Temperature Dependence of Chlorine Kinetic Isotope Effects for Aliphatic Chlorides

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Abstract: The temperature dependence of chlorine kinetic isotope effects (k_{35}/k_{37}) has been established by experimental measurements in the range 0–60° for model SN1 and SN2 systems (*tert*-butyl chloride solvolysis and *n*-butyl chloride plus thiophenoxide anion reaction, respectively) in anhydrous methanol. The temperature dependence predicted by the Bigeleisen–Mayer heavy atom approximation using measured ground state carbon–chlorine stretch frequencies and isotopic splitting is found to agree well with the experimental values for these two systems. The KIE dependence on temperature was found to vary linearly with $1/T$ over the limited range 0–60°. The magnitude of k_{35}/k_{37} is higher for the SN1 reaction than for the SN2 reaction at any given temperature (*i.e.*, 1.0106 *vs.* 1.0089 ± 0.00015 at 20°) also as predicted by theory.

The observation and measurement of kinetic isotope effects in chemical reactions have provided considerable insight into reaction mechanisms and have led to choices among probable transition state structures.[1–7] The development of theoretical models to describe kinetic isotope effects was pioneered by Bigeleisen and has been further developed by Wolfsberg and Stern.[8–10] Their general case equation[9] may be represented by the product of factors given in eq 1

$$k_1/k_2 = \frac{\nu_{1L}^{\ddagger}}{\nu_{2L}^{\ddagger}}(\mathrm{VP})(\mathrm{EXC})(\mathrm{ZPE}) \qquad (1)$$

where k_1/k_2 is the ratio of the reaction rate constant of the light isotope to that of the heavy isotope; $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$ is the ratio of the imaginary frequencies for the light isotope in the transition state to the analogous frequencies for the heavy isotope; VP is the vibrational product, a classical factor resulting from translational and rotational motion; EXC is a quantum factor, a correction for thermal excitation of vibrations to levels higher than the zero-point levels; and ZPE is an expression of the zero-point energy differences of the isotopic shifts of vibrations in the transition state and reactants.

In applying Bigeleisen's isotope effect model to heavy isotopes, such as chlorine, eq 2, the heavy atom approximation[9] of eq 1 is quite useful.

$$k_1/k_2 = \frac{\nu_{1L}^{\ddagger}}{\nu_{2L}^{\ddagger}}\left(1 + \sum^{3n-6} G(u_i)\Delta u_i - \sum^{3n-7} G(u_i^{\ddagger})\Delta u_i^{\ddagger}\right) \qquad (2)$$

$$G(u_i) = [{}^1/_2 - 1/u_i + 1/(e^{u_i} - 1)]$$

$$u_i = hc\nu_i/kT$$

$\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$ is often referred to as the "temperature-independent factor" (TIF), following the terminology of Yankwich and coworkers.[11,12] In the region of infinite temperature limiting behavior, $u \rightarrow 0$, ZPE $\rightarrow$ 1, and EXC $\rightarrow$ EXC/VP so that the $k_1/k_2 \rightarrow \nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$. The KIE thus becomes the ratio of the imaginary frequencies describing transmission over the barrier.[13]

Most previous studies have involved a measurement of the heavy atom isotope effects at one temperature and the investigators have used variation of the transition state structures to achieve correspondence between theory and experimental results.[3,10,14] A more extensive investigation of the expected variations in temperature dependences has been accomplished by Stern and coworkers[15] for isotope-exchange equilibria. Yankwich and coworkers have done the calculations for intramolecular carbon decarboxylation reactions.[11] One study measured the temperature dependence of central carbon k_{12}/k_{13} isotope effects in 1-bromo-1-phenylethane with the aim of differentiating between SN2 and SN1 reaction mechanisms.[16,17] The results indicated that this differentiation could be accomplished with either of two experimental parameters: (a) the magnitude of the observed carbon isotope effect (SN1 reactions produced smaller effects contrary to the theoretical calculations where larger values might be expected for the two-center transition state than for the three-center state); (b) the direction of the temperature dependence (SN1 reactions gave carbon isotope effects which varied directly with temperatures whereas the SN2 reaction was inversely proportional to temperature). The work of Kresge, *et al.*,[18] and later conclusions by Bron and Stothers[19] suggest that these contradictions between experiment and simple theory may be due to strengthening of the bonds in the re-

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(17) J. Bron and J. B. Stothers, *Can. J. Chem.*, **46**, 1435 (1968).

