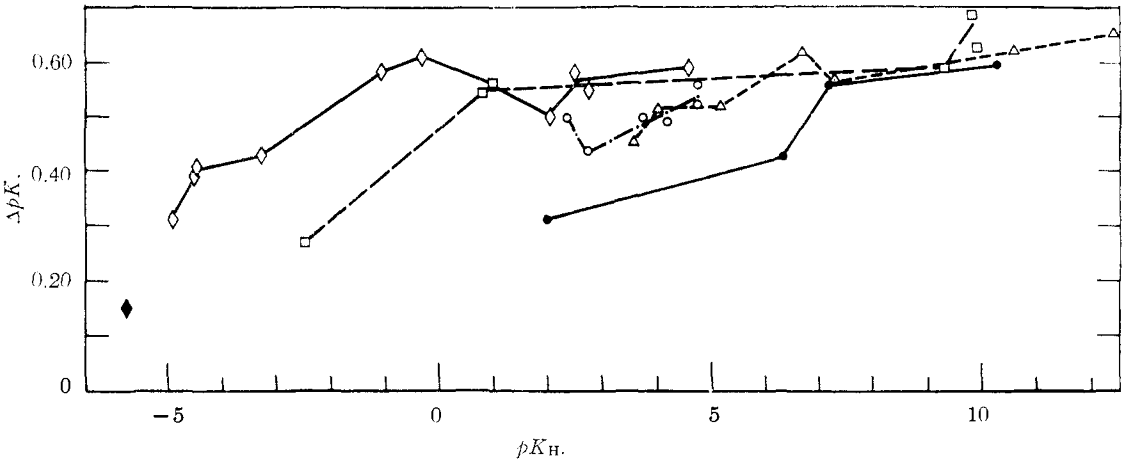

Fig. 6.—Δ*pK* as a function of acid strength: ◇, substituted anilines; □, amines; ◆, ketones; △, phenols and alcohols (data of D. C. Martin and J. A. V. Butler (*J. Chem. Soc.*, 1366 (1939), and P. Ballinger and F. A. Long, THIS JOURNAL, 81, 1050, 2347 (1959).); ○, carboxylic acids; ●, $MO_x(OH)_y$.

$H_2CO_3$, is abnormally low. This is due to the fact that an appreciable contribution to the acidity of carbonic acid comes from dissolved $CO_2$. Our point for *p*-nitrodiphenylamine appears to be somewhat low. The experimental uncertainty in Δ*pK* is large for this indicator and no conclusions can be drawn at present for Δ*pK* for amines with *pK* values less than zero.

In solutions concentrated in sulfuric acid, medium effects on Δ*pK* are to be expected. These arise in part from the correction necessary to equation 8 from the relative fugacities of $H_2O$ and $D_2O$ in $H_2SO_4$ and $D_2SO_3$, respectively. Furthermore reactions of the type

$$BH^+ + H_2SO_4 = B(H_2SO_4) + H_3SO_4^+ \quad (16)$$

become of importance. Even in the approximations used in equation 8 we would find

$$\Delta pK = \log f_{BD^+} + \log f_{D_2SO_4} - \log f_{D_3SO_4^+} \quad (17)$$

These effects may be responsible for the drop in Δ*pK* for the substituted anilines with negative *pK* values.

NOTE ADDED IN PROOF.—Bascombe and Bell (*J. Chem. Soc.*, 1096 (1959)) have recently reported measurements of *pK* ($H_2O$ solutions) for some of the indicators studied by us. Their measurements include solutions of $H_2SO_4$ among a number of different acids. Wherever comparisons can be made, our values of *pK* and $H_0$ are in agreement with those of Bascombe and Bell. For the indicator *p*-nitrodiphenylamine they find a medium and wave length effect on *pK* and $H_0$. From three different assumptions, *pK* and $H_0$ are calculated from measurements at 4100 Å. $H_0$ is less sensitive to the nature of the assumption than *pK*. Our values of *pK*, $H_0$, and $D_0$ were obtained from measurements at 4100 Å. The medium effects observed by Bascombe and Bell for this indicator probably explain the fact that our value of Δ*pK* for this indicator is anomalously low.

