

Hydrogen Isotope Fractionation between HCl_2^- Ion and HCl

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Hydrogen isotope fractionation between hydrogen dichloride ion in the condensed phase and gaseous hydrogen chloride has been studied both theoretically and experimentally. Quite good agreement between the experimental tritium fractionation factor and that theoretically calculated for two sets of vibrational data was found. Theoretical calculations of the fractionation factors of both deuterium and tritium over the large temperature range of 100–2000 K revealed some anomalies (minima and crossover points) in their temperature dependences. The relative tritium-deuterium isotope effect has also been discussed within the framework of the presently accepted statistical-thermodynamic theory in the harmonic approximation and recent works by Stern et al.

Introduction

Recently, the exchange of tritium between pyridine hydrochloride (PyHCl) and hydrogen chloride has been studied^{1,2}. It has been proposed that the exchange reaction occurs in two ways, one of which is the isotope exchange of tritium between hydrogen dichloride ion (HCl_2^-) in liquid phase and gaseous hydrogen chloride (the former appears in the system studied as a result of the reaction of PyHCl with HCl).

The occurrence of the HCl_2^- – HCl system presents a great opportunity for the determination of the experimental fractionation factor of tritium between HCl_2^- and HCl . It should be noticed that direct study of isotope fractionation in the system mentioned is extremely difficult, if at all possible because of the low stability of hydrogen dichloride ions. Furthermore, cations usually obscure the exchange of tritium in HCl_2^- . Since hydrogen dihalide ions play an important role in the hydrogen bond theory, it seems useful to determine the fractionation factor in question. As the suitable vibrational data are available, theoretical calculations of isotope effects on equilibria in the system mentioned are also possible.

Thus, the paper presents both the experimental and theoretical results concerning the fractionation of hydrogen isotopes between hydrogen dichloride ion in the condensed phase and gaseous hydrogen chloride.

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Method and Calculations

A) Experimental Fractionation Factor

Usually the isotope fractionation factor between two phases is defined as follows:

$$\alpha = \frac{N_1}{1 - N_1} \bigg/ \frac{N_2}{1 - N_2} \quad (1)$$

where N_1 , N_2 are atom fractions at equilibrium of exchangeable labelled atom in the condensed and in the gas phase, respectively. In this work, as $N_1 \ll 1$, $N_2 \ll 1$, α may be approximated as:

$$\alpha = N_1/N_2. \quad (2)$$

Since the radioactive isotope of hydrogen, tritium, was used, atom fractions N_1 , N_2 may be replaced by the specific activities $A_\infty(c)$, $A_\infty(g)$ of the condensed and gas phase, respectively³:

$$\alpha = [A_\infty(c)/A_\infty(g)]. \quad (3)$$

The specific activities of tritium in the condensed phase, $A_\infty(c)$, have not been directly determined. Instead, from the material balance, $A_\infty(c)$ can always be expressed in terms of the initial and equilibrium specific activities of tritium in the gas phase. From the fact that at the beginning of the process the entire activity is in the gas phase and that some measurable amount of gaseous hydrogen chloride dissolves in the condensed phase² the following equation results:

$$A_\infty(c) = \frac{A_0(g)m - (m-s)A_\infty(g)}{n+s} \quad (4)$$

Combining Eq. (3) and (4) one can obtain:

$$\alpha = \frac{m}{n+s} \frac{A_0(g)}{A_\infty(g)} - \frac{m-s}{n+s} \quad (5)$$



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where:

m is the amount of labelled hydrogen chloride used in experiment,

n is the amount of the condensed phase,

s denotes the amount of dissolved hydrogen chloride,

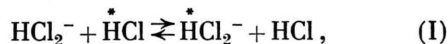
$A_0(\text{g})$ and $A_\infty(\text{g})$ refer to the initial and equilibrium activities of the gas phase, respectively.

The experiments do not directly provide the data concerning the equilibrium activities of the gas phase for the reaction:



But it seems to be very likely that the experimental data previously presented^{1,2} are quite sufficient to determine suitable values, and hence to calculate the fractionation factor according to Equation (5).

