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Solvent Deuterium Isotope Effect in the Acid Catalyzed Decarboxylation of Phenylpropiolic Acid in 85% D_3PO_4 in D_2O

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A comparative study of the solvent deuterium isotope effect in the decarboxylation of phenylpropiolic acid (PPA) in 85% perdeuteriated orthophosphoric acid, D_3PO_4/D_2O, has been carried out and the ratio of the decarboxylation rate constants, $k(H_2O)/k(D_2O)$ equal 1.88±0.07, interpreted as caused by different dissociation constants, K_h/K_d, of normal and perdeuteriated phosphoric acids in H_2O and in D_2O respectively, and by the deuterium discriminations in the subsequent steps of hydrogen transfer from the solvent H_3O^+/D_3O^+ to triple bond of PPA and finally by proton transfer from π-complex to nearest C_α-carbon and $sp^2(C_\alpha\text{-H})$ covalent bond formation. The detachment of carbon dioxide from PPA (decarboxylation step) is the fast process taking place or directly after the rate determining T.S. formation or stepwise by hydration of the vinyl cation and formation of the benzoylacetic acid intermediate compound, which then decarboxylates in the kinetically insignificant step. The discussion is supplemented by calculating the $k(H_2O)/k(D_2O)$ ratios for decarboxylation scheme involving protonation of the triple bond in the rate determining step and for the reaction scheme involving fast isotope equilibrium between protonated water and protonated triple bond, followed by the rate determining transfer of proton from π-complex to the usual sp^2 (C–H) covalent bond. A good agreement between experimental solvent D_2O I.E. and values calculated for reaction scheme involving proton transfer in the r.d.s. (what follows also from the ^{13}C K.I.E. determinations in decarboxylation of PPA in H_3PO_4/H_2O and D_3PO_4/D_2O solvents) was found.

Key words: solvent isotope effect, phenylpropiolic acid, decarboxylation, rate determining step

^{13}C- and D-KIEs are usually studied in different laboratories and the direct comparison of the corresponding data is not always possible [1,2]. We, therefore, carried out the simultaneous determination of ^{13}C-KIE and D-KIE in the decarboxylation of PPA in 85% D_3PO_4 in D_2O to assess the magnitude of the expected "sizeable" D-KIE, which should accompany the small ^{13}C decarboxylation KIE [3,4].

EXPERIMENTAL

Phenylpropiolic acid, PhC≡C-COOH, Aldrich, 99% purity, 1.573 mmoles in the first series, 1.631 mmoles in the second series of decarboxylation experiments was mixed under vacuum in the reaction vessel with 85% D_3PO_4 in D_2O (Isotope Center Swierk/Warsaw). 10 cm^3 of this solution in the first series, 20 cm^3 in the second series of decarboxylation experiments were used. The r.v. was placed in the thermostat at temperatures indicated in column (1) of Table 1. Decarboxylations were interrupted by fast withdrawals of the reaction vessels from thermostat at preset times, rapid cooling, and then extraction of the carbon dioxide in the vacuum line by "freeze-pump-thaw" cycles repeated several times. The amount of CO_2 measured in the specially designed mercury manometer served to determine the degree "f" of decarboxylation of PPA and the absolute rates of decarboxylation of PPA, both in 85% D_3PO_4/in D_2O and in 85% H_3PO_4/in H_2O, column (3), Table 1. The carbon dioxide probes purified by cryogenic methods were flame sealed under vacuum in standard glass tubes and analysed by MS using a Europa-Scientific 20-20 mass spectrometer as described in [4].

Table 1. Experimental comparison of decarboxylation rate constants of phenylpropiolic acid (PPA) in 85% perdeuteriated orthophosphoric acid respectively.

Exp. No/Temp.K/reaction time in min.	Fraction "f" of decarboxylation	Decarboxylation rate constant "k" min^{-1}	$k(H_2O)/k(D_2O)$
1.631 mmoles of PPA in 20 cm^3 of 85% H_3PO_4 in H_2O			
OL-6/334.16/410	0.2549	7.176×10^{-4}	2.66
OL-8/343.16/130	0.2766	2.490×10^{-3}	1.81
OL-10/353.96/75	0.5081	9.459×10^{-3}	1.95
1.537 mmoles of PPA in 20 cm^3 of D_3PO_4 (85% in D_2O)			
OL-7/334.16/463	0.1174	2.697×10^{-4}	
OL-9/343.16/166	0.2047	1.38×10^{-3}	
OL-11/353.96/10	0.3851	4.863×10^{-3}	

