The Vibrational Spectra and Assignments of *t*-Butyl Chloride and *t*-Butyl-d_9 Chloride, and the Calculated Ionization–Equilibrium, Deuterium-Isotope Effect

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Abstract: Raman and infrared spectra supported by a calculation of the vibrational frequencies using transferred Urey–Bradley force constants were used to obtain complete vibrational assignments for *t*-butyl chloride and *t*-butyl-d_9 chloride. These assignments, taken with previously calculated vibrational frequencies for the carbonium ions, $(CH_3)_3C^+$ and $(CD_3)_3C^+$, were used to calculate the equilibrium deuterium isotope effect for the ionization of *t*-butyl chloride. This was found to be very similar in its magnitude and its temperature variation to the published experimental kinetic isotope effect for the solvolysis of *t*-butyl chloride in a number of widely different solvents. This correlation was interpreted to be an indication that the transition-state structure during the rate-determining step of this SN1 reaction is very close to an ion pair.

An understanding of the vibrational spectra of *t*-butyl chloride and its perdeuterio derivative is of considerable spectroscopic value in itself, but it becomes of greater interest when its thermodynamic and kinetic implications can also be exploited. One such application, which is of direct concern to the study of nucleophilic substitution reaction mechanisms, is to the calculation of the equilibrium constant K for the isotope exchange reaction

$$(CH_3)_3CCl + (CD_3)_3\overset{+}{C} \xrightleftharpoons{K} (CH_3)_3\overset{+}{C} + (CD_3)_3CCl \qquad (1)$$