As was noted above, the reaction studied had been suggested to proceed along two different paths — namely:



The reaction (I) is considered to be fast and the reaction (II) is very slow (Figure 1). These conclusions have been drawn on the basis of the detailed analysis of the experimental kinetic data.

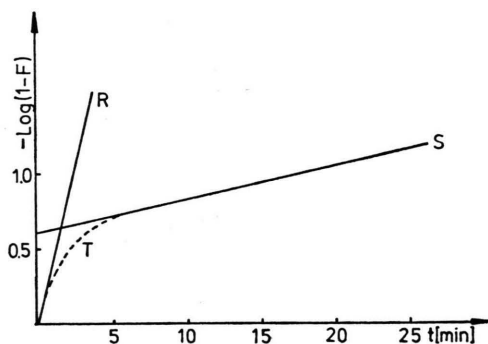


Fig. 1. Kinetics of tritium exchange between pyridine hydrochloride and hydrogen chloride. R — rapid process, corresponding to the exchange between HCl_2^- and HCl ; S — slow process, corresponding to the exchange in pyridinium species; T — resultant process.

It may be assumed that the total activity of the gaseous phase at any time t is the sum of two components:

$$A_t = A_t(\text{R}) + A_t(\text{S}) \quad (6)$$

the first corresponding to the rapid exchange process and the second — to the slow one. Hence the total exchange fraction:

$$F = (A_0 - A_t) / (A_0 - A_\infty) \quad (7)$$

is also the sum of two components:

$$F = F(\text{R}) + F(\text{S}). \quad (8)$$

For sufficiently large t $A_t(\text{R}) \approx 0$ and the second, slow process can be easily determined. Graphical analysis shown in Figure 1 enables one to determine the first rapid process, and further simple calculations based on Eq. (7) and (8) lead to $A_\infty(\text{R})$ value, which is the activity of the gas phase in the equilibrium for the rapid process. This value is necessary to evaluate the tritium isotope effect on equilibrium. Other required data can be found elsewhere². In all experiments m and n were practically the same, and s was also practically constant over the temperature range studied. Using the data presented in the earlier works, the following equation results:

$$\alpha = 0.60[A_0(\text{g})/A_\infty(\text{g})] - 0.20. \quad (9)$$

Using this equation, the experimental fractionation factor of tritium between hydrogen dichloride ion and hydrogen chloride can be easily calculated. In Table I the results obtained are listed.

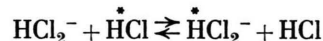
Table I. Experimental data and experimental fractionation factor.

Temperature °K	Specific activities ^a		Experimental fractionation factor α
	initial A_0	equilibrium A_∞	
313	33.6	17.9	0.93 ± 0.02
323	33.6	18.8	0.90 ± 0.02
333	26.4	15.2	0.85 ± 0.06
343	33.6	19.7	0.83 ± 0.08

^a Specific activities are given in arbitrary units.

B) Theoretical Fractionation Factor

For the exchange reaction:



the fractionation factor α is defined by:

$$\alpha = \{[\dot{\text{H}}]/[\text{H}]\}_{\text{HCl}_2^-} / \{[\dot{\text{H}}]/[\text{H}]\}_{\text{HCl}} \quad (10)$$

and can be expressed in terms of reduced partition function ratio:

$$\alpha = (s_2/s_1 f)_{\text{HCl}_2^-} / (s_2/s_1 f)_{\text{HCl}}. \quad (11)$$

The "exact" equation for isotopic reduced partition function ratio $s_2/s_1 f$ in the harmonic approximation, neglecting effects owing the quantum-mechanical rotation, is ^{4, 5}:

$$s_2/s_1 f = \prod_i \frac{u_{2i}}{u_{1i}} \times \exp \left(\sum_i \frac{u_{1i} - u_{2i}}{2} \right) \times \prod_i \frac{1 - \exp(-u_{1i})}{1 - \exp(-u_{2i})} \quad (12)$$

where:

$u = h \nu / k T$, ν – normal-mode vibrational frequency, k, h, T have their usual meaning, s – symmetry number and the subscripts 1 and 2 refer to the light and heavy isotopic species, respectively. The products and sums are taken over all normal mode vibrational frequencies of the molecule.