RESULTS AND DISCUSSION

The results of the first preliminary series of determinations of the solvent deuterium isotope effect indicated that the ratio $k(H_2O)/k(D_2O)$ for decarboxylation of 0.16 M. solution of PPA in 85% H_3PO_4/in H_2O and in 85% D_3PO_4/in D_2O are in the range 1.7–2.1 (mean value 1.86±0.18 [4]). The mean value 1.88±0.07 of the $k(H_2O)/k(D_2O)$ ratio for 343–353 K (70–80°C) obtained in the second series of comparative decarboxylation experiments with phenylpropiolic acid dissolved in 20 cm^3 of 85% D_3PO_4 in D_2O, presented in Table 1, agrees with the preliminary published value [4], but the Arrhenius plots of the decarboxylation rate constants $k(H_2O)$ and $k(D_2O)$, given by (1) and (2) indicated that the difference of the Arrhenius activation energies $\Delta Q = [Q(D_2O) - Q(H_2O)] = 15.07$ kJ/mol and the ratio of the preexponential factors, $A(H)/A(D) = 0.01$ are characteristic of kinetic processes involving tunneling.

$$\ln k(H_2O) = 38.846 - 15396/T, \text{ correl. coef.} = 0.99988 \qquad (1)$$

$$Q_{Arrh} = 127.96 \text{ kJ mol}^{-1}, \quad A_{Arrh} = 1.24\times10^{15} \text{ s}^{-1}$$

$$\ln k(D_2O) = 43.377 - 17208/T, \text{ correl. coef.} = 0.994 \qquad (2)$$

$$Q_{Arrh} = 143.03 \text{ kJ mol}^{-1}; \quad A_{Arrh} = 1.15\times10^{17} \text{ s}^{-1}$$

We conclude, therefore, that the transition state of the investigated decarboxylation reaction of PPA in 85% orthophosphoric acid is located on the trajectory of the proton moving from its highly polar initial state to the covalently bound sp^2 "C–H" bond. The last remark is supported by the calculational approach presented below.

The negligible ^{13}C KIE found in the decarboxylation of PPA in 85% orthophosphoric acid medium indicated that the bond between C_α and the carboxylic group is not broken in the transition state and that a sizeable solvent D_2O KIE should be observed if the decarboxylation reaction is carried out in 85% D_3PO_4 in D_2O. The determined simultaneously experimental ^{13}C KIEs and solvent D_2O KIE are internally consistent and in agreement with the above expectations. The carboxyl ^{13}C decarboxylation KIE depends largely on the skeletal vibrations and on changes of the nearby C–H bond also but not on the distant proton bonding. The values of solvent D_2O I.E. permit in principle to localise the position of hydrogen in the transition state of the decarboxylation of PPA if the dissociation constants K_h and K_d for light and heavy mineral acids (in H_2O and D_2O respectively) are known and the necessary corrections to the observed resulting solvent isotope effect can be introduced. The aliphatic carboxylic acids are about $(3)^{1/2}$ times more dissociated in H_2O than in D_2O, but there are no data concerning the K_h/K_d ratio for $PhC{\equiv}C\text{-}COOD/D_2O$ as well as for large temperature and large concentration ranges of D_3PO_4/D_2O solutions including diphosphoric acid, $D_4P_2O_7$, [8]. The observed D_2O/H_2O solvent isotope effect in the decarboxylation of PPA may originate in three-four subsequent physical/chemical steps:

1. Dissociation of orthophosphoric acid and hydronium ion formation:

$$D_3PO_4 + D_2O \Leftrightarrow D_2PO_4^- + D_3O^+, \quad (K_h/K_d) > 1$$

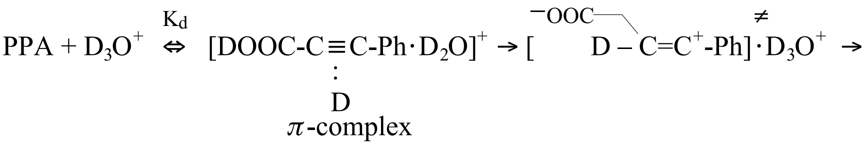
$$H_3PO_4 + H_2O \Leftrightarrow H_2PO_4^- + H_3O^+$$

2. Transfer of proton/deuteron from H_3O^+/D_3O^+ to triple bond of PPA and the formation of π-complex.
3. Internal transformation of H^+/D^+ from π-complex to usual covalent sp^2(C-H)/(C-D) bonds.