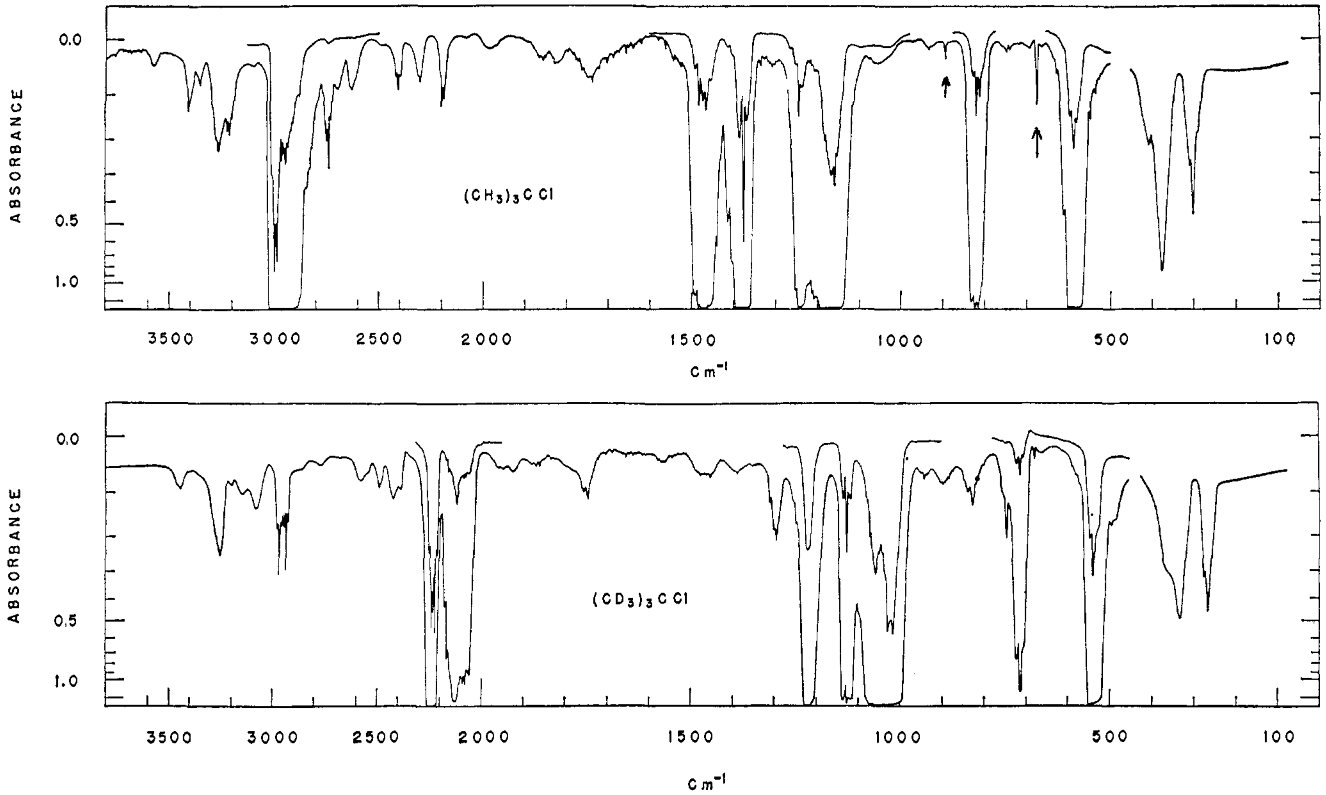

Figure 1. (a) Infrared absorption spectrum of *t*-butyl chloride vapor (upper): 10-cm path with vapor pressures of approximately 240 and 8 mm. The two weak, arrowed features were shown by vpc separation to be impurity bands. (b) Infrared absorption spectrum of *t*-butyl-d_9 chloride vapor (lower): 10-cm path length with vapor pressures of approximately 260 and 10 mm.

This equilibrium may be considered as a combination of the two ionization equilibria

$$(CH_3)_3CCl \xrightleftharpoons{K_H} (CH_3)_3\overset{+}{C} + Cl^- \qquad (2)$$

$$(CD_3)_3CCl \xrightleftharpoons{K_D} (CD_3)_3\overset{+}{C} + Cl^- \qquad (3)$$

so that

$$K = \frac{K_H}{K_D}$$

Table I. Infrared and Raman Data for *t*-Butyl Chloride

Infrared, cm^{-1}		Raman, cm^{-1}		
Vapor[a]	Solution[b]	Liquid	Depolarization	Assignment[c]
3398 vw	3395 vw			$\nu_{13} + \nu_{22}$
3347 vw				$\nu_8 + \nu_{13}$
3260 w				$\nu_{14} + \nu_{23}$
3218 vw				$\nu_{15} + \nu_{23}$
2993 vw	2986 vs	2985 ms	D	ν_{13}
2981 vs	2975 vs	2973 ms	D (?)	ν_1, ν_{14}
2957 m	2946 m	2945 w	P	$2\nu_{16}$
2937 m	2927 ms	2922 s	P	ν_2, ν_{15}
2903 w	2900 m	2897 m	P	$\nu_{16} + \nu_{17}$
2874 vw	2865 w	2863 mw	P	$2\nu_3$
2732 vw	2725 vw	2722 mw	P	$2\nu_4$
2690 vvw				$\nu_{17} + \nu_{19}$
2627 vvw				$\nu_5 + \nu_{16}$
2406 vvw				$\nu_4 + \nu_{20}$
2301 vvw	2295 vvw			$2\nu_5$
2191 vw	2180 vvw			$\nu_4 + \nu_6$
~1970 vvw				$\nu_5 + \nu_6$
~1850 vvw				$\nu_6 + \nu_{20}$
~1820 vvw				$\nu_8 + \nu_{17}$
1740 vw				$\nu_4 + \nu_8$
1480 m	1474 m			ν_{16}
1462 m	1456 ms	1460 sh, w	D	ν_{17}
		1448 s		ν_3
	1437 w, sh	1437 w, sh		$\nu_{20} + \nu_{22}$
1402 vw	1396 w	1392 vvw		$\nu_6 + \nu_7$
1375 vw	1370 vs	1366 w	D (?)	ν_4, ν_{18}
1241 ms	1238 ms	1236 m	D	ν_{19}
1155 vs	1158 vs	1156 ms	D (?)	ν_5
~1175 sh, m	1135 m, sh	1130 w		$2\nu_7$ (FR)
		1030 w	D	ν_{20}
930 vvw		927 mw	D	ν_{21}
890 vvw				Isobutene impurity
818 ms	810 ms	810 s	P	ν_6
674 vw	676 vvw			Impurity
585 s	571 s	569 vs	P	ν_7
545 vvw				$2\nu_{24}$
408 w	407 w	404 w	D	ν_{22}
372 m	372 m	369 s	P	ν_8
301 m	303 m	302 s	D	ν_{23}
	197 vw			$\nu_7 - \nu_8$
	Increasing absorption with peak beyond range of instrument; liquid spectrum only			Absorption due to dipole–dipole interaction