Hydrogen dichloride ion is the second member of the hydrogen dihalide ions series. Unfortunately its molecular properties are much less known than those of hydrogen difluoride ion. In earlier studies on the basis of residual entropy arguments ⁶ and from the similarity of its infrared spectrum to that of hydrogen difluoride ion ⁷, the same structure as that of HF_2^- (that is – linear centrosymmetric) has also been proposed for HCl_2^- ions.

In the recent years new vibrational data have been reported, especially those of Evans and Lo ⁸ and those of Nibler and Pimentel ⁹. Evans and Lo were able to postulate two kinds of HCl_2^- ions, both presumed to be linear. Type I was considered to be unsymmetrical and type II was proposed to possess a centrally located proton. Nibler and Pimentel ⁹ confirm, at least partially, the above conclusions but they also suggest a second possible structure – nonlinear symmetrical one. As a result of these studies, several different sets of vibrational data corresponding to hydrogen dichloride ions are obtained. They are listed in Table II (Column 2).

Under the given experimental conditions (temperature range is 313–343 K) pyridinium hydrogen dichloride salt is found to be liquid ¹. Because of the lack of vibrational data for liquid one must use the solution and/or solid-phase spectra. The use of solution-phase vibrational data seems to be more appropriate because they appear to be almost independent upon the nature of the cation (contrary to the solid-phase spectra). Nevertheless, as the measurable frequency shifts between solution and solid-phase spectra corresponding to the unsym-

Table II. Representative vibrational data of hydrogen dichloride ion (frequencies in cm^{-1}). The frequencies are given in order: ν_1, ν_2, ν_3 for all sets. ν_2 is doubly degenerate frequency. Geometry used in calculations from Nibler and Pimentel ⁹.

Type of anion	HCl_2^- obs.	DCl_2^- obs.	DCl_2^- calc.	TCl_2^-	Ref.
<i>Solution</i>					
A) Symmetrical anion	$\begin{Bmatrix} 240 \\ 1050 \\ 805 \end{Bmatrix}$	$\begin{Bmatrix} ? \\ 750 \\ 565 \end{Bmatrix}$	$\begin{Bmatrix} 240 \\ 749 \\ 573 \end{Bmatrix}$	$\begin{Bmatrix} 240 \\ 614 \\ 471 \end{Bmatrix}$	8
B) Unsymmetrical anion	$\begin{Bmatrix} 240 \\ 1100 \\ 1600 \end{Bmatrix}$	$\begin{Bmatrix} 225 \\ 780 \\ 1170 \end{Bmatrix}$	$\begin{Bmatrix} 241 \\ 782 \\ 1148 \end{Bmatrix}$	$\begin{Bmatrix} 242 \\ 654 \\ 970 \end{Bmatrix}$	8
<i>Solid</i>					
A') Symmetrical anion	$\begin{Bmatrix} 240 \\ 1050 \\ 810 \end{Bmatrix}$	$\begin{Bmatrix} ? \\ 750 \\ 590 \end{Bmatrix}$	$\begin{Bmatrix} 240 \\ 749 \\ 578 \end{Bmatrix}$	$\begin{Bmatrix} 240 \\ 614 \\ 473 \end{Bmatrix}$	8
B') Unsymmetrical anion	$\begin{Bmatrix} 210 \\ 1185 \\ 1575 \end{Bmatrix}$	$\begin{Bmatrix} 200 \\ 880 \\ 1180 \end{Bmatrix}$	$\begin{Bmatrix} 211 \\ 851 \\ 1120 \end{Bmatrix}$	$\begin{Bmatrix} 211 \\ 705 \\ 919 \end{Bmatrix}$	7, 8

metrical species exist, set B' must be also taken into account.