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(19) J. Bron and J. B. Stothers, *Can. J. Chem.*, **47**, 2506 (1969).

sulting carbonium ion which offset the loss of the carbon–chlorine bond. Thus the heavy atom diagnostic criteria offered by Bron and Stothers may be a special case only for carbon (central atom) isotope effects. Based on this conclusion, it seemed reasonable to expect that observations of the temperature dependence on chlorine leaving group isotope effects might serve to circumvent a portion of the problems found with the carbon isotope effects and lead to a direct measurement of the $G(u_i)$ factor in eq 2. This factor, involving $G(u_i)$, is composed of the real vibrations of the substrate in the ground state and of the nonimaginary vibrations of the substrate in the reaction transition state. It is the purpose of this paper to contrast and compare the chlorine isotopic temperature dependence calculated for a given substrate with the experimentally observed temperature dependence using two test cases involving the SN2 reaction of *n*-butyl chloride and the SN1 reaction of *tert*-butyl chloride.

Experimental Section

Materials. ***n*-Butyl chloride** (Aldrich) was distilled under a nitrogen atmosphere, bp 78° (lit.[20] bp 78.5° at 760 mm).

Thiophenol (Eastman) was vacuum distilled, bp 59° at 14 mm (lit.[21] bp 169.1° at 760 mm).

Laboratory **distilled water** was further purified by distilling it from an alkaline permanganate solution and then again from a sulfuric acid solution in an all-glass still.

For *n*-butyl chloride reactions, 0.250 *M* **lithium methoxide** in methanol was prepared by dissolving 6 g of clean 0.5 in. lithium rod (Alfa Inorganics) in 3 l. of anhydrous methanol (Mallinckrodt Chemical).

***tert*-Butyl chloride** (Columbia Chemical) was distilled, bp 51°, through a well-insulated glass column (lit.[22] bp 50.5° at 760 mm).

For the *tert*-butyl chloride reactions, **lithium methoxide** (Alfa Inorganics) was added to anhydrous methanol (Mallinckrodt Chemical) to achieve a concentration of 0.25 *M* by adding 950 mg to 100 ml of methanol.

Procedure. Kinetics of the *n*-Butyl Chloride Reaction. The reactions were run in a controlled temperature bath measured to ±0.01° with a calibrated thermometer. Typically the 0.25 *M* lithium methoxide in methanol solution was deoxygenated in a 100-ml volumetric flask; the ratio of reactant to nucleophile was established as 1:1 by adding 257 μl of thiophenol (2.5 mmol) *via* syringe, then 261 μl of *n*-butyl chloride (2.5 mmol) was injected to start the reaction. Quenching was accomplished by pouring the reaction mixture into a cold aqueous solution of acid (0.13 *M* HNO_3) which stopped the reaction by protonating the thiophenoxide anion. This mixture was then extracted three times with 250 ml of toluene to remove unreacted *n*-butyl chloride. After extraction, the aqueous layer was made basic and boiled down to approximately 50 ml. The water solution was then acidified with HNO_3, and the ionic strength adjusted to approximately 1 *M* with potassium nitrate (Baker), and titrated potentiometrically with 0.1 *M* silver nitrate. The silver chloride produced was washed and dried at 105°.

Kinetics of the *tert*-Butyl Chloride Solvolysis. The reactions were all run in a calibrated and controlled temperature bath. The reaction vessels were 125-ml erlenmeyer flasks which allowed injection of the *tert*-butyl chloride (540 μl, 5 mmol) through a septum/valve arrangement (Mininert Valve-HV-6) after temperature equilibration of the 0.25 *M* lithium methoxide solution in methanol at the given reaction temperature. Three samples at each temperature were typically taken to allow better precision in determining the kinetic rate constants and the chlorine kinetic isotope effects. The temperature quench was critical and was accomplished by bathing the reaction vessel in a Trichlor/Dry Ice mixture for 30 sec. The vessel was then opened and the reaction mixture poured into a separatory funnel containing 100 ml of chilled water and 200 ml of reagent grade heptane. Two more heptane extractions were made, then the aqueous layer was boiled down to approximately 50 ml. The solution was then acidified to phenolphthalein, and the ionic strength adjusted to approximately 1 *M* with potassium nitrate (Baker, reagent grade), and treated as previously described.