UPTON, N. Y.

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

# Ion Pairs. I. Isotope Effects Shown by Chloride Solutions in Glacial Acetic Acid[1]

BY REED A. HOWALD[2]

RECEIVED JUNE 25, 1959

Appreciable isotopic separation has been obtained in countercurrent columns using the distribution of chlorine between HCl gas and solutions of inorganic chlorides in glacial acetic acid. The isotope effects[3] *vs.* Cl atoms, calculated from the observed enrichments for various species present in the solutions are: HCl (dissolved), 1.0050 ± 0.0002; $HgCl_2$, 1.0061 ± 0.0009; $HCl·H_2O$, 1.0039 ± 0.0003; $SrCl_2$, 1.0042 ± 0.0003; LiCl, 1.0040 ± 0.0003. These results are consistent with a picture involving strong Hg–Cl bonds, but much "looser" interaction between the metal and chlorine atoms in the ion pairs from LiCl and $SrCl_2$.

## Introduction

This is the first in a series of papers describing experiments designed to provide a more detailed understanding of the nature of ion pairs in solvents of low dielectric constant. Most previous investigations have been concerned primarily with the dissociation constants of ion pairs. Data on at least three other general aspects of ion pairs should also be available to complete the picture: 1, average vibration frequencies and the stiffness of the bonding present, 2, the lability of various ion pairs as measured by rates of isotopic exchange, and 3, the effects of other salts on the activity coefficients of ion pairs. Such information should prove useful in interpreting kinetic data for organic reactions which apparently involve intermediates with con-

[1] This work was supported by the William F. Milton Fund of Harvard University. It was presented at the September 1958 American Chemical Society meeting in Chicago.

[2] Chemistry Department, Oberlin College, Oberlin, Ohio.

[3] The isotope effect for a given species is the equilibrium constant, corrected for symmetry, for the isotopic exchange reaction with free atoms. It is numerically equal to the $Cl^{37}/Cl^{35}$ ratio which would be present in the species in equilibrium with equal concentrations of free gaseous $Cl^{37}$ and $Cl^{35}$ atoms.

siderable charge separation such as carbonium ions. This paper presents some data bearing on points 1 and 2 above for various inorganic chlorides in glacial acetic acid obtained by the use of countercurrent columns adapted to the separation of chlorine isotopes. Such countercurrent columns provide a means of measuring the small isotope effects shown by chlorine, which are in turn related to the average stiffness of the vibrations in which the chlorine atoms are involved. In addition such columns, which provide efficient contact between liquid and gas phases together with continuous separation, can yield fairly large lower limits for the rates of the rapid isotopic exchange reactions of ion pairs.

The shifts of vibration frequencies upon isotopic substitution have been widely studied both experimentally and theoretically,[4] principally to aid in the interpretation of complex spectra. Both exact expressions[5,6] and convenient approximate relations[6] are available for the resulting changes in partition functions. The isotope effect for a given species is by convention the equilibrium constant, corrected for symmetry, for an isotopic exchange reaction with free atoms such as

$$MCl^{35}{}_{n+1} + Cl^{37} = MCl_n{}^{35}\,Cl^{37} + Cl^{35}$$

which is given by the appropriate ratio of partition functions. Such corrected equilibrium constants are unity in the classical limit, so that it is only the deviations from classical behavior, and principally only the stiffest vibrations involving the isotopic atom, which contribute to the observed isotope effects. Isotope effects often are calculated from vibration frequencies observed spectroscopically, but where spectroscopic data are lacking, the reverse calculation can give some sort of average of the highest vibration frequencies involved. Direct spectroscopic observation of the vibration frequencies of ion pairs in solution will be very difficult and possibly impossible due to a combination of absorption by the solvent and broadening of the lines due to strong interactions with the solvent.