Thus three different sets of the vibrational data, denoted as A, B and B', will be used in the following calculations. In order to calculate the reduced partition function ratio we must know all normal-mode vibrational frequencies for both isotopic species. The linear triatomic molecule, HCl_2^- , should have three vibrational frequencies: ν_1 , Cl–Cl stretching motion (H centrally located); ν_2 , doubly degenerate bending motion and ν_3 , the hydrogen stretching motion. The vibrational frequencies of HCl_2^- are known, they are presented in Table II (Column 2). Unfortunately, there are no vibrational data for tritiated (TCl_2^-) molecule. However, these data may be easily calculated using the Wilson FG method ¹⁰ with an isotope – independent F matrix. General valence force field calculations ¹¹ were carried out for both symmetrical and unsymmetrical hydrogen dichloride ion. Valence force constants obtained were used to compute the frequencies of isotopic HCl_2^- molecules.

Table II shows the results of the calculations in comparison with the observed spectrum. Since the force constants were adjusted to fit the observed frequencies of HCl_2^- , only the comparison of the observed and calculated values of DCl_2^- serves as a test for the correct choice of the force field. In view of the limited accuracy of both the observations (very broad bands) and calculations (the use of the

observed instead of zero-order frequencies) the agreement between theoretical and experimental values seems to be satisfactory. Only the agreement of the values corresponding to the frequency of unsymmetric hydrogen stretching mode ν_3 is a little poorer, especially for the unsymmetrical species in the solid phase. This is likely due to anharmonicity which is expected to be large^{8,9,11} but there was no way to properly assess anharmonic corrections.

However, on account of rather large uncertainties in the observed frequencies, the use of the calculated frequencies based on a common force field seems to be a better approach because this procedure minimizes the error in isotopic partition function.

The contribution of external vibration frequencies to the isotopic reduced partition function ratio cannot be directly calculated because of lack of data but it is expected to be very small. This expectation results from the following considerations. The highest lattice frequency is found⁸ near 100 cm^{-1} . Thus all external frequencies are very small and their contribution to the partition function ratio will be in the form of a first order quantum correction:

$$\ln f_{\text{ext.}} = \frac{1}{24} \left(\frac{h}{kT} \right)^2 \sum_i^6 (\nu_{1i}^2 - \nu_{2i}^2). \quad (13)$$

Assuming that the rotational frequencies are dependent on the reciprocal square root of the moments of inertia and the translational frequencies are dependent on the reciprocal square root of the molecular mass one can obtain:

$$\ln f_{\text{ext.}} = \frac{1}{24} \left(\frac{h}{kT} \right)^2 \left\{ \sum^3 \nu_{\text{rot.}}^2 \left(1 - \frac{I_1}{I_2} \right) + \sum^3 \nu_{\text{tr.}}^2 \left(1 - \frac{M_1}{M_2} \right) \right\}. \quad (14)$$

Using the highest observed external frequency (this is the only lattice frequency observed in spectrum⁸), the upper limit of the contribution of the external frequencies can be estimated. This rather crude approximation gives at 100 K $\ln f_{\text{ext.}} < 9 \times 10^{-3}$ which is very small value in comparison with $\ln f_{\text{int.}} = 5.08$.

The partition function ratio of HCl is also calculated in harmonic approximation², though there is possibility to make corrections for anharmonicity. However, it is known¹² that the neglect of anharmonicity corrections for both molecular species in an exchange reaction appears to be a better approximation than to include them for only one species.

Results and Discussion

Calculated fractionation factors of tritium for $\text{HCl}_2^- - \text{HCl}$ system are compared with the experimental results on tritium isotope exchange in Table III. As can be seen, only two sets are fairly consistent with the experimental results but the better agreement is observed for the set B than for the set B'.

Table III. Comparison of the experimental and theoretical tritium isotope effects for $\text{HCl}_2^- - \text{HCl}$ system.

Temperature °K	Experimental fractionation factor $\alpha_{\text{exp.}}$	Theoretical fractionation factor $\alpha_{\text{theoret.}}$		
		set A	set B	set B'
313	0.93	0.445	0.944	0.995
323	0.90	0.451	0.931	0.975
333	0.85	0.455	0.911	0.955
343	0.83	0.457	0.898	0.936

The results obtained suggest that in this particular case, i. e. in pyridinium hydrogen dichloride molecule, hydrogen dichloride ion is noncentrosymmetric species of $C_{\infty v}$ symmetry, and can be described as an anion to type I according to the classification of Evans and Lo⁸. Moreover, hydrogen dichloride ions of such a symmetry are expected to possess much weaker hydrogen bond than symmetrical ones^{8,9}. The latter conclusion seems to be in a good agreement with the results obtained previously in the kinetic studies¹.