Potentiometric Titration. The silver ion concentration throughout the titration was followed by a silver wire electrode. The reference electrode was a saturated calomel electrode which was connected to the solution through an agar|potassium nitrate salt bridge to prevent chloride ion contamination from the sce. The conversion of the microcrystalline, dry silver chloride *via* reaction with excess methyl iodide to methyl chloride, purification of the methyl chloride, and chlorine isotopic analysis by isotope ratio mass spectrometry have been described previously.[23] For the data reported herein, however, only a twofold mole excess of methyl iodide was used and the isotopic analysis employed positive ion ratios. The collection system previously described was modified such that any high mass ions above *m/e* 52 are excluded as are the ions lower in mass than *m/e* 50. These collector alterations lead to a lower positive ion δ correction factor of 1.036 compared to the previously reported 1.056 value.[23]

Infrared Measurements. The acquisition of the high resolution infrared data utilized herein is described elsewhere by Williams and Taylor.[24]

Product Analysis of *tert*-Butyl Chloride Solvolysis in Methanol. The glc system used was an F & M Scientific Corp. Model 720 programmed temperature gas chromatograph equipped with a Model 1609 flame ionization attachment. The column used was 0.25 in. o.d. by 15 ft in length and the liquid support was 20% diisooctyl sebacate on 60–80 mesh Gas-Chrom Q support. At 50° column temperature the corrected retention time of isobutene was 80 sec while *tert*-butyl methyl ether appeared at 9 min 20 sec on the tail of the methanol solvent peak. A second column composed of 0.25 in. i.d. by 6 ft 20% Carbowax 20-M on 60–80 mesh silanized Chromosorb P support allowed a clearer distinction of the ether peak without the solvent overlap.

For the solvolysis reaction mixture, 98 mg of lithium methoxide was dissolved in 10 ml of methanol at room temperature to give a 0.25 *M* solution; 55 μl of *tert*-butyl chloride was injected into the solution giving a reactant concentration of 0.049 *M*. One milliliter of the reaction mixture was put into each of six opticlear vials. Each vial was suspended in a 60° temperature bath and the time noted. The six data points were taken over 15-min intervals. The growth of the isobutene was linear with time with an approximate rate constant of 1.88×10^{-5} sec^{-1} and the growth of the *tert*-butyl methyl ether peak was also linear. However, the growth of the ether was approximately three times faster than the growth of the olefin.

Results and Discussion

The temperature dependent factor (TDF) of eq 2 has usually been simplified to allow calculation of TDF from available physical constants. For organo chlorides the assumption is as follows. The R–Cl stretching frequency becomes imaginary in the transition state and all other vibrations cancel between the ground and transition states. This assumption implies that the TDF is controlled by the ground vibrational stretching frequency and isotopic separation of the R–Cl vibrations. This is shown in eq 3, where ν_f =

$$\mathrm{TDF_I} = 1 + G(u_f)\Delta u_f \qquad (3)$$

C–Cl stretching frequency, and will constitute a type I temperature dependence. Of the terms in eq 1, only EXC and ZPE are temperature dependent. When EXC is assumed to be unity at reasonable reaction temperatures (*i.e.*, u_i is not too small), then the kinetic isotope effect temperature dependence is mainly a function of the ZPE factor.

$$\mathrm{ZPE} = \exp\left[\sum^{3n-6}(u_{1i} - u_{2i}/2)\right] \Big/ \exp\left[\sum^{3n-7}(u_{1i}{}^{\ddagger} - u_{2i}{}^{\ddagger})/2\right] \qquad (4)$$

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[20] I. Heilbron, "Dictionary of Organic Compounds," Vol. 1, Oxford University Press, New York, N. Y., 1953, p 272.

[21] "Handbook of Chemistry and Physics," 45th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1964, p C-168.

[22] L. M. Kushner, R. W. Crowe, and C. P. Smyth, *J. Amer. Chem. Soc.*, **72**, 1091 (1950).

[23] J. W. Taylor and E. P. Grimsrud, *Anal. Chem.*, **41**, 805 (1969).

[24] R. C. Williams and J. W. Taylor, *J. Amer. Chem. Soc.*, **95**, 1710 (1973).

When the temperature dependence of the KIE is determined by the ZPE factor, this temperature dependence can take the form of an Arrhenius equation

$$\ln (k_1/k_2) = \ln A + \Delta E_a/kT \tag{5}$$

where

$$\Delta E_a = \sum^{3n-6} {}^1\!/_2 hc(\nu_{1i} - \nu_{2i}) - \sum^{3n-7} {}^1\!/_2 hc(\nu_{1i}{}^{\ddagger} - \nu_{2i}{}^{\ddagger})$$

$$A = (\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger})\mathrm{VP}$$

ΔE_a is the energy difference of the isotopic shifts of vibrations in the transition state and in the reactants. ΔE_a for a given reaction can be evaluated from the slope of a plot of ln (k_{35}/k_{37}) *vs.* $1/T$. In the type I situation where only the R–Cl stretching frequency is assumed to be isotopically important, the ΔE_a found should be one-half the value of the isotopic shift for the R–Cl stretching frequency of the ground vibration state.