[a] Only the prominent central peaks of the vapor bands are recorded here. [b] Solvents used were CCl_4 (3800–1333 cm^{-1}), CS_2 (1333–450 cm^{-1}), and *n*-hexane (below 450 cm^{-1}). Concentrations were approximately 10% by volume. [c] Only one combination tone is suggested for each band although, for many, several possibilities arise. [d] Abbreviations used are: s = strong, m = medium, w = weak, sh = shoulder, P = polarized, D = apparently depolarized, FR = Fermi resonance.

which gives the deuterium isotope effect upon the ionization equilibrium of *t*-butyl chloride. A knowledge of all of the fundamental vibrational frequencies of the four molecular species in equilibrium[1] allows the use of Bigeleisen and Mayer's[1] formulation to calculate *K*. Complete vibrational assignments based on complete spectral data are not yet available and may not be obtained for the carbonium ions for some time. However, during earlier studies,[2] a calculation of all of the vibrational frequencies of the two carbonium ions was made and comparison of these with the limited spectral data obtainable showed no serious discrepancies; in particular, the higher frequency modes which are the most significant for the present purpose were reasonably well reproduced by the calculation. The present study of the vibrational spectra of *t*-butyl chloride and *t*-butyl-d_9 chloride was aimed at obtaining frequency values for all of the vibrational modes. Since values for spectrally inactive modes are also required, a calculation of all of the vibrational frequencies was made using assumed force constants based on those found suitable for other related molecules.

Experimental Section

Infrared absorption spectra were recorded using Beckman IR 9 and IR 11 instruments over the 50–3800-cm^{-1} range for the vapor, solution, and liquid phases; the uncertainties in the quoted wavenumber values, Tables I and II, should not exceed ±1 cm^{-1}. The vapor phase infrared spectra are reproduced in Figure 1. Raman spectra for the liquid phase were recorded photographically using a Hilger E612 spectrograph (16 A/mm) with mercury arc excitation (4358 A); wavenumber values are probably better than ±2 cm^{-1}. Qualitative depolarization measurements were made using Polaroid cylinders wrapped around the sample tube.[3]

Fractionally distilled *t*-butyl chloride, the purity of which was checked by vapor phase chromatography, was used. The *t*-butyl-d_9

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

(2) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, **86**, 1360 (1964).

(3) D. H. Rank and R. E. Kagarise, *J. Opt. Soc. Am.*, **40**, 89 (1950).