There are no data concerning the dependence of the (K_h/K_d) ratio on the concentration of D_3PO_4 in D_2O for temperature interval pertinent to the decarboxylation experimental studies. $(K_h/K_d) > 1$ is expected but the exact value of this ratio is unknown. The knowledge of the above ratio for direct protonation of PPA and of the triple bond of PPA with H_3PO_4/D_3PO_4 would be very useful also. The magnitude of D_2O solvent KIE in steps 2 and 3 depends on the mechanism and the structure of the transition state. A view has been frequently expressed that $k(H_2O)/k(D_2O) > 1$ implies the transfer of proton/deuteron from H_3O^+/D_3O^+ to unsaturated (triple) bond in the rate determining step (3):

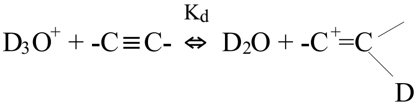
$$PPA + D_3O^+ \rightarrow (DOOC\text{-}C{\equiv}\underset{\underset{D}{\vdots}}{C}\text{-}Ph\cdot D_2O)^+ \qquad (3)$$

while the $k(H_2O)/k(D_2O) < 1$ indicates the occurrence of the reversible step of proton/deuteron transfer from H_3O^+/D_3O^+ to (-C=C-) or to (-C≡C-) (4):



$$PPA + D_3O^+ \overset{K_d}{\Leftrightarrow} [DOOC\text{-}C{\equiv}\underset{\underset{\underset{\pi\text{-complex}}{D}}{\vdots}}{C}\text{-}Ph\cdot D_2O]^+ \rightarrow [\ {}^{-}OOC\diagdown\ D - C{=}C^+\text{-}Ph]\cdot D_3O^{+\,\neq} \rightarrow \qquad (4)$$

Approximate guess calculations of the equilibrium (K_h/K_d) for hydrations of olefins have been carried out [11,12]. We are presenting explicitly the analogous assessment for the reversible scheme (5) but using the fractionation factors “f” introduced to chemistry of isotopes by Bigeleisen and Goeppert-Mayer [17] given by (6) and explained by the exchange reaction (7) [18] correspondingly.



$$D_3O^+ + \text{-}C{\equiv}C\text{-} \overset{K_d}{\Leftrightarrow} D_2O + \text{-}C^+{=}C\begin{smallmatrix}\diagup\\ \diagdown D\end{smallmatrix} \qquad (5)$$

$$f_i = (u_{2i}/u_{1i})[\sinh(u_{1i}/2)/\sinh(u_{2i}/2)] \qquad (6)$$

where: $u_i = (hc\omega_i/kT)$ and h, c, ω_i, k, T have usual meaning [18].

$$A^1X(\sigma_1) + {}^2X \overset{K}{\Leftrightarrow} A^2X(\sigma_2) + {}^1X \qquad (7)$$

$f = (\sigma_2/\sigma_1)K$, σ_1 and σ_2 are the symmetry numbers.

Neglecting the contribution of the system of hydrogen bonds to D_3O^+ on the left side of the equation (5) and to the carbon cation on the right side of this equation, then considering only the stretching vibrations, we can write the K_h/K_d ratio for equilibrium (5) approximately as given by (8), since the contribution of bending vibrations cancels to great extent and the symmetry numbers cancel in the K_h/K_d ratio also.

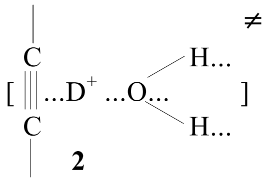
$$(K_h/K_d) \approx (f_{OD^+})^3/(f_{OD})^2(f_{CD^+}) \qquad (8)$$

