species [1, 2]. Therefore, a study of isotope exchange equilibria involving carboxylic acids is useful to probe into the vibrational characteristics of the hydrogen bonds of carboxylic acids which have become subject of numerous investigations [3].

Recently, the deuterium isotope exchange between liquid acetic acid and hydrogen gas has been studied, and the isotope fractionation factor, α, for this exchange reaction has been determined at 25 °C and 65 °C [4]. A comparison of this value of α with that calculated from spectroscopic data provides a test of the validity of the molecular force fields of monomeric and dimeric acetic acid, which have been evaluated recently [5].

If dimers are assumed to be the only associated species in the liquid, the isotope exchange may be characterized, for small deuterium concentrations, by two independent isotope exchange reactions which involve acetic acid either as monomer or as monodeuterated dimer. The exchange reactions are:

$$\mathrm{CH_3COOH(l) + HD(g) \lesssim CH_3COOD(l) + H_2(g)} \quad (1)$$

and

$$\mathrm{(CH_3COOH)_2(l) + HD(g) \lesssim CH_3COOH \cdot CH_3COOD(l) + H_2(g)} \quad (2)$$

The isotope fractionation factor, α, defined as the ratio of the atom fractions of exchangeable [6] deuterium and hydrogen in the liquid, divided by the ratio of the atom fractions of deuterium and hydrogen in the gas, is related to the mole fractions of the exchanging species of the reactions (1) and (2) by

$$\alpha = \frac{x_{1\mathrm{D}} + x_{2\mathrm{D}}}{x_{1\mathrm{H}} + 2x_{2\mathrm{H}}} \bigg/ \frac{x_{\mathrm{HD}}}{2x_{\mathrm{H_2}}}. \quad (3)$$

$x_{1\mathrm{D}}$, $x_{2\mathrm{D}}$, $x_{1\mathrm{H}}$ and $x_{2\mathrm{H}}$, respectively, are the mole fractions of $\mathrm{CH_3COOD}$, $\mathrm{CH_3COOH.CH_3COOD}$, $\mathrm{CH_3COOH}$ and $\mathrm{(CH_3COOH)_2}$; x_{HD} and $x_{\mathrm{H_2}}$, respectively, are the mole fractions of HD and $\mathrm{H_2}$.

The right hand side of Eqn. (3) can be written as the weighted average of the equilibrium constants K_1 and K_2 of reaction (1) and (2), respectively, i. e.

$$\alpha = 2K_1\,\xi + K_2\,(1-\xi) \quad (4)$$

the weights, ξ, and $1-\xi$, being the atom fractions of exchangeable hydrogen in the monomeric and dimeric species, respectively;

$$\xi = x_{1\mathrm{H}}/(x_{1\mathrm{H}} + 2x_{2\mathrm{H}})\ . \quad (5)$$

Since the force fields of the liquid species are as yet unknown, the calculations of K_1 and K_2 have to be based on force fields of the gaseous species. Using the vapor pressure isotope effect of acetic acid [7] and data on the association in the liquid [8], the influence of the condensed phase on K_1 and K_2 is readily estimated. Since the acid is highly associated [8], the isotope fractionation factor, α, and the vapor pressure isotope effect are predominantly determined by the acid dimer and become almost insensitive to monomer contributions. Further, a vapor pressure isotope effect of approximately unity [7] indicates that the effect of condensation on K_2 is negligible. Consequently, for the calculation of α, it seems justified to use values of K_1 and K_2 which are derived from the force fields of gaseous acetic acid[5].

Calculations of α via Eqn. (4) were carried out[9] using a harmonic forcefield for the isotopic species of acetic acid[5]. The calculations result in a significant discrepancy between the theoretical and experimental values. Thus, for example, the calculated value of α for room temperature is $\alpha = 4.123$ which compares with an experimental value of 3.10. A similar discrepancy exists for higher temperatures.

It can be shown that discrepancies of this order of magnitude are to be expected if anharmonicities in the vibration of the H-bonding proton are not taken into account. Recently, MARECHAL, WITKOWSKI and coworkers demonstrated the significance of anharmonic coupling between the hydroxyl bond stretching vibrations and the hydrogen bond stretching vibrations of the dimer in order to reproduce the infrared absorption spectrum of carboxylic acids in the hydroxyl bond stretching region[10, 11, 12]. Previously, similar anharmonic potential functions have been used to describe the isotope effect on the hydrogen bond length (Ubbelohde effect)[13, 14]. In their quantum mechanical treatment, Marechal and Witkowski assume that the hydroxyl bond stretching frequency, ω_H, depends linearly on the amplitude, Q_A, of the hydrogen bond stretching vibration, i. e.

$$\omega_H(Q_A) = \omega_H(0) + Q_A\,(d\omega_H(Q_A)/dQ_A)_{Q_A=0} \tag{6}$$

$\omega_H(0)$ is the frequency of the hydroxyl bond stretching vibration, if the proton is in its equilibrium position, and $(d\omega_H(Q_A)/dQ_A)_{Q_A=0}$ measures the change of $\omega_H(Q_A)$ with respect to Q_A at the equilibrium position[10, 11]. In this model, the hydroxyl bond stretching vibrations and the antisymmetric hydrogen bond stretching mode of the dimer are assumed to be harmonic. The symmetric hydrogen bond stretching mode is assumed to obey a Morse potential. Equation (6) implies cubic and quartic interaction terms in the potential function. The harmonicity of the hydroxyl bond stretching vibration imposes an isotope dependence on $\omega_H(Q_A)$ of the form

$$\omega_H(Q_A)/\omega_D(Q_A) = \sqrt{2}\ . \tag{7}$$

This, in turn, implies via Eqn. (6) different anharmonic force fields for the isotopic species of the dimer. Although this constitutes a weakness of the model, it should, in view of its success, nevertheless be useful to estimate the magnitude of the anharmonic contribution to the isotope effect.

