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Chlorine Kinetic Isotope Effect Models. II.[1] Vibrational Analysis and KIE Calculations of *tert*-Butyl Chloride Transition State Models

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Abstract: A transition state model is advanced for the methanol solvolysis of *tert*-butyl chloride, and various transition state structures are evaluated in terms of their calculated chlorine kinetic isotope effects. The best model gives chlorine KIE values of 1.01087 and 1.00951 at 10 and 60°, respectively, *vs.* the experimentally determined values of 1.01087_7 and 1.00953_3, and does not require large imaginary values of ν_L. The influence of transition state geometry on calculated KIE is appreciable; there is a good correlation between the transition state carbon–chlorine bond length and the difference in KIE values at 10 and 60°. The degree of planarity of the $C(CH_3)_3$ group correlates well with the temperature-independent factor ν_{1L}/ν_{2L}, as does the carbon–methyl group bond length. The most probable transition state configuration in the methanol solvolysis of *tert*-butyl chloride is estimated to be C–Cl = 1.89 Å, C–CH_3 = 1.50 Å, and $Z(CH_3)$ = −0.16 Å, relative to the central carbon. The effects of various transition state force constant assumptions are studied, and methods of estimating transition state force constants are enumerated.

Heavy atom kinetic isotope effects (KIE) have shown promise as a useful tool both for studying fundamental chemical processes and for elucidating the transition state.[2–8] Unfortunately, this promise has only been partially fulfilled to date, and most of the information about transition state structures has been obtained by inference.[6–14] In testing other techniques for improving this situation Wolfsberg and Stern have extensively studied the KIE temperature dependence of model systems resembling methyl halides but have cautioned against applying their generalized results to specific experimental systems.[15] Stern and coworkers[16,17] have also made a rather elegant study of the variation in temperature dependence of isotope equilibrium. Because these were equilibrium calculations, somewhat less information could be inferred about transition states. For intramolecular decarboxylation reactions Yankwich and coworkers have made a very complete model study of the temperature dependence and have derived conclusions about the transition state for this class of reactions.[18,19]

As a continuation of previous work from these laboratories where the ground state force constants and isotopic separations of the skeletal vibrational frequencies of *tert*-butyl chloride were considered using a methyl chloride type model,[20] it was decided to attempt

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to describe the transition state in terms of the transition state geometry, the transition state force field, and the calculated temperature dependence of the kinetic isotope effect for this model. Particular emphasis was placed on determining the effect that each of several geometric parameters (C–Cl transition state bond length, degree of nonplanarity, and carbon–carbon transition state bond length) has on the temperature dependence and final KIE value. The influence of off-diagonal (interaction) force constants and bending vibrations was also of special interest. It was expected that in the studies with the transition state models, it would also be possible to evaluate several commonly used approximations and determine their accuracy relative to the more rigorous calculations involving the complete partition functions.

Selection of Transition State Models. As in the ground state case, methyl groups were assumed to be point masses, the skeletal vibrations were assumed to be separable from hydrogen modes, and the hydrogen vibrations were assumed to be negligibly affected by chlorine substitution on the central carbon. The choice of a transition state geometry is more complicated than in the previously discussed ground state case[20] because no vibrations can be measured directly. The approach must essentially be that of choosing extremes, which encompass all reasonable transition state geometries, then working within these extremes. The three geometric parameters, which together completely describe the molecule and whose extremes must be determined, are the carbon–chlorine distance, the carbon–methyl distance, and the Z coordinate of the methyl groups relative to the central carbon, where the carbon–chlorine bond lies colinear with the Z axis. One might reasonably expect these extremes to be represented by the reactant and product cation geometries. Olah and coworkers[21] have shown that the carbon skeleton of *tert*-butyl cation is planar by correlation of its infrared spectrum with that of trimethylboron, a molecule with which it is isoelectronic. However, the central carbon–methyl distance is not well known. Olah, *et al.*,[22] used a value of 1.50 Å for their normal coordinate analysis of the cation, but other workers have used values as small as 1.42 Å, which is the measured (nonaromatic) intercarbon distance for the crystalline trimethyl cation.[23,24] A conservative assignment for the *tert*-butyl chloride case might be between the bounds 1.42 and 1.53 Å. For the carbon–chlorine distance preliminary calculations[25] have shown that 4.5 Å (2.5 times the ground state C–Cl distance) could be taken as the extreme. Finally, the methyl Z coordinate which represents the degree of planarity, or nonplanarity, of the $C(CH_3)_3$ portion might be expected to have a value of 0 Å if completely planar. Values of Z between the planar extreme and the ground state value (−0.47 Å) were chosen for this parameter.