As can be seen, the direction of changes of the fractionation factors corresponding to the sets B and B' with temperature is rather unexpected. Therefore it seemed very interesting to calculate the fractionation factor over larger temperature range for both tritium and deuterium. Such calculations were carried out over the temperature range of $100 - 2000\text{ K}$. The theoretical curves obtained are presented in Figure 2.

It is seen that the fractionation factor is rather a complicated function of the temperature. However, in a general way it can be described by the equation:

$$\ln = a + b/T + c/T^2 \quad (15)$$

where a, b, c are constants. The least squares treatment gives approximate values of these constants. They are listed in Table IV.

It is seen in Fig. 2 that the differences between the fractionation factor corresponding to the sets B and B' disappear at higher temperatures. Thus, the

curves of the fractionation factor temperature dependence of deuterium mix at the neighborhood of 400 K and those of tritium in the neighborhood of 500 K. Moreover, the theoretical curves presented in Fig. 2 revealed some interesting features. Both H/D and H/T fractionation factors corresponding to the sets B and B' of the vibrational data exhibit minima. They are placed in the range of 500–600 K. Furthermore these fractionation factors exhibit crossover points. They are placed at 270 K and 280 K for set B, and at 290 K and 305 K for set B', for H/D and H/T fractionation factors, respectively.

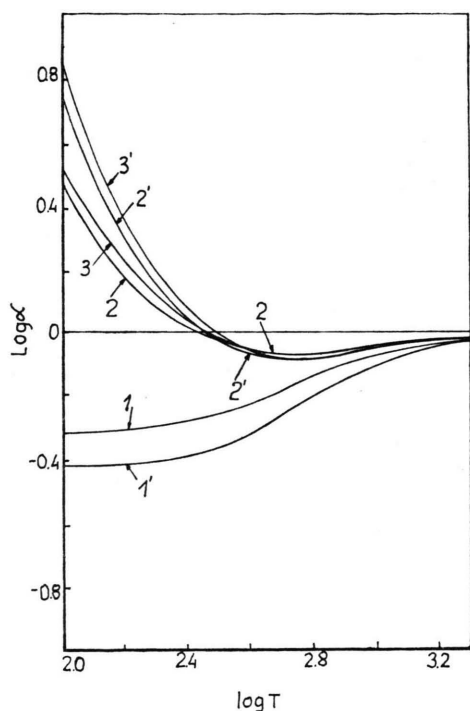


Fig. 2. Temperature dependences of deuterium and tritium isotope effects in the exchange of hydrogen isotopes between HCl_2^- and HCl . Theoretical curves correspond to the following sets of the vibrational data: Deuterium — 1 — set A; 2 — set B; 3 — set B'; Tritium — 1' — set A; 2' — set B; 3' — set B'.

Table IV. Numerical values of parameters a , b , c [Equation (15)].

No. of curve	a	b	c
1	-0.0369	-208.5	14358
1'	-0.0269	-305.8	21827
2	-0.1688	-4.947	12270
2'	-0.1958	-32.79	18586
3	-0.1325	-39.67	9937
3'	-0.2299	-13.52	17467

The fractionation factor corresponding to the set A of the vibrational data does not exhibit any temperature anomalies.

Direct comparison of the tritium and deuterium fractionation factors reveals other interesting features. Thus, it is seen that temperature dependence of the fractionation factors corresponding to the set A is approximately what it was expected. For the sets B and B' at the range of low temperatures regular temperature dependences are observed. After having passed the crossover points $\ln \alpha$'s proceed to their minima and then to their high temperature limits which are expected to be equal to zero ($\ln \alpha = 0$ — no isotope effect). However, the ratios, r , of the fractionation factors of H–D and H–T exchange are not exactly what they were expected. According to the Bigeleisen's treatment¹³ the relative fractionation factors of tritium and deuterium, r , should be placed in the range of 1.33–1.55. However, in this particular case the value of r is beyond the limits mentioned above. For example, in the case of B r is equal to 1.55 at 100 K, 1.97 at 250 K and 1.20 at 1000 K.