In order to account for the effect of the anharmonic coupling on the equilibrium constant K_2, the hydroxyl bond stretching frequency calculated from the original harmonic force fields is replaced, in the partition functions of the dimer, by the average frequencies $\langle\omega_H\rangle$ and $\langle\omega_D\rangle$ which arise from the anharmonic coupling according to Equation (6)[15]. The average frequency $\langle\omega_H\rangle$ is expressed in terms of the parameters of the anharmonic potential by

$$\langle\omega_H\rangle = \omega_H(0) - (V_0 + b_H^2)\omega_{00} + b_H\,\omega_{00}\,\langle Q^+\rangle\ . \tag{8}$$

ω_{00} is the frequency of the hydrogen bond vibration, V_0 is a constant associated with the dipole-dipole-interaction between the two hydrogen bonds in the dimer, b_H is a coupling constant proportional to $(d\omega(Q_A)/dQ_A)_{Q_A=0}$ of equation (6), and $\langle Q^+\rangle$ is the mean of the amplitude Q^+ of the symmetric hydrogen bond stretching mode, for which a Morse potential of the form $\hbar\,\omega_{00}\,\delta^{-1}\,\{1-\exp\,[-(\frac{1}{2}\,\delta)^{\frac{1}{2}}\,Q^+]\}^2$ has been assumed; approximately[16],

$$\langle Q^+\rangle = \tfrac{3}{4}(\tfrac{1}{2}\delta)^{\frac{1}{2}}\ \coth\ (\hbar\,\omega_{00})/2kT\ . \tag{9}$$

The parameters of Eqn. (8) reported for acetic acid are[11] $\omega_H(0) = 3230\ cm^{-1}$, $\omega_D(0) = 2340\ cm^{-1}$, $V_0 = -0.68$, $\omega_{00} = 160\ cm^{-1}$, $b_H = -1.4$, $b_D = -0.95$, $\delta = 0.04$. Since the hydroxyl bond stretching frequencies are large, only the zeropoint energy contribution to the isotope exchange equilibrium is affected by the anharmonicity correction.

Table 1 shows the result of the calculations for $T = 298.16$ °K and $T = 338.16$ °K. The table contains the reduced partition function ratios $s/s'f^2$ of the pairs HD-H_2[17], CH_3COOD-CH_3COOH and $(CH_3COOH)_2$-$CH_3COOH.CH_3COOD$, respectively, as well as the quantities K_1, K_2^* and α^* derived from the harmonic force field[5] of the exchanging species. The values K_2^{**} and α^{**} are obtained by applying to K_2 the anharmonicity correction discussed above.

It is to be noted that K_2 and α change significantly, if anharmonicity is taken into account. The change is due primarily to the anharmonic coupling represented by the constant b in Eqn. (8) which tends to reduce the difference between the zeropoint energies of the protonated and the deuterated dimer, as compared to the zeropoint energy difference of the harmonic oscillators. This results in a decrease of the equilibrium con-

Table 1. Calculated and Observed Data on the Deuterium Isotope Exchange between Acetic Acid and Hydrogen Gas.

T(°K)	Reduced Partition Function Ratios $s/s'f$			Equiblibrium Constants				Isotope Fractionation Factor		
	$\frac{HD}{H_2}$	$\frac{CH_3COOD}{CH_3COOH}$	$\frac{CH_3COOH \cdot CH_3COOD}{(CH_3COOH)_2}$	K_1	K_2*	K_2**	ξ	α obs.	α*	α**
298.16	3.4096	15.237	13.976	2.234	4.099	2.761	0.065	3.10±0.03	4.123	2.872
338.16	2.8965	10.171	9.331	1.756	3.222	2.274	0.114	2.86±0.09	3.254	2.415

* Calculated using harmonic force field [5], ref. 9.
** Calculated including anharmonicity correction, this work.
α obs. Observed, ref. 4.

stant K_2 which, in turn, via Eqn. (4) decreases the isotope fraction factor α.

The discrepancy between the experimental values of α and the harmonic force field calculations is likely to be caused by the neglect of the anharmonic coupling, since the anharmonicity correction has the same order of magnitude and the same direction as the observed discrepancy. The inherent approximations and simplifications of the anharmonic model do not warrant a detailed evalution of the isotope effect. This has to await a normal coordinate analysis of the dimer based on a common anharmonic force field for all isotopic species. For a similar reason, the effect of proton tunnelling has not been considered here [17]. However, even in its preliminary form, the model suggests that anharmonic coupling contributes appreciably to isotope effects involving hydrogen bonded species. This is particularly interesting, since, in general, anharmonicity corrections to isotope effects are small [18].

In conclusion, the preceding calculations show that isotope effects appear to be sensitive to the structure of hydrogen bonded species. Therefore, the study of appropriate isotope exchange reactions, similar to Eqn. (2), should yield, in conjunction with spectroscopic observations, valuable information about the force fields associated with weak and intermediate hydrogen bonds.

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