Another possibility, which we will specify as type II, may arise when there is more than one isotopically important vibration in a given substrate. This case is more complex and for complete description would require evaluation of all frequencies in both the ground and transition state. A simplification, however, would be to consider the TDF as given in eq 6.

$$\mathrm{TDF_{II}} = 1 + G(u_1)\Delta u_1 + G(u_2)\Delta u_2 \tag{6}$$

In this formulation both frequencies, u_1 and u_2, are assumed either to become imaginary or the respective Δu values are assumed to become zero in the transition state such that terms such as $-G(u^{\ddagger})(\Delta u^{\ddagger})$ are omitted from the equation. Thus $\mathrm{TDF_{II}}$ may be expected to be larger than the true value by the magnitude of these $G(u^{\ddagger})(\Delta u^{\ddagger})$ terms. Experimentally, however, a comparison of the $\mathrm{TDF_{II}}$ values with those observed from a plot of k_1/k_2 *vs.* $1/T$ should give an indication of the error in these simplifying assumptions.[25]

One of the first temperature studies of chlorine leaving groups investigated in these laboratories was the reaction of *n*-butyl chloride with thiophenol anion in methanol. This reaction was chosen to be representative of the SN2 mechanism and is characterized by second-order kinetics, as shown in Table I,[26] and is not complicated by elimination reactions.[28] For *n*-butyl chloride, gas phase infrared measurements of the isotopic shift[24] show that the ground-state vibrations are complicated slightly by the fact that although the carbon–chlorine stretching frequency is the only isotopically important vibration in *n*-butyl chloride, there are three isomers of the molecule attributable to rotation of the $-\mathrm{CH_2{-}Cl}$ group around an axis colinear with the C–C bond joining this group to the rest of the molecule.[29] These rotational isomers are designated $\mathrm{P_H}$ (chlorine trans to hydrogen, two isomers) and $\mathrm{P_C}$ (chlorine trans to carbon, one isomer), after the notation of Mizushima, *et al.*[30] The $\mathrm{P_H}$ isomers have a measured gas-phase stretching frequency of 665.1 $\mathrm{cm^{-1}}$ with a chlorine 35/37 splitting of 4.0 $\mathrm{cm^{-1}}$ while the $\mathrm{P_C}$ isomer has a measured gas-phase stretching frequency of 747.6 $\mathrm{cm^{-1}}$ with a chlorine 35/37 splitting of 3.5 $\mathrm{cm^{-1}}$.[24] A combination of these isomers is taken to give the calculated shift by combining two-thirds of the value for the $\mathrm{P_H}$ isomer and one-third of the value for the $\mathrm{P_C}$ isomer. Using this weighting with the $G(u)\Delta u$ values and assuming a type I case pertains, the $\mathrm{TDF_I}$ values shown in Table II can be calculated. The slope of the ln $(\mathrm{TDF_I})$ *vs.* $1/T$ plot yields a value of 1.55 $\mathrm{cm^{-1}}$ and is shown in Figure 1.

Table I. Reaction of *n*-Butyl Chloride (0.025 *M*) with Thiophenol Anion (0.025 *M*) in Methanol (0.25 *M* in $\mathrm{LiOCH_3}$)

Temp, °C	Fract of react	k_2, l./(mol sec)	KIE[a]
0	0.019	1.77×10^{-6}	1.0096_4
20	0.105	2.50×10^{-5}	1.0089_5
40	0.281	2.27×10^{-4}	1.0084_0
60	0.102	1.68×10^{-3}	1.0079_4

[a] Estimated precision in the determination of the KIE values is ±0.00015 or better.

Table II. Predicted Temperature Dependence of *n*-Butyl Chloride KIE Calculated from Eq 3 ($\mathrm{TDF_I}$ Values)

Temp, °C	$G(u_A)$	Δu_A	$G(u_B)$	Δu_B	$\mathrm{TDF_I}$[a]
0	0.2456	0.0211	0.2661	0.0185	1.00509
20	0.2335	0.0197	0.2537	0.0172	1.00451
40	0.2223	0.0184	0.2423	0.0161	1.00403
60	0.2119	0.0173	0.2316	0.0151	1.00361

[a] $\nu_A = \mathrm{P_H}$ C–Cl stretch = 665.1 $\mathrm{cm^{-1}}$; $\Delta\nu_A$ = 4.0 $\mathrm{cm^{-1}}$. $\nu_B = \mathrm{P_C}$ C–Cl stretch = 747.6 $\mathrm{cm^{-1}}$; $\Delta\nu_B$ = 3.5 $\mathrm{cm^{-1}}$.

When the experimental values for the temperature dependence of the chlorine kinetic isotopic effect for this same reaction are plotted in the same manner (data in Table I, Figure 1), the experimentally determined slope[31] is 1.77 $\mathrm{cm^{-1}}$. This compares quite favorably with the 1.55 $\mathrm{cm^{-1}}$ calculated and may suggest that although the transition state does involve bonding of the central carbon to the nucleophile, as evidenced by the kinetic order, the influence of this bonding does not strongly effect the bonding to the leaving group because the ground state value appears to predominate in the TDF.