Table II.[a] Infrared and Raman Data for *t*-Butyl-d_9 Chloride

Infrared, cm^{-1}		Raman, cm^{-1}		
Vapor	Solution	Liquid	Depolarization	Assignment
3453 vvw				$\nu_{13} + \nu_{19}$
3262 vw	3257 vw			$\nu_1 + \nu_3$
3154 vvw				$\nu_2 + \nu_3$
3088 vw				$\nu_{13} + \nu_{20}$
2968 vw	2961 vw			H impurity
2936 vw	2929 vw			H impurity
2581 vvw				$\nu_{13} + \nu_{22}$
2495 vvw				$\nu_{13} + \nu_{23}$
2424 vw				$2\nu_{19}$
2391 vvw				$\nu_{15} + \nu_{23}$
2242 vs	2240 vs	2244 vs	D	ν_{13}
2223 vs	2222 vs	2227 vs	D (?)	ν_{14}, ν_1
		2191 w	P	$\nu_3 + \nu_5$
2163 vw	2156 vw			H-containing impurity
	2138 vw	2138 s	P	$\nu_4 + \nu_5$
2124 mw	2116 m	2117 vs	P	ν_2, ν_{15}
~2089 vw	2083 vw	2082 m	P	$2\nu_3$
~2079 vw	2071 vw			$\nu_3 + \nu_4$
~2061 vw	2050 vw	2048 s	P	$\nu_{19} + \nu_{20}$
1955 vvw				$\nu_{19} + \nu_{21}$
1926 vvw				$\nu_6 + \nu_{19}$
1866 vvw				$\nu_{16} + \nu_{20}$
1744 vw				$\nu_7 + \nu_{19}$
1570 vvw				$\nu_3 + \nu_7$
~1460 vvw				$\nu_{19} + \nu_{23}$
1387 vvw				$\nu_{16} + \nu_{22}$
1295 w	1285			$\nu_{16} + \nu_{23}$
	1260 vw			$\nu_{18} + \nu_{23}$
1217 s	1214 s	1216 m	D	ν_{19}
1200 vvw	1190 vvw			$\nu_{18} + \nu_{24}$
1124 s	1117 s	1119 mw	D (?)	ν_5
	1087 vw			$\nu_{21} + \nu_{22}$
1070 m, sh	1065 sh	1067 w		$2\nu_7$
1054 s	1048 s	1045 s	D	$\nu_3, \nu_{16}, \nu_{17}$
1016 vs	1005 vs	1005 vs	P	ν_4, ν_{18}
941 vvw				$\nu_{21} + \nu_{24}$
897 vvw				$\nu_7 + \nu_{22}$
824 w		824 mw	D	ν_{20}
740 w	740 w	740 w	D	ν_{21}
710 s	709 s	708 s	P	ν_6
	~529 sh, w			H impurity
534 vs	521 vs	523 vs	P	ν_7
491 vvw		486 vw		$\nu_{23} + \nu_{24}$
	398 vw			$2\nu_{24}$
352 w	347 w	343 w	D	ν_{22}
330 m	326 s	324 s	P	ν_8
261 m	263 s	263 s	D	ν_{23}
	193 vw			$\nu_7 - \nu_8$
	Gradually increasing absorption with peak beyond 50 cm^{-1} (liquid only)			Dipole–dipole interaction absorption

[a] Footnotes to Table I are applicable here also.

chloride was a sample of Merck Sharp and Dohme material which was used as received; the infrared spectrum showed the H content to be very low.

Discussion

Earlier studies of the vibrational spectra of $(CH_3)_3CX$ type molecules, with X = H and D[4,5] and F,[6] were based on the assumed, sterically favored C_{3v} structure. A microwave study[7] of *t*-butyl chloride gave the structure of the heavy atom skeleton but gave no information on the hydrogen positions. The C_{3v} structure was also assumed for the present purpose; tetrahedral angles and the following bond lengths were used: C–Cl = 1.803, C–C = 1.530, and C–H = 1.104 A. The calculated principal moments of inertia were, in atomic mass $(A)^2$ units: for *t*-butyl chloride, 109.48 and 170.44, and for *t*-butyl-d_9 chloride, 144.0 and 201.41. The band contours of the vapor infrared bands of these symmetric tops are predicted[8] to be similar in appearance for both perpendicular- and parallel-type vibrations; this prediction was confirmed and no assistance in making vibrational assignments was obtained from the band shapes. The spectra were assigned largely on the basis of the Raman polarization data and the results of a calculation of the vibrational frequencies which

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(4) J. C. Evans and H. J. Bernstein, *Can. J. Chem.*, **33**, 1037 (1956).

(5) J. K. Wilmshurst and H. J. Bernstein, *ibid.*, **35**, 969 (1957).

(6) D. E. Mann, N. Acquista, and D. R. Lide, *J. Mol. Spectry.*, **2**, 575 (1958).

(7) D. R. Lide and M. Jen, *J. Chem. Phys.*, **38**, 1504 (1963).

(8) S. L. Gerhard and D. M. Dennison, *Phys. Rev.*, **43**, 197 (1933).