## Experimental

The principal part of the apparatus used was a 135 cm. column, 1 cm. in diameter, packed with $^1/_{16}$ inch glass helices. A stream of HCl gas was passed in at the bottom of this column while the chloride solution flowed down the column. At the top of this column was a device for sampling the gas phase, and above this a shorter column in which reflux was obtained by reaction of the HCl with an appropriate solution flowing in at the top of the column, usually a solution of an acetate in acetic acid.

This essentially simple apparatus was complicated by a number of less important but necessary additional features. A cartesian manostat was used to maintain a constant low pressure (usually about 210 mm.) thus reducing the solubility of HCl in the solutions. An indicator such as *p*-naphtholbenzein or cupric ion was added to the solutions so that the point of reflux could be observed and regulated (within a 25 cm. range near the bottom of the upper column). A slow adjustable leak out at the top of the column was necessary to compensate for air carried into the column with the solution and any other leaks at joints or stopcocks. A flowmeter and needle valve (glass and Teflon) were used to regulate the flow of solution (within ±10%). At the bottom of the column excess HCl bubbled out through a portion of the solution so that the HCl supply did not require precise regulation. The bottom of the column was also designed so that a measured portion of the solution could be isolated and removed for titration of the dissolved HCl with a solution of lithium acetate in glacial acetic acid.

Two HCl samples were taken from most runs, at least one of them long before the column had reached equilibrium so that the number of theoretical plates present could be calculated from the observed rate of approach to equilibrium. The samples were treated with dimethyl sulfate.[7] The methyl chloride produced was separated from unreacted HCl and analyzed in an isotope ratio mass spectrometer (Consolidated-Nier, model 21-201). A standard sample of methyl chloride was run along with each of the samples. The instrument gave directly the ratio of the mass 52 peak to the sum of peaks 53, 51, 50, 49, 48 and part of 47, from which, using the ratio given by the standard methyl chloride, the percentage decrease in the $Cl^{37}/Cl^{35}$ ratio was calculated. Thus a positive enrichment corresponds to a favoring of the heavy isotope in the solution compared to HCl gas.

The equations describing the approach of a countercurrent column to equilibrium have been derived by Cohen.[8] His equations need only slight modification to adapt them to the case of chlorine in which both isotopes are present in appreciable quantity. After the enrichment has reached about $^1/_3$ of the equilibrium value only one term of the Fourier expansion used in the solution is important, giving the simple solution

$$X_t = X_\infty(1 - Ae^{Bt})$$

where $X_t$ is the per cent. enrichment at time *t*, "*A*" depends only on the amount of holdup in the column above the point of sampling, and "*B*" is inversely proportional to the number of theoretical plates present. From the two values of *X* for each run it was possible to calculate both $X_\infty$ and "*B*" by successive approximations using Newton's method or from a table constructed for the case where one time was a factor of 3 longer than the other. Since the point of reflux varied during each run, the value of *A* is somewhat uncertain, and calculations were made for both 10 and 20% of the chlorine present above the point of sampling, giving values for "*A*" of 0.89 and 0.96, respectively. The results of the calculations are tabulated in terms of the H.E.T.P. (height equivalent theoretical plate, or column length per theoretical plate), and $\epsilon$, the deviation of the single stage fractionation factor from unity.

## Results

The type of data obtainable is shown in Fig. 1 which shows the results of a series of blank runs with no solutes other than HCl and $H_2O$ present. The observed enrichments are plotted against the square root of a normalized time, the normalization factor, $\theta$, being the holdup of the column divided by the flow rate. It is clear that water has a marked effect on the observed enrichments, even to changing the sign at concentrations above 1.5 *M*, at which point the solubility of HCl has increased to about twice its value in dry acetic acid. If all the increase in solubility is formally ascribed to the species $H_3OCl$, an essentially linear relation is obtained between the observed values of $\epsilon$ and the fraction of the dissolved HCl present as either HCl or $H_3OCl$ as shown in Fig. 2. The effect of small quantities of water, under 0.1 *M*, should be negligible, and since excess acetic anhydride used as a drying agent had a larger effect, most runs were made with small amounts of water present.