The effect of solvent on the pertinent vibration frequencies was investigated and the isotopic splitting was found to be relatively unaffected although the $\mathrm{P_C}$ and $\mathrm{P_H}$ values dropped by approximately 20 $\mathrm{cm^{-1}}$.[24] These observations suggest that the gas-phase values used in these calculations for *n*-butyl chloride are appropriate for the solution case as well. This was demonstrated

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(25) The exact calculations of the KIE derived from GF matrix programs to obtain frequencies and force fields for *tert*-butyl chloride, a case similar to the one described, will be published by R. C. Williams and J. W. Taylor. These calculations provide an additional test for the assumptions of eq 6. For *tert*-butyl chloride this slope appears to yield a value which is one-half the average isotopic splitting of the two frequencies.

(26) A plot of ln (rate constant) *vs.* $1/T$ for these data was linear. The slopes indicated an activation energy (E_a) of 20.4 kcal/mol for the *n*-butyl chloride reaction and an E_a of 24.5 kcal/mol for the *tert*-butyl chloride solvolysis. These E_a's are within the energy range encountered for these types of reactions.[27]

(27) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 148.

(28) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 485.

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(31) The value of the slope was determined by the following equation

$$\Delta E_a = \left(\frac{\Delta \ln (k_{35}/k_{37})}{\Delta 1/T} \times R\right) \Big/ (2.859\ \mathrm{cal/(mol\ cm^{-1})})$$

where R is the gas constant expressed in cal/(deg mol).

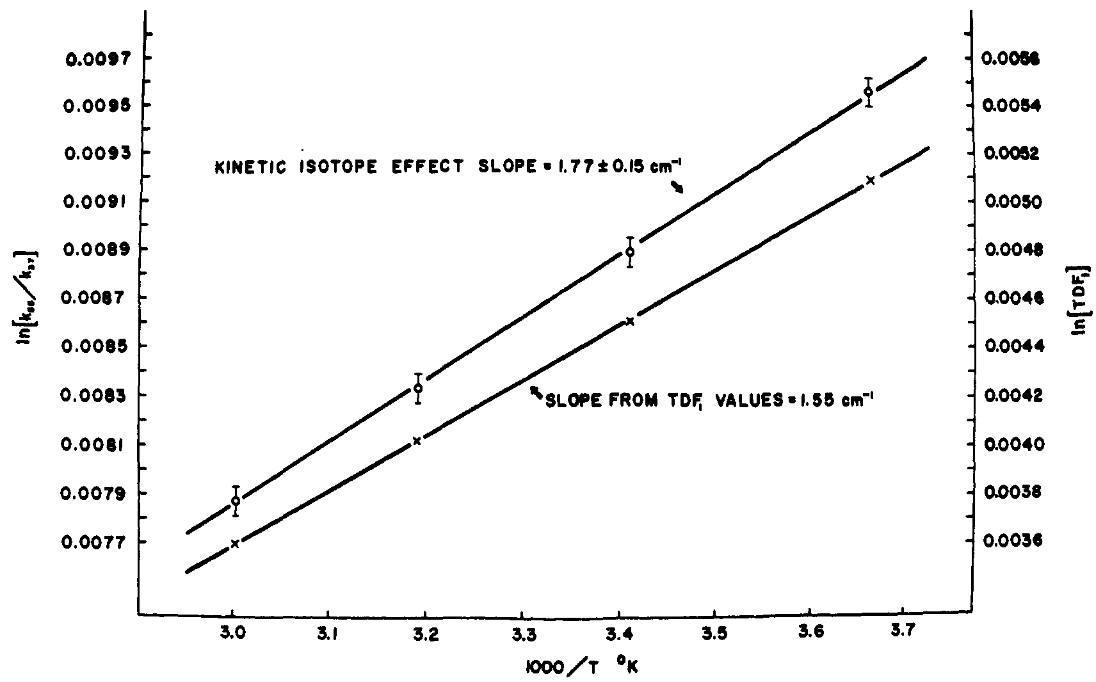

Figure 1. The temperature dependence of the chlorine kinetic isotope effect (left ordinate) for the reaction of *n*-butyl chloride with thiophenol anion in methanol compared to the temperature dependence predicted by eq 3 (right ordinate) for *n*-butyl chloride.

by recalculation of TDF$_\mathrm{I}$ assuming a 20-cm^{-1} reduction in the P_C and P_H isomer vibrations and a 0.1-cm^{-1} reduction in each isotopic splitting. This calculation yields TDF$_\mathrm{I}$ values with a slope of 1.49 cm^{-1} *vs.* the 1.55 cm^{-1} slope found from the TDF$_\mathrm{I}$ values for the gas-phase data.