Table III. Urey–Bradley Force Constants Used for Calculating Vibrational Frequencies of *t*-Butyl Chloride and *t*-Butyl-d_9 Chloride[a]

Force constant	Description	Value used[b]
K_{CCl}	C–Cl stretching	1.50
K_{CC}	C–C stretching	2.45
K_{CH}	C–H stretching	4.43
H_{CCl}	C$\hat{C}$Cl bending	0.10
H_{CC}	C$\hat{C}$C bending	0.84
H_{CH}	C$\hat{C}$H bending	0.32
H_{HH}	H$\hat{C}$H bending	0.51
F_{CC}	C···C interaction	0.33
F_{CCl}	C···Cl interaction	0.87
F_{HH}	H···H interaction	0.05
F_{CH}	C···H interaction	0.56
τ_{CH_3}	CH_3 torsion	0.03
ρ_{CH_3}	Intramolecular tension	0.025
ρ_{CC_3}	Intramolecular tension	−0.02

[a] The usual assumption that $F_{ij}' = -0.1F_{ij}$ was made. Units: K, F in mdynes/A; H, ρ, and τ in mdynes A/(radian)^2. [b] The values used for the three force constants associated with the Cl were based on the compilation of ref 10, and the remainder, ref 9.

was made using force constants transferred from other molecules, and which gave frequencies in good agreement with those observed for both molecules. This calculation used the Urey–Bradley force field with 14 constants chosen by comparison with those found suitable for the paraffins[9] and for some chlorinated hydrocarbons;[10] they are given in Table III. Programs prepared by Scherer[11] for the IBM 7090 computer were used to calculate the frequencies and the potential energy distributions of the normal modes. The approximate descriptions of the modes given in Table IV are based on these calculated data; Table IV also shows the comparison of calculated and observed frequencies, and this indicates that there are no gross errors in the frequency assignment.

A feature which introduces complexity into the correlation of the bands of the light and heavy molecules is the mixed nature of several modes which contain C–C stretching and CH_3 or CD_3 rocking motions. ν_5 and ν_6 in the a_1 species and ν_{19} and ν_{21} in the e species are quite different in the light and in the heavy molecules. This explains why Zeil, *et al.*,[12] who obtained partial infrared data for *t*-butyl-d_9 chloride but were without the benefit of a normal coordinate calculation, reached assignments which were quite different from those presently made. Mann, *et al.*,[6] on the other hand, were able to assign correctly most of the observed Raman bands of *t*-butyl chloride by comparison with the assignments for the fluoride and other *t*-butyl derivatives.

Table IV. Comparison of Calculated and Observed Frequencies[a] for $(CH_3)_3CCl$ and for $(CD_3)_3CCl$[b]

	$(CH_3)_3CCl$				$(CD_3)_3CCl$			
	Mode no.	Calcd, cm^{-1}	Obsd, cm^{-1}	Approx description	Mode no.	Calcd, cm^{-1}	Obsd, cm^{-1}	Approx description
	1	2973	2981	CH_3 stretch	1	2207	2226	CD_3 stretch
	2	2897	2937	CH_3 stretch	2	2080	2124	CD_3 stretch
	3	1445	1448	CH_3 def	3	1045	1054	CD_3 def
a_1	4	1368	1375	CH_3 def	4	1018	1016	CD_3 def
	5	1158	1155	CH_3 rock	5	1092	1124	$\nu(CC_3) + CH_3$ rock
	6	823	818	CC_3 stretch	6	699	710	$\nu(CC_3) + CH_3$ rock
	7	599	585	CCl stretch	7	555	534	CCl stretch
	8	378	372	CC_3 def	8	330	330	CC_3 def
	9	2971	...	CH_3 stretch	9	2202	...	CD_3 stretch
a_2	10	1438	...	CH_3 def	10	1032	...	CD_3 def
	11	980	...	CH_3 rock	11	746	...	CD_3 rock
	12	460	...	CH_3 tors	12	326	...	CD_3 tors
	13	2974	2993	CH_3 stretch	13	2210	2244	CD_3 stretch
	14	2972	2981	CH_3 stretch	14	2204	2226	CD_3 stretch
	15	2898	2937	CH_3 stretch	15	2080	2124	CD_3 stretch
	16	1444	1480	CH_3 def	16	1037	1054	CD_3 def
	17	1439	1456	CH_3 def	17	1034	1054	CD_3 def
	18	1364	1375	CH_3 def	18	1031	1016	CD_3 def
e	19	1220	1241	CC_3 stretch + CH_3 rock	19	1185	1217	CC_3 stretch + CD_3 rock
	20	992	1030	CH_3 rock	20	767	824	CD_3 rock
	21	927	927	CH_3 rock + CC_3 stretch	21	744	740	CD_3 rock + CC_3 stretch
	22	415	408	CC_3 def	22	356	352	CC_3 def
	23	314	301	CCl bend	23	279	261	CCl bend
	24	465	(~290)	CH_3 tors	24	331	(~210)	CD_3 tors