The results of calculations for the five blank runs with almost dry acetic acid are listed in part A of

---

[4] E. B. Wilson, Jr., J. C. Decius and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955.

[5] H. C. Urey, *J. Chem. Soc.*, 562 (1947).

[6] J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947).

[7] This is an adaptation of the procedure given by H. R. Owen and O. A. Schaeffer, THIS JOURNAL, **77**, 898 (1955). The conversion to methyl chloride was not quantitative, however, in agreement with the results of Owen and Schaeffer, any isotopic fractionation in the conversion was less than the limits of experimental error in the mass spectrometric determination, about ±0.2%.

[8] K. Cohen, "The Theory of Isotope Separation," National Nuclear Energy Series III-1B.

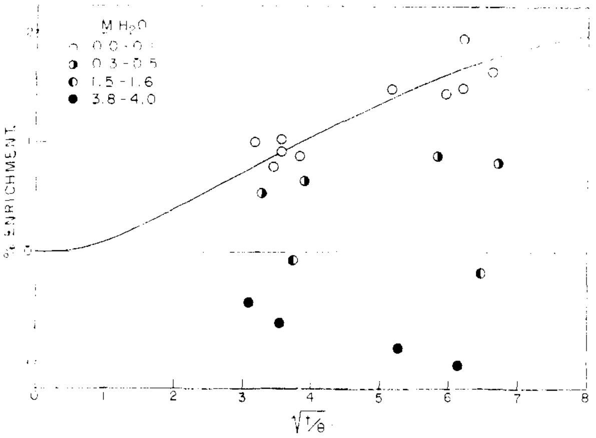

Fig. 1.—Observed isotopic enrichments in runs with HCl alone and with $HCl \cdot H_2O$ present *vs.* $\sqrt{t/\theta}$, where $t/\theta$ is a normalized time of operation of the column.

Table I. The average of the values for the isotope effect (dissolved HCl *vs.* HCl gas) is 1.00044, and a range of ±0.00016 includes the results of almost all the individual calculations. The solid curve in Fig. 1 calculated for $\epsilon = 0.00044$ and a value of 50 theoretical plates fits the experimental points quite well.

The runs with mercuric chloride present at a concentration of about 0.15 *M* listed in part C of Table I show ultimate enrichments comparable to the blank runs, but a somewhat faster approach to equilibrium. This indication of a larger isotope effect balanced by a decrease in the number of theoretical plates is borne out by the calculations which yield a value for $\epsilon$ of $0.00079 \pm 0.00025$. Dissolved HCl is still the principal species in these solutions, and a long extrapolation is necessary to obtain the value of $1.0015 \pm 0.0009$ for the isotope effect for $HgCl_2$. Converting to the usual standard of chlorine atoms instead of HCl gas gives the value of $1.0061 \pm 0.0009$. (The value of 1.0046 for the isotope effect of HCl gas calculated by Urey[6] was used for this conversion.) This is in satisfactory agreement with the value of 1.007 calculated for $HgCl_2$ gas from its known vibration frequencies.[9]

Both LiCl and $SrCl_2$ which are more soluble than $HgCl_2$ were studied over a wider range of concentration with the results listed in parts D and E of Table I. With both of these species, as with $H_3OCl$, the isotope effect is in the opposite direction from dissolved HCl, giving large cancellations and only small observed enrichments. The experimental error is too large a fraction of the observed enrichments to permit meaningful calculations of both the isotope effect and the number of theoretical plates from each single run as was done with the $HgCl_2$ data. Assuming a value of 25 theoretical plates leads to the values for $\epsilon$ shown in Fig. 2 which extrapolate to give isotope effects *vs.* chlorine atoms of 1.0040, 1.0042 and 1.0039 for LiCl, $SrCl_2$ and $H_3OCl$, respectively, with an uncertainty of ±0.0003 in each case. These extrapolated values are not very sensitive to the value used for the number of theoretical plates. The presence of a change in sign of the observed enrichments at concentrations corresponding to a fraction of HCl of about 0.5 to 0.6, which is clearly evident in all three cases, is sufficient to fix the intercept within the range of −0.0003 to −0.0010 for $\epsilon$ or 1.0043 to 1.0036 for the isotope effect *vs.* chlorine atoms. The smallest value for the number of theoretical plates which would still give a roughly linear dependence of $\epsilon$ on the fraction of the chlorine present as HCl is about 8. A value of less than 8 would lead to over 99% of the equilibrium enrichment in 60 minutes and so is also inconsistent with the observed further enrichments at longer times.