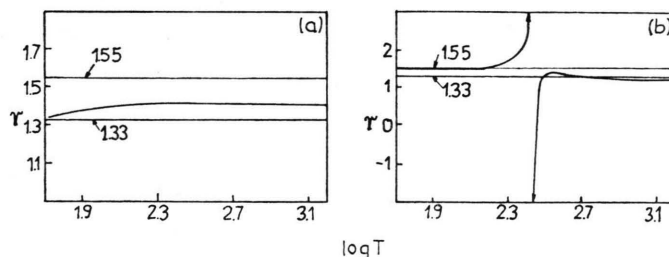


Fig. 3. Relative tritium-deuterium equilibrium isotope effects in hydrogen isotope exchange reaction between HCl_2^- and HCl . (a) refers to the set A, (b) to the set B.

It should be pointed out that in the case of the set A the relative isotope effect of tritium and deuterium appears to be completely in the range of 1.33–1.55.

All these findings are summarized in Figure 3. It is seen that in the case, when isotope effect temperature dependence is quite regular (data corresponding to the set A) then r vs. $\log T$ curve is confined to 1.33–1.55 range exhibiting relatively little structure (see Figure 3 a). In Fig. 3 b the temperature dependence of the relative T–D fractionation factor for the set B is shown (similar dependence is expected for the set B'). Such a dependence is due to the fact that both temperature dependences of tritium and deuterium isotope effects exhibit some

anomalies. Taking this fact into account, the relative T – D fractionation factor vs. $\log T$ behaviour seems to be exactly what one would expect from previous works by Stern et al.^{14, 15}. Thus, when $\ln \alpha$ exhibits crossovers, the resulting r vs. $\log T$ plot exhibits a pole with the value of r outside the 1.33 – 1.55 range.

In conclusion it should be noted that some error can be involved in the calculation of the fractionation factor. They arise mainly from the un-

certainities in the frequencies used to evaluate the partition function ratios. However, it seems that the general picture presented above is true.

Acknowledgement

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- ¹ J. Szydłowski and M. Zieliński, *Roczniki Chemii* **47**, 123 [1973].
- ² J. Szydłowski, Ph. D. Thesis, Warsaw University, Warsaw 1971.
- ³ J. Szydłowski and M. Zieliński, *Radiochem. Radioanal. Letters* **8**, 291 [1971].
- ⁴ J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.* **15**, 261 [1947].
- ⁵ H. C. Urey, *J. Chem. Soc.* **1947**, 562.
- ⁶ S. Chang and E. F. Westrum, *J. Chem. Phys.* **36**, 257 [1962].
- ⁷ T. C. Waddington, *J. Chem. Soc.* **1958**, 1708.
- ⁸ J. C. Evans and G. Y.-S. Lo, *J. Phys. Chem.* **70**, 11 [1966].
- ⁹ J. W. Nibler and G. C. Pimentel, *J. Chem. Phys.* **47**, 710 [1967].
- ¹⁰ E. B. Wilson, Jr., J. C. Decius, and P. L. Cross, *Molecular Vibrations*, McGraw-Hill, New York 1955.
- ¹¹ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, D. Van Nostrand Co., Inc., New York 1945.
- ¹² R. E. Weston, Jr., *Z. Naturforsch.* **28 a**, 177 [1973].
- ¹³ J. Bigeleisen, *Tritium in the Physical and Biological Sciences Vol. 1*, IAEA, Vienna 1962, p. 161.
- ¹⁴ M. J. Stern, W. Spindel, and E. U. Monse, *J. Chem. Phys.* **48**, 2908 [1968].
- ¹⁵ M. J. Stern and P. C. Vogel, *J. Amer. Chem. Soc.* **93**, 4664 [1971].