[a] Observed frequencies are, wherever possible, vapor phase values. [b] The CH_3 torsional modes are determined almost entirely (100% for the a_2 mode and 99% for the e mode) by the torsional force constant; the assumed value of this constant was apparently too large.

The Teller–Redlich products were satisfactory: for the a_1 class, the observed product was 0.195 and that calculated was 0.186; for the e species: observed 0.0510, and calculated 0.0502. The e species contains one mode, the CH_3 torsional mode, which was not observed directly, but estimates of 290 and 210 cm^{-1} for the light and heavy molecules, respectively, were based on bands assigned to the first overtones; these estimates are in agreement with the estimates for the torsional mode

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(9) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).

(10) T. Shimanouchi, *Pure Appl. Chem.*, 7, 131 (1963).

(11) J. R. Scherer and J. Overend, *J. Chem. Phys.*, **32**, 1720 (1960).

(12) W. Zeil, H. Buchert, H. Heel, and H. Pförtner, *Z. Elektrochem.*, **64**, 769 (1960).

values obtained[6] for *t*-butyl fluoride, 298 cm^{-1}, and for isobutane, 280 cm^{-1}, from their microwave spectra.

None of the four a_2 modes, which are inactive in Raman and infrared, was observed. The calculated values for ν_9, ν_{10}, and ν_{11} should not be greatly in error because similar modes in the other symmetry classes are reasonably well reproduced by the calculation. ν_{12}, the a_2 torsional mode, is, however, probably best estimated by comparison with the microwave values for the same mode in *t*-butyl fluoride, 223 cm^{-1}, and in isobutane, 225 cm^{-1}.[6] The values 220 and 170 cm^{-1} were assumed for *t*-butyl chloride and *t*-butyl-d_9 chloride, respectively.

Calculated Ionization–Equilibrium Isotope Effect

The Bigeleisen–Mayer formulation[13] of the equilibrium constant for the equilibrium

$$(\mathrm{CH_3})_3\mathrm{CCl} + (\mathrm{CD_3})_3\overset{+}{\mathrm{C}} \overset{K}{\rightleftharpoons} (\mathrm{CD_3})_3\mathrm{CCl} + (\mathrm{CH_3})_3\overset{+}{\mathrm{C}}$$

is

$K =$

$$\frac{\prod_i \frac{\mu_i(\mathrm{D})}{\mu_i(\mathrm{H})}\frac{1 - \exp\{-\mu_i(\mathrm{H})\}}{1 - \exp\{-\mu_i(\mathrm{D})\}}\exp\left\{\frac{1}{2}\left[\mu_i(\mathrm{H}) - \mu_i(\mathrm{D})\right]\right\}}{\prod_j \frac{\mu_j(\mathrm{D})}{\mu_j(\mathrm{H})}\frac{1 - \exp\{-\mu_j(\mathrm{H})\}}{1 - \exp\{-\mu_j(\mathrm{D})\}}\exp\left\{\frac{1}{2}\left[\mu_j(\mathrm{H}) - \mu_j(\mathrm{D})\right]\right\}}$$