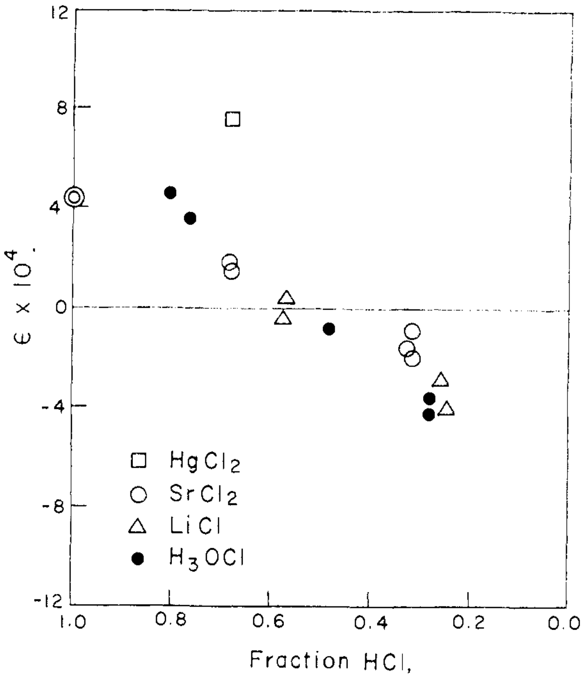

Fig. 2.—Plot of $\epsilon$ *vs.* the composition of the liquid phase. The observed single stage enrichment factors are equal to $1 + \epsilon$.

## Discussion

The $Cl^{37}/Cl^{35}$ isotope effect for the LiCl gaseous molecule can be calculated from the $LiCl^{35}$ vibration frequency,[10] giving the value 1.0035. The contribution of the LiCl bond to the isotope effect should be considerably decreased in a dielectric, and thus most of the observed value of 1.0040 for LiCl dissolved in glacial acetic acid must be ascribed to the vibrations involved in the solvation of the chloride ion. The increase in the isotope effect in going from HCl gas to dissolved HCl must also be due to solvation, and the isotope effect observed for $H_3OCl$ further demonstrates that O—H—Cl hydrogen bonds may make a sizable contribution. The numerical agreement of the values for LiCl, $SrCl_2$ and $H_3OCl$ may be coincidental, or it may be a valid indication that these species exist in glacial acetic acid solutions in a "solvent separated" form with the cation sufficiently distant that it is not importantly involved in the vibrations of the chloride ion. The presence of strong Hg–Cl bonds in acetic acid solutions of

---

(9) W. Klemperer and L. Lindeman, *J. Chem. Phys.*, **25**, 397 (1956).

(10) W. Klemperer and S. A. Rice, *J. Chem. Phys.*, **26**, 618 (1957).