Taking: $\omega = 3400\ cm^{-1}$ for (OH) in H_2O,
2475, 234 cm^{-1} for (OD) in D_2O,
2900 cm^{-1} for (OH^+) in H_3O^+,
2111, 229 cm^{-1} for (OD^+) in D_3O^+,
2900 cm^{-1} for (CH^+), and 2129, 267 cm^{-1} for (CD^+),

calculating the corresponding fractionation factors (reduced partition functions ratios “f” of eq. (6) for O-D, O-D^+, and for C-D^+ in liquid D_2O, in D_3O^+ in D_2O and for carbocation (or for D^+ bound in π complex) and substituting the calculated values of “f” into (8) we find that the (K_h/K_d) for equilibrium process (5) equals:

$$(K_h/K_d) = (4.88291)^3/[(6.77907)^2(4.71488)] = (116.42225/216.67586) =$$
$$= 0.5373 \text{ at } 298.16\text{ K } (25°\text{C}),$$
$$= 0.5634 \text{ at } 323.16\text{ K } (50°\text{C}),$$
$$= 0.60795 \text{ at } 373.16\text{ K } (100°\text{C}).$$

Thus, within the above calculational approach, the positively charged heavy hydrogen should concentrate in organic transient carbocation or in π-complex (see footnote on p. 218). Within the decarboxylation scheme (5), the equilibrium K_d should be followed by the rate determining migration of proton/deuteron from π-complex to $(C–D)sp^2$ bond. To great extent arbitrarily, invoking the “principle of microscopic reversibility” [12,19] a value $(k_h/k_d) = 1.8$ (or 2.0) is taken for the deuterium isotope effect in the proton migration from π-complex to carbocation. Multiplying the equilibrium isotope effect (K_h/K_d) by 1.8 (or by 2), we obtain the total solvent D_2O decarboxylation KIE values close to unity (0.967 or 1.0746). The experimental solvent D_2O isotope effect is close to 2.0. Thus, within the scheme (5) of decarboxylation of PPA we should admit that the $(k(H_2O)/(k(D_2O))$ is larger, due to tunneling, which increases the deuterium isotope effect especially at low temperatures or reject the mechanism of decarboxylation of PPA involving the preequilibrium (5) and consider the mechanism of decarboxylation of PPA as presented in (3). The gas phase proton affinity of water (equal 166.5±2 kcal/mol) is higher than the gas phase H^+ affinity of acetylene (equal 155.3 kcal/mol) [20]. The electron withdrawing carboxylic group should decrease the electron density at the triple bond and the “symmetric or slightly late” transition states could be suggested. Especially attractive is a “free proton” model of the transition state as given by **2**. Accepting this model of the T.S., we can calculate the solvent D_2O decarboxylation isotope effect using



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$$(k(H_2O)/k(D_2O)) \approx (f(OD^+))^3/(f(OD))^2 \tag{9}$$

since the “free proton” does not change the basicities of water molecule, which was left behind and of the acetylenic bond which is attacked. A surprising agreement is found between experimental values determined in the temperature interval 333–354 K (60–81°C) and deuterium solvent isotope effects calculated with (9) for these temperatures, as listed below:

Temp. K/°C	k(H_2O)/k(D_2O)	
	calculated values	experimental values
333.16 /60°C	2.2227	2.479
343.16/70	2.1518	2.116
353.96/80.8	2.0820	1.801

Probably the omitted in (9) factors (libration, deformation vibrations) in numerator and denominator, compensate each other and the "free proton" model reproduces well the experimental results in the rather narrow temperature interval studied. There are no experimental data for temperatures below 60℃ (333 K), where the calculated and the extrapolated experimental data diverge.

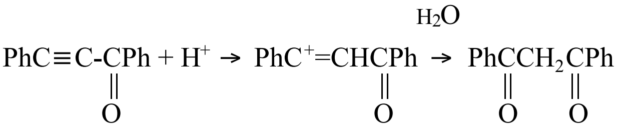
This introductory study of the D_2O solvent isotope effect in decarboxylation of phenylpropiolic acid in 85% D_3PO_4/D_2O are in line with the previous more detailed investigations of ^{13}C KIEs in decarboxylations of PPA in mineral acids diluted with water [3,4,21]. The negligible heavy atom ^{13}C KIEs indicated that the rupture of carbon–carbon bond does not take place in the rate determining step of the decarboxylation of PPA. The kinetic solvent D_2O determinations, (k(H_2O)/k(D_2O)) > 1, showed more precisely that protonation of the triple bond of PPA takes place in the r.d.s. and that the "free-proton" model of the T.S. reproduces quite well the experimental solvent D_2O isotope effect in the 85% D_3PO_4/D_2O medium but only in the narrow temperature interval investigated. Below 50°C and especially in the (0–25°) temperature interval the extrapolated $(k(H_2O)/k(D_2O))_{exp.}$ values diverge greatly from the corresponding values calculated using the simple "free proton" model of the T.S., but they are comparable with solvent deuterium isotope effect for hydration of phenylpropiolic acids, $XC_6H_4C{\equiv}CCOOH$, [22,23], in moderately concentrated H_2SO_4/D_2SO_4 extrapolated to 50% H_2SO_4 from 53–75.6 wt % H_2SO_4, found to be equal:

$$(k(H_2SO_4)/k(D_2SO_4)_{50\%} = 3.73 \text{ (for X = p-Me)},$$
$$4.06 \text{ (for X = H)},$$
$$3.75 \text{ (for X = p-Cl)}.$$