The solvolysis of *t*-BuCl in methanol was chosen as a model for the SN1 reaction mechanism because *tert*-butyl chloride solvolysis is assumed to be a classic SN1 reaction.[32] Calculations on the ground state of the *t*-BuCl molecule were made by computer in this laboratory utilizing a vibrational analysis program. This computer analysis has shown that there are *two* isotopically important vibrations in *tert*-butyl chloride, apparently due to its symmetry. The two vibrations are the carbon–chlorine stretching frequency and the symmetric bending frequency between the central carbon and the three methyl groups.[24] High resolution infrared studies in this laboratory have shown the carbon–chlorine stretching frequency to be 585 cm^{-1} with an isotopic shift of 2.63 cm^{-1} and the trimethylcarbon symmetric bend to be 372 cm^{-1} with an isotopic shift of 3.77 cm^{-1}.[24]

Because *tert*-butyl chloride falls into the type II situation with two isotopically important vibrations, its expected temperature dependence may be approximated by eq 6. The calculated TDF$_\mathrm{II}$ values for *tert*-butyl chloride are presented in Table III. The slope obtained from a plot of ln (calculated TDF$_\mathrm{II}$) *vs.* $1/T$ (Figure 2) yields a value of 1.94 cm^{-1}. This value is slightly higher than the experimental slope of 1.76 cm^{-1} found from the plot of ln (k_{35}/k_{37}) *vs.* $1/T$ for the solvolysis of *tert*-butyl chloride (Table IV,[24] Figure 2) but gives support to the simplifying assumptions in eq 6. Again for these calculations the gas-phase vibrational data were used. If the solution values of 560 and 370 cm^{-1} are employed with a scaling to yield an isotopic separation of 2.52 for the 560 cm^{-1} stretch and essentially an unchanged C–C$_3$ bend, the TDF$_\mathrm{II}$ calculated value becomes 1.89 cm^{-1}.

The significance of the agreement of the two slopes for *tert*-butyl chloride may require further scrutiny, however, because of several contributing factors which were not present for the *n*-butyl chloride case. Although no nucleophile is kinetically involved in the transition state, the *tert*-butyl chloride does undergo elimination reactions in methanol solvent. At 60° the observed products of the solvolysis were *ca.* 30%

Table III. Predicted Temperature Dependence of *tert*-Butyl Chloride KIE Calculated from Eq 6 (TDF$_\mathrm{II}$ Values)

Temp, °C	$G(u_1)$	Δu_1	$G(u_2)$	Δu_2	TDF$_\mathrm{II}$[a]
10	0.2176	0.0134	0.1488	0.0192	1.00576
20	0.2120	0.0129	0.1443	0.0185	1.00541
40	0.2011	0.0121	0.1359	0.0174	1.00479
60	0.1911	0.0114	0.1286	0.0163	1.00427

[a] $\nu_1 = 585.0$ cm^{-1}; $\Delta\nu_1 = 2.63$ cm^{-1}; $\nu_2 = 372.0$ cm^{-1}; $\Delta\nu_2 = 3.77$ cm^{-1}; TDF$_\mathrm{II}$ calculated according to eq 6.

Table IV. Solvolysis of *tert*-Butyl Chloride (0.050 *M*) in Methanol (0.25 *M* LiOCH$_3$)

Temp, °C	Fract of react	k_1, sec^{-1}	KIE[a]	Av KIE
10	0.068	6.89×10^{-8}	1.01089	
10	0.088	6.65×10^{-8}	1.01090	
10	0.133	7.04×10^{-8}	1.01082	1.01087
20	0.213	3.47×10^{-7}	1.01046	
20	0.276	3.50×10^{-7}	1.01063	
20	0.380	3.46×10^{-7}	1.01065	1.01058
40	0.074	6.51×10^{-6}	1.00996	
40	0.092	6.17×10^{-6}	1.00995	
40	0.116	6.22×10^{-6}	1.00982	1.00994
60	0.063	6.78×10^{-5}	1.00959	
60	0.207	6.81×10^{-5}	1.00947	1.00953

[a] Estimated precision in the determination of the KIE values is ±0.00015 or better.