TABLE I

| | HCl, *M* | $H_2O$, *M* | Flow[a] rate | Time, min. | % enrich. | H.E.T.P., | | $\epsilon \times 10^4$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | b | c | b | c |
| (A) | 0.64 | 0.08 | 3 | 60 | 0.78 | 2.0 | 3.8 | 3.1 | 5.1 |
| | | | | 180 | 1.45 | | | | |
| | .33[d] | .1[e] | 4 | 60 | 0.92 | 3.6 | 5.2 | 4.1 | 6.3 |
| | | | | 180 | 1.49 | | | | |
| | .65 | .08 | 4 | 60 | 1.03 | 1.5 | 3.2 | 3.5 | 6.0 |
| | | | | 180 | 1.95 | | | | |
| | .56 | .09 | 4.5 | 60 | 0.88 | 1.5 | 3.0 | 2.7 | 4.6 |
| | | | | 180 | 1.65 | | | | |
| | .50 | .09 | 6 | 40 | 1.00 | 5.6 | 7.8 | (6.7) | (9.0) |
| | | | | 107 | 1.49 | | | | |
| | | | | | | | Av. | 4.4 ± 1.6 | |
| (B) $H_3OCl$, *M* | | | | | | | | | |
| 0.13 | 0.5[e] | 0.35 | 6 | 60 | 0.65 | 6.6 | 8.7 | 4.0 | 5.2 |
| | | | | 180 | .81 | | | | |
| .19 | .6[e] | 0.44 | 4 | 60 | .54 | 4.4 | 6.4 | 3.2 | 4.5 |
| | | | | 190 | .88 | | | | |
| .62 | .6[e] | 1.55 | 5.5 | 60 | − .08 | 5.4[e] | | −0.8 | |
| | | | | 180 | − .19 | | | | |
| 1.5 | .6[e] | 3.9 | 3 | 60 | − .46 | 5.4[e] | 4.3 | −3.9 | −3.7 |
| | | | | 180 | − .88 | | | | |
| 1.6 | .6[e] | 3.9 | 4.5 | 60 | − .65 | 4.0 | 5.8 | −3.4 | −4.8 |
| | | | | 180 | −1.03 | | | | |
| (C) $HgCl_2$, *N* | | | | | | | | | |
| 0.32 | 0.67 | 0.08 | 3 | 60 | 0.88 | 4.4 | 6.6 | 5.7 | 8.3 |
| | | | | 180 | 1.49 | | | | |
| .32 | .40[d] | .11 | 3 | 60 | 1.03 | 3.9 | 6.0 | 6.1 | 9.0 |
| | | | | 180 | 1.76 | | | | |
| .30 | .69 | .14 | 3.5 | 60 | 1.11 | 4.8 | 6.9 | 6.9 | 9.8 |
| | | | | 180 | 1.76 | | | | |
| .31 | .55 | .14 | 4 | 60 | 1.23 | 4.9 | 6.9 | 7.6 | 10.6 |
| | | | | 180 | 1.91 | | | | |
| .35 | .6[e] | .1[e] | 5.5 | 75 | 1.57 | 4.6 | 6.5 | 8.0 | 11.2 |
| | | | | 195 | 2.18 | | | | |
| .31 | .63 | .14 | 4 | 60 | 1.19 | 4.5 | 6.3 | 6.7 | 9.3 |
| | | | | 180 | 1.84 | | | | |
| .23 | .49 | .1[e] | 5.5 | 60 | 0.96 | 7.1 | 9.6 | 6.3 | 8.5 |
| | | | | 120 | 1.15 | | | | |
| .32 | .72 | .11 | 5.5 | 65 | 1.03 | 3.2 | 4.7 | 4.3 | 6.2 |
| | | | | 155 | 1.53 | | | | |
| .23 | .64 | .1[e] | 5.5 | 50 | 0.84 | 11.1 | 14.6 | 7.9 | 10.4 |
| | | | | 150 | 0.96 | | | | |
| | | | | | | | Av. | 7.9 ± 2.5 | |
| (D) LiCl, *M* | | | | | | | | | |
| 0.53 | 0.70 | 0.04 | 3 | 180 | 0.08 | 5.4[e] | | 0.4 | |
| 0.53 | .72 | .04 | 4 | 60 | .00 | 5.4[e] | | −0.4 | |
| | | | | 144 | − .08 | | | | |
| 2.0 | .66 | .07 | 2 | 60 | − .23 | 5.4[e] | | −4.0 | |
| | | | | 180 | − .77 | | | | |
| 2.0 | .70 | .07 | 2 | 60 | − .27 | 4.0 | 7.5 | −2.2 | −3.5 |
| | | | | 180 | − .50 | | | | |
| (E) $SrCl_2$, *N* | | | | | | | | | |
| 0.30 | 0.64 | 0.09 | 2 | 60 | 0.23 | 5.4[e] | | 1.5 | |
| | | | | 180 | .31 | | | | |
| 0.30 | .65 | .09 | 4 | 60 | .38 | 5.4[e] | | 1.8 | |
| | | | | 180 | .42 | | | | |
| 1.6 | .74 | .0[e] | 1 | 240 | − .31 | 5.4[e] | | −1.6 | |
| 1.6 | .77 | .0[e] | 2 | 60 | − .11 | 5.4[e] | | −0.9 | |
| | | | | 180 | − .19 | | | | |
| 1.6 | .74 | .0[e] | 2 | 60 | − .27 | 4.0 | 6.0 | −1.6 | −2.3 |
| | | | | 180 | − .46 | | | | |