They were rationalized also as resulting from the rate-limiting protonation of the α-carbon of the acetylenic acid:

$$PhC{\equiv}C\text{-}COOH + H^+ \rightarrow PhC^+{=}CHCOOH \qquad (10)$$

The rate of the acid-catalyzed hydration of phenylacetylene (measured spectrophotometrically) is smaller in deuteriosulfuric acid media, k(H_2O)/k(D_2O) being about 2 [24]. Similarly the solvent D_2O isotope effect, equal about 2 in 60% sulfuric acid and about 4 in 80% sulfuric acid, has been used also to support the conclusion that the rate limiting step for the hydration of acetylenic ketone, phenylbenzoylacetylene, to dibenzoylmethane involves a proton transfer from acidic medium to carbon (11) [25].



$$\mathrm{PhC{\equiv}C\text{-}\underset{\displaystyle O}{\underset{\|}{C}}Ph + H^{+} \rightarrow PhC^{+}{=}CH\underset{\displaystyle O}{\underset{\|}{C}}Ph \xrightarrow{H_2O} Ph\underset{\displaystyle O}{\underset{\|}{C}}CH_2\underset{\displaystyle O}{\underset{\|}{C}}Ph} \qquad (11)$$

The more detailed quantitative interpretation of the ^{13}C decarboxylation KIE and solvent D_2O hydration KIE in the reactions of phenylpropiolic acid in deuteriophosphoric and deuteriosulfuric acid media require to extend the actual deuterium solvent D_2O and ^{13}C KIE studies for decarboxylation of benzoylacetic acid to wider concentration ranges of phosphoric and sulfuric acid media, at least as it has been done in the case of ^{13}C KIE studies of decarboxylation of PPA in phosphoric acid media. Interpretation of solvent D_2O isotope effects in deuteriosulfuric acids, for which the K_h/K_d ratio is close to 1 [8], is simpler than in deuteriophosphoric acids media. The interaction between H_3O^+ (and D_3O^+ respectively) and the investigated substrates in solution need to be considered only (that is the transfer of D^+ from D_3O^+ to π-complex and from π-complex to "C–D" bond). The $k_{(RCOOH)}/k_{(RCOOD)}$ isotope effects in the decarboxylation of substituted benzoylacetic acids in benzene at 50°C were found to depend largely on substituents in accord with a cyclic proton transfer mechanism [26]. The k(H)/k(D) equal: 2.8 (for Z = *m*-nitro), 1.7 (for *p*-chloro), 1.4 (for unsubstituted), and 0.85 (for *p*-methyl) reflect the variations in the bonding of hydrogen in the T.S. [26]. There are no ^{13}C KIEs data for the above system, needed for a full clarification of the problem. More pertinent to our study are deuterium isotope effects in the decarboxylation of benzoylacetic acid determined in 62.33–71.71 wt% sulfuric acid media, $ArCOCD_2COOD$ in D_2O-D_2SO_4, [27]. The combined medium, D_2O, and secondary isotope effects from CD_2 moiety were of 0.98 (for 68.64 wt% D_2SO_4) and 1.15 (for 71.71 wt% D_2SO_4).

Determinations of solvent D_2O isotope effects, measured usually spectrophotometrically in two related series of experiments, are less precise than ^{13}C KIEs determined using the contemporary isotope ratio MS. Nevertheless, if determined simultaneously with ^{13}C KIEs in a given competitive experiment, they permit to obtain the unambiguous information about the reaction rate determining step and to locate properly the positions of H/D in transition state, rather difficult to establish by heavy atom isotope effect determinations alone. Our introductory D_2O solvent I.E. determination confirmed the correct conclusion drawn from ^{13}C KIE study that the C–C bond cleavage is not the decarboxylation r.d.s. in the decarboxylation of phenylpropiolic acid in 85% orthophosphoric acid and showed that protonation of the triple bond of PPA is the crucial step in the carbon dioxide production.