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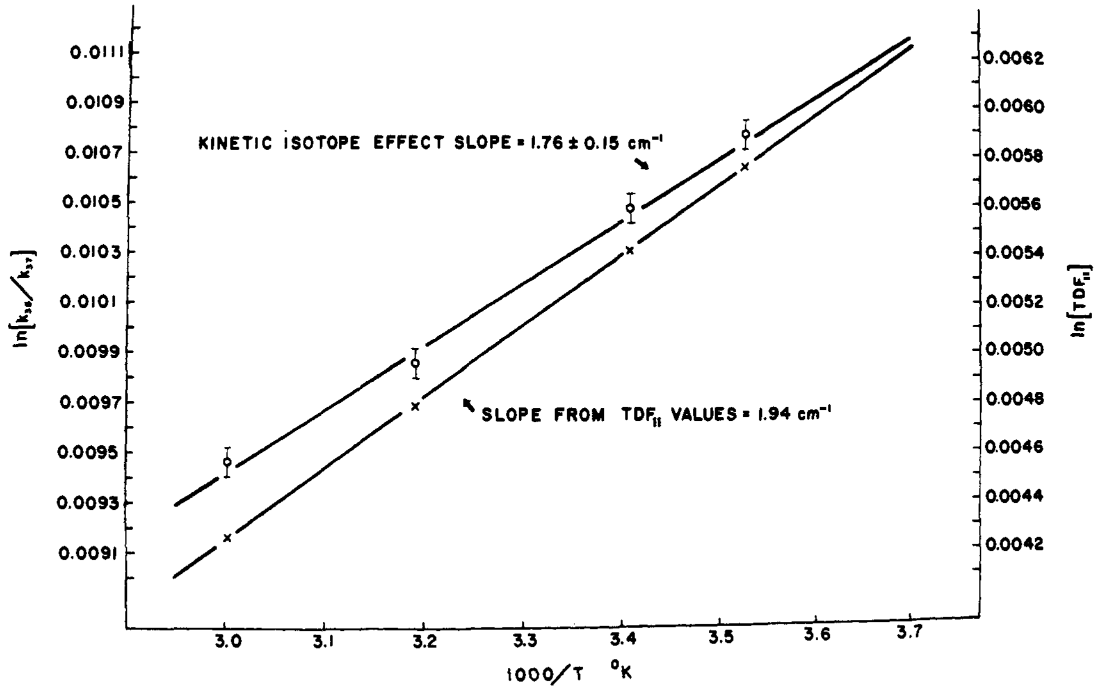

Figure 2. The temperature dependence of the chlorine kinetic isotope effect (left ordinate) for the solvolysis of *tert*-butyl chloride in methanol compared to the temperature dependence predicted by eq 6 (right ordinate) for *tert*-butyl chloride.

isobutene and 70% *tert*-butyl methyl ether. The glc analysis showed that the rate for growth of isobutene is first order as is the rate for growth of *tert*-butyl methyl ether. The sum of the two rate constants approximates the overall first-order rate constant, observed by titration, for the solvolysis. Cocivera and Winstein[33] have studied the reactions of various substituted *tert*-butyl groups and have shown that both the rates of the solvolysis reaction and the product composition were leaving group dependent in alcohol solvents. In ethanol they obtained nearly 45% olefin from the *tert*-butyl chloride reaction, and they interpreted all their observations in terms of ion-pair intermediates. Although the kinetic isotope effect (KIE) data may not exclude ion pairs as intermediates in the solvolysis reaction, the values of the chloride KIE are sufficiently large to suggest that the transition state must involve considerable translational motion of the chlorine atom, and if any ion pairing occurs, it does not involve a great deal of internal return. The fact that the slope of the observed ln (k_1/k_2) *vs.* $1/T$ plot is quite linear may be interpreted to give some information on the timing of the elimination reaction. If the slow step of the reaction involved initial loss of hydrogen, no isotope effect would be observed. If the ionization reaction producing the ether and the elimination producing the isobutene were synchronous, the ΔE_a's for both reactions would have to be equal in order to fit the linear slope found for the plot of ln (k_1/k_2) *vs.* $1/T$ found in Figure 2. The glc data can be cited to suggest that this is not the case because the elimination reaction proceeds at a slower rate than the solvolysis to ether. The remaining conclusion is that the elimination reaction occurs after the slow step and consequently the elimination plays no part in determining the isotope effect.

If this latter conclusion is valid, the $\mathrm{TDF_{II}}$ calculation and the observed experimental slope are in very good agreement (*cf.* Figure 2). The calculated value is higher than the experimental value as expected from the approximation made in eq 6. How much of the difference between the calculated and experimental values is due to the neglect of the transition state vibrations and how much may be due to solvent participation are questions we presently are investigating.[25,34]

For the chlorine leaving groups (SN2, *n*-butyl chloride; SN1, *tert*-butyl chloride), esentially the same experimental slopes are obtained, 1.77 and 1.76 cm^{-1}, respectively. At this point it is not known if the observed close agreement in slopes for these two mechanistic extremes is general or if these results are fortuitous. If further work reveals that this observation is general, it would imply that the primary contribution to differences in observed KIE for chlorine as a leaving group arise from the TIF. This factor is sensitive to transition state geometry and thus the KIE values could be made to reflect that geometry in a more quantitative fashion.