where $\mu_i = hc\omega_i/kT$ and ω_i is the wavenumber of the *i*th normal mode. The product in the numerator is over the 36 normal modes of $(\mathrm{CH_3})_3\mathrm{CCl}$ and the 36 of $(\mathrm{CD_3})_3\mathrm{CCl}$, while the denominator runs over the 33 normal modes of $(\mathrm{CH_3})_3\mathrm{C}^+$ and of $(\mathrm{CD_3})_3\mathrm{C}^+$. The carbonium ion frequencies were taken directly from the calculation[14] described in ref 2, where a planar carbon skeleton and C_{3h} symmetry were assumed. The frequencies, which were not all quoted in the earlier report, were for $(\mathrm{CH_3})_3\mathrm{C}^+$: 2799, 2734, 1438, 1360, 970, 756 for the a′ species; 2800, 1444, 1076, 315, 271 for the a′′ species; 2802, 2737, 1445, 1354, 1298, 941, 403 for the e′ species; 2800, 1439, 980, 282 cm^{-1} for the e′′ species; for $(\mathrm{CD_3})_3\mathrm{C}^+$: 2074, 1964, 1070, 1032, 738, 669 (a′ species); 2076, 1037, 892, 272, 192 (a′′ species); 2082, 1964, 1277, 1038, 1022, 748, 340 (e′ species); 2077, 1034, 754, 203 (e′′ species). For the *t*-butyl chloride pair, liquid phase frequencies were chosen for the observed modes, the calculated values for the a_2 modes, and the estimated values for the two torsional modes. The calculated values for K at two temperatures were 2.358 (25°) and 2.511 (5.686°). The contribution made by the CH and CD stretching modes alone was approximately 2.0.

There appear to be no experimental data for direct comparison, but these $K_\mathrm{H}K_\mathrm{D}$ values are strikingly similar to the experimental rate ratios, $k_\mathrm{H}k_\mathrm{D}$, for the solvolysis of *t*-butyl chloride and *t*-butyl-d_9 chloride in water–ethanol solutions[15] and in a number of other solvent mixtures;[16] thus, the $k_\mathrm{H}/k_\mathrm{D}$ values observed by Hakka, *et al.*,[15] were 2.387 at 25° and 2.542 at 5.686°. If we accept the hypothesis that this is significant, it implies that the transition state in the rate-determining step of the solvolysis of *t*-butyl chloride is structurally similar to the carbonium ion. It is generally accepted that this reaction proceeds by the SN1 mechanism for which the rate-determining step is

$$(\mathrm{CH_3})_3\mathrm{CCl} \overset{K_\mathrm{H}^*}{\rightleftharpoons} \text{transition state} \rightleftharpoons (\mathrm{CH_3})_3\overset{+}{\mathrm{C}} + \mathrm{Cl}^-$$

so that, according to absolute reaction rate theory,[17] the isotope effect on the reaction rate is

$$\frac{k_\mathrm{H}}{k_\mathrm{D}} = \frac{X_\mathrm{H}K_\mathrm{H}^*}{X_\mathrm{D}K_\mathrm{D}^*}$$

where the X values are the transmission coefficients and the K^*'s are the constants of the quasi-equilibrium between the transition state and alkyl halide. The transmission coefficient ratio depends on the model assumed for the transition state, but it should not depart appreciably from unity for this reaction.[17] One approximation, which considers the ratio of transmission coefficients to be equivalent to the ratio of effective reduced masses along the reaction coordinate, gives in this case a ratio of 1.028 when the *t*-butyl group is taken as a point mass.

However, the calculation described here applies strictly to the equilibrium of molecules uninfluenced by solvation, whereas the experimental data quoted were obtained in solution. Closer comparison of calculated and observed data and an attempt to attribute further mechanistic significance to the small differences between these data seem unwarranted for this reason, and also for the reason that the vibrational data for the two cations are only partially supported by experimental data.

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(13) E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 125 (1963).

(14) Note that the list of force constants given in Table XI of ref 2 contains a minor error; the set actually used did not include the small C···C (*cis*) interaction constant.

(15) L. Hakka, A. Queen, and R. E. Robertson, *J. Am. Chem. Soc.*, **87**, 161 (1965).

(16) G. J. Frisone and E. R. Thornton, *ibid.*, **86**, 1900 (1964).

(17) J. Bigeleisen and M. Wolfsberg, *Advan. Chem. Phys.*, **1**, 15 (1958).