[a] Flow rate in ml. $min.^{-1}$ $cm.^{-2}$. [b] Values in this column were calculated on the basis of 10% of the total holdup present above the point of sampling, *i.e.*, $A = 0.89$. [c] Values in this column were calculated assuming that the amount of holdup above the point of sampling is 20% of the total holdup, *i.e.*, $A = 0.96$. [d] These two runs were made at a pressure of about 130 mm. instead of approximately 210 mm. as used for the other runs. [e] These values were not directly measured or calculated but are estimated from corresponding figures in other runs. [f] This run was made in a column packed with Podbelniak Heli-Pak 3014 instead of Pyrex helices.

$HgCl_2$ is to be expected since $HgCl_2$ is largely unionized even in water solutions.

An isotope effect of about 1.0040 for a solvated chloride ion is not inconsistent with the limited data available on the vibration frequencies of O–H–Cl hydrogen bonds[11] as is shown by the approximate calculation to be given. The relations between the frequencies of stretching vibrations and the masses and force constants involved for a linear triatomic system are given by Herzberg[12] as $4\pi^2(\nu_1^2 + \nu_3^2) = k_1(1/m_x + 1/m_y) + k_2(1/m_y + 1/m_z)$ and $16\pi^4\nu_1^2\nu_3^2 = k_1k_2(m_x + m_y + m_z)/m_x \cdot m_ym_z$. For hydrogen bonds in which the mass of the central atom, $m_y$, is considerably smaller than the other two, one of the frequencies, $\nu_3$, hereinafter called the hydrogen stretching frequency, will be considerably higher than the other, and a sufficiently accurate solution is $4\pi^2\nu_3^2 = (k_1 + k_2)/m_y + (1/m_x)(k_1^2/(k_1 + k_2)) + (1/m_z)(k_2^2/(k_1 + k_2))$ and $4\pi^2\nu_1^2 = ((m_x + m_y + m_z)/m_xm_z)(k_1k_2/(k_1 + k_2))$. $k_1$ is the force constant for stretching the x–y bond and $k_2$ refers to the y–z bond. These expressions are readily differentiated with respect to $m_z$, and then multiplying by $\Delta m_z = 2$ awu. one obtains the changes in frequency on changing from $Cl^{35}$ to $Cl^{37}$. Substituting directly into Bigeleisen's equations[6] one obtains

$$\epsilon = \sum_i G(u_i)\Delta u_i = n\left(\frac{1}{8\pi^2}\right)\left(\frac{h}{kT}\right)^2\left(\frac{k_2\Delta m_z}{m_z^2}\right)\left(\frac{k_1G(u_1)}{(k_1 + k_2)u_1} + \frac{k_2G(u_3)}{(k_1 + k_2)u_3}\right)$$