For the two systems studied, the magnitude of the total isotope effects is larger for the SN1 case than for the SN2 case, in agreement with theoretical predictions. (At 20°, *tert*-butyl chloride KIE = 1.0106 while *n*-butyl chloride KIE = 1.0089.) Thus the magnitude of the leaving group KIE does distinguish the two mechanisms and the numerical difference between SN1 and SN2 isotope effect values is approximately that observed by Hill and Fry for benzyl chlorides,[14] although the absolute values are not the same. If the TDF are assumed to be equal and have a value of 1.00496 at 20°, the TIF value for the SN1 case becomes 1.00559 and that for the SN2 case, 1.00397. The TIF values are in the expected direction for product-like and reactant-

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(34) C. R. Turnquist, unpublished results from these laboratories.

like transition states, respectively, but the magnitudes and their more quantitative comparison with geometry must await further calculations.

The temperature dependences of these leaving groups do show that for both the SN2 and SN1 reactions the KIE values are inversely proportional to temperature as predicted by simple theory. The experimental results for the two cases reveal that the temperature dependence of the kinetic isotope effects is best evaluated from consideration of the ground-state configuration plus information on the number of isotopically important ground-state vibrational frequencies for a given reactant. The good correlation achieved between the slopes found for the experimental data and the slopes derived from calculated TDF values demonstrates the utility and specificity of the chlorine kinetic isotope effect probe for isotopically important vibrations and the necessity of consideration of the isotopically important ground-state vibrations in deriving models for the transition state from the observed KIE values.

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Beam Maser Measurement of ^{19}F Hyperfine Structure and Relation to Magnetic Shielding in Carbonyl Fluoride

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Abstract: Hyperfine structure on the $1_{10} \rightarrow 1_{11}$, $2_{11} \rightarrow 2_{12}$, $4_{31} \rightarrow 4_{32}$, and $6_{51} \rightarrow 6_{52}$ rotational transitions in COF_2 was observed with a molecular beam maser spectrometer. The resonance line width (fwhm) ranged from 1.5 kHz on the $1_{11} \rightarrow 1_{10}$ transition to 6 kHz on the highest frequency transitions. The diagonal elements of the spin–rotation tensor obtained are $M_{aa} = -19.77 \pm 0.21$ kHz, $M_{bb} = -13.46 \pm 0.14$ kHz, and $M_{cc} = -7.80 \pm 0.26$ kHz. Magnetic shielding parameters are calculated from experimental results and comparison is made with other molecules.

The dependence of the nuclear magnetic shielding or chemical shift on the molecular structure and chemical properties is very important in nuclear magnetic resonance. Many theoretical calculations[1,2] of the diamagnetic and paramagnetic contributions to the magnetic shielding have been made for small fluorine-containing molecules using either minimal or extended Slater type orbital (STO) basis sets. It is known[1,2] that the diamagnetic contribution, which depends only on the ground electronic state, is insensitive to the choice of basis set. One can calculate the diamagnetic shielding within a few per cent accuracy using a reasonable basis set or the empirical atom dipole model. However, the paramagnetic shielding, which depends on electronic excited states, is very sensitive to the basis wave functions. Unfortunately, there are very few experimental paramagnetic shielding results which can be used to test the choice of basis sets and better understand the relation to the molecular structure. The data most often used in the comparison are the average magnetic shieldings from nmr experiments.

Recently, the magnetic shielding and spin–rotation interaction of fluorine have been studied for a number of small molecules. A direct measurement of the shielding anisotropy for CH_2F_2 was made in the gas phase,[3] and shielding anisotropies for CH_3F, CH_2F_2, and CHF_3[4] were measured in a liquid crystal. An alternative approach to obtain the shielding tensor is to use the measured spin–rotation tensor and calculated values for the diamagnetic shielding. This method was used for CH_3F.[5] In order to better understand the contributions to magnetic shielding and spin–rotation in small molecules, we believe that it is important to have accurate experimental data on spin–rotation and shielding interactions.

Measurements of magnetic hyperfine interactions in a few diatomic molecules, HF,[6] DF,[7] and F_2,[8] were made using molecular beam methods. Some components in the hyperfine structure of COF_2[9] and OF_2[10] were resolved in a microwave spectrometer previously. However, the resolution was not high enough to allow a meaningful comparison with calculations made using different basis sets. In the present experiments, we observe several rotational transitions in COF_2 using a molecular beam maser spectrometer. This system provides improvements in resolution of a factor of 5 to 20 over previous microwave measurements. The high

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