Foot note to pages 216–217 supporting the conclusion concerning the preferential concentration of deuterium in organic carbocation:

Ruff and Csizmadia [16] presented in chapter 8 of their monograph the selected by them set of vibrational frequencies for H_2O/D_2O, H_3O^+/D_3O^+ for water vapors and for conjugate acids, $(R_2)O^+\text{-}H/(R_2)O^+\text{-}D$, (in which hydrogen is bonded to oxygen), to reproduce the average experimental value $(K_b^D/K_b^H)_{exp}$ of 3 [12a] corresponding to protonation equilibrium of a base (B) in water (H_2O) and in heavy water (D_2O) (Eq. 5a and 5b):

$$H_3O^+ + B \overset{K_b^H}{\Leftrightarrow} B\text{-}H^+ + H_2O \tag{5a}$$

$$D_3O^+ + B \overset{K_b^D}{\Leftrightarrow} B\text{-}D^+ + D_2O \tag{5b}$$

For $(H_2O)/(D_2O)$ they took the $\nu(OL)$ and $\delta(OL)$ values of the stretching and of the deformation vibrations to be equal: (3760 cm^{-1}/2786 cm^{-1})(1), (3650/2667)(1) and (1595/1178)(1) respectively. For $(H_3O^+)/(D_3O^+)$ species the $\nu(OL)$ and $\delta(OL)$ frequencies were taken by them to be: (3235/2445)(2), (2590/2000)(1) and (1700/1255)(2), (1150/785)(1) respectively. To obtain the agreement between the calculated and the average experimental value of (K_b^D/K_b^H), both of 3.0, they used not the deformation frequencies (1060/785) = 1.350 [28,29] for (H_3O^+/D_3O^+) but the higher values (1150 cm^{-1}/785 cm^{-1}) = 1.465 > 1.4142 = $(2)^{1/2}$. Inserting their wave numbers into the equation expressing the ZPV energy approximation for (K_b^D/K_b^H), one obtains a value 3.03 at 298.16°K. This coincident of theory and experiment cannot be considered as the complete solution of the problem of the certain class of the deuterium solvent isotope effects, reviewed in the past by K.B. Wiberg [12a]. The mean value of the first fifteen $k(D_2O)/k(H_2O)$ entries, expressing the effect of solvent deuterium on the rate of acid- and base-catalyzed reactions equals 3.004±2.389, but two entries included into the averaging procedure, equal 4.0–7.0 in the case of the oxidation of bromide by iodate and about 10 in the oxidation of iodide by iodate deviate from the mean value by more than $2(\sigma_n = \pm 2.31)$. The mean value of the left 13 entries equals 2.149 ±0.692, commonly found in the specific acid catalysis, which enhances rates in D_2O and quite close to the calculational result presented, using the set of vibrational frequencies given in the main text. If to consider all vibrational modes in the course of calculation of (K_h/K_d) for equilibrium process (5) by taking the stretching modes as given on pages 6–7 of the main text and the values of deformation vibrations in H_3O^+/D_3O^+, in $(C^+)H/D$, and in H_2O as given in the above footnote to page 7, then the approximate values of the (K_h/K_d) listed in the text increase by about 6.7–5.5% and are equal: 0.573 $(1.745)^{-1}$/at 25°C; 0.599 $(1.669)^{-1}$/at 50°; and 0.642 $(1.558)^{-1}$/at 100°C. For comparative purposes the (K_b^D/K_b^H) values for equilibria between D_3O^+ and "conjugate acids" $(R_2O^+)^{H/D}$ and $(C^+)^{H/D}$ are calculated below for temperature interval 298.16–373.16 K using gas phase frequencies but taking (1060 cm^{-1}/785 cm^{-1}) = 1.350 [28,29].

Temp. K (℃)	$(K_b^D/K_b^H)^{a)}$	
	for $(R_2O^+)^{H/D}$	for $(C^+)^{H/D}$
298.16 (25°C)	3.4977	3.2436
323.16 (50)	3.1534	2.9350
333.16 (60)	3.0386	2.8318
343.16 (70)	2.9343	2.7380
353.16 (80)	2.8392	2.6523
373.16 (100)	2.6723	2.5018

[a)] calculated considering all vibrational frequencies and full expression for the deuterium isotope equilibrium constant [17,18].

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