for the isotope effect due to $n$ hydrogen bonds to the $Cl^-$ ion. $u_i = h\nu_i/kT$ and $G(u)$ is a function tabulated by Bigeleisen.[6] $u_1$ lies in the range for which $G(u)/u = {}^1/_{12}$ is a valid approximation; however $G(u_3)/u_3$ must be obtained by successive approximations, or the value of 0.041 calculated from the hydrogen stretching frequency in the HCl–methyl ether complex,[11] may be used. $k_2$ is probably considerably smaller than $k_1$ due to the lower charge density on a chlorine atom as compared to an oxygen atom. Assuming that $k_1 = 1.5k_2$[13] and putting in the experimentally determined isotope effect, one obtains: $\epsilon = 0.0040 = nk_2(3.19 \times 10^{-7})[({}^3/_5)\ 0.083 + ({}^2/_5)0.041]$ and $nk_2 = 1.9 \times 10^5$ dynes cm.$^{-1}$.[14] The hydrogen stretching vibrations of O–H–Cl hydrogen bonds have been observed in HCl–methyl ether complexes[11] at about 2250 cm.$^{-1}$, corresponding to $k_1 + k_2 = 3 \times 10^5$, which in turn gives an estimate of 1.6 for $n$, the number of hydrogen bonds per Cl atom. A similar estimate can be made for the aqueous chloride ion, based on the isotopic enrichment data of Urey, *et al.*[15] Assuming that their column gave a H.E.T.P. between 0 and 15 cm., the isotope effect for aqueous chloride ion is in the range of 1.0043 ± 0.0003, which gives $nk_2 = 2.0_3 \times 10^5$ and an estimate of 1.7 for $n$.

TABLE II

| | | H.E.T.P. | $\tau$,[b] sec. | $k_2$,[c] l. mole$^{-1}$ sec.$^{-1}$ |
|---|---|---|---|---|
| $HgCl_2$ | 0.3 *N* | 6 | 20 | 0.079 |
| LiCl | 2.0 *M* | 17[a] | 18 | .014 |
| $SrCl_2$ | 1.6 *N* | 17[a] | 17 | .036 |

[a] Maximum value for the H.E.T.P. consistent with the data. [b] Maximum value for the half time for isotopic exchange with HCl present at 0.6 to 0.7 *M*. [c] Minimum value for the rate constant for exchange assuming second-order kinetics.

The rate of isotopic exchange reactions within the liquid phase is only one of a number of factors determining the H.E.T.P. Some of these contributions are additive, but there is a complicated interaction between the exchange reactions and mixing and diffusion processes in the liquid phase. Not enough is known about the flow in packed columns to calculate the effect of this interaction; however a lower limit for the rate of isotopic exchange can be calculated by neglecting all contributions to the H.E.T.P. other than that of the exchange reaction. The results of this calculation are summarized in Table II. There is an additional uncertainty in the LiCl and $SrCl_2$ results due to the smallness of the observed enrichments, and the maximum value for the H.E.T.P. consistent with the data, 17 cm., has been used to get an absolute minimum for the exchange rates. The H.E.T.P.'s for the $HgCl_2$ runs are only slightly larger than those of the blank, HCl only, runs, so the exchange rate is probably much faster than the calculated minimum. A study of the HCl–acetyl chloride exchange in the same columns at various concentrations of $ZnCl_2$ catalyst is under way in this Laboratory and eventually should permit the setting of higher minimum values for the exchange reactions reported here.

CAMBRIDGE, MASS.

---

[11] G. L. Vidale and R. C. Taylor, THIS JOURNAL, **78**, 294 (1956).

[12] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co. Inc., New York, N. Y., 1945.

[13] The assumption that $k_1 = k_2$ gives $nk_2 = 2.0_5 \times 10^5$ and an estimate of 1.4 for $n$.

[14] The approximations used in the above calculations are similar to those used by Bigeleisen and Mayer[6] for $SnCl_4$, etc. Unfortunately their equations cannot be used directly in the present case because of the high frequency of the hydrogen stretching vibrations.

[15] H. D. Urey, A. Mills, I. Roberts, H. G. Thode and J. R. Huffman, *J. Chem. Phys.*, **7**, 138 (1939).