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Using these boundaries, a set of models was generated as shown in Table I where one or more of these parameters was varied. The MMI (mass times moment of of inertia) term ratios are fixed by the geometry,[15] and these are also listed as part of Table I. In order to probe the importance of each parameter and its influence on the KIE calculations, model 19 was chosen as the primary planar model and model 23 was chosen as the nonplanar model. Other models were generated by variation of one or two parameters from these basic configurations. These choices were made on the basis of preliminary calculations initiated from the expectation (Hammond postulate[26]) that the transition state for the SN1 reaction should more closely resemble the product than the reactant. On this basis, the most reasonable central carbon–methyl distance was taken to be 1.50 Å, in accordance with Olah's work. Similarly, the $C(CH_3)_3$ fragment was expected to be planar or near planar. In choosing the C–Cl bond length, qualitative aides such as Pauling's[27] and Badger's[28] rules indicate that even small displacements from ground state equilibrium cause drastic changes in force constants. This could be expected to be even more severe in solution, where solvent shielding is possible. In other calculations when changes in bond length have been made,[7,14,15] the maximum changes seem to be no more than 25% of the ground state bond distance, and most of the changes are on the order of a few per cent. Both Models 19 and 23 increase the C–Cl distance only 5% over the ground state value.

Table I. Initial Transition State Models

Model	Bond distances, A (C–Cl)	(C–CH_3)	$Z(CH_3)$[a]	MMI[b]
0[c]	1.80	1.53	−0.473	1.0000
16	1.80	1.46	0.0	1.0025
17	1.98	1.46	0.0	1.0011
18	1.89	1.53	0.0	1.0026
19	1.89	1.50	0.0	1.0023
20	1.89	1.46	0.0	1.0018
21	1.89	1.42	0.0	1.0014
22	1.89	1.50	−0.01	1.0022
23	1.89	1.50	−0.16	1.0012
24	1.89	1.50	−0.32	1.0001
25	1.89	1.50	−0.473	0.9991
26	1.80	1.50	0.0	1.0030
27	1.98	1.50	0.0	1.0015
28	2.16	1.50	0.0	1.0002
29	2.70	1.50	0.0	0.9972
30	4.50	1.50	0.0	0.9927
31	1.89	1.50	−0.08	1.0017
32	1.89	1.50	−0.24	1.0007
33	1.80	1.50	−0.16	1.0019
34	1.98	1.50	−0.16	1.0005
35	1.89	1.53	−0.16	1.0015
36	1.89	1.46	−0.16	1.0007

[a] The axis Z lies colinear with the C–Cl bond and is centered about the central carbon. [b] $[(I_{35}\ddagger/I_{37}\ddagger)/(I_{35}/I_{37})]^{1/2}[(M_{35}\ddagger/M_{37}\ddagger)/(M_{35}/M_{37})]^{3/2}$. [c] Ground state configuration.

Selection of the Transition State Force Field and Evaluation of Transition State Models. The choice of a transition state force field for these calculations is difficult because a unique set is not apparent, but a reasonable set of force constants may be selected,

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Table II. Correlation between *tert*-Butyl Chloride and *tert*-Butyl Cation Skeletal Numbers

tert-Butyl chloride (C_{3v} symmetry)				*tert*-Butyl cation (D_{3h} symmetry)		
Skeletal no.[a]	Obsd freq[b]	Symmetry type	Approx kinetic description	Symmetry type	Obsd freq[c]	Skeletal no.[a]
ν_1	806	a_1	Symmetric methyl group stretch	a_1'	667?	ν_1
ν_2	560	a_1	C–Cl stretch			
ν_3	370	a_1	Symmetric methyl group deformation	a_2''	347	ν_2
ν_4	1210[d]	e	Degenerate methyl group stretch	e′	1295	ν_3
ν_5	404	e	Degenerate methyl group deformation	e′	306	ν_4
ν_6	296	e	CH_3–C–Cl deformation			

[a] Frequency numbers are assigned assuming point methyl groups and ignoring hydrogen vibrations. [b] Liquid-phase data; see ref 20. [c] Solution phase, taken from ref 21. [d] Adjusted value, see ref 20.

Table III. Summary of Force Field Variations Studied for Liquid Models[a,b]

Force field	F_{11}	F_{22}	F_{33}	F_{12}	F_{13}	F_{23}	F_{44}	F_{55}	F_{66}	F_{45}	F_{46}	F_{56}
Ground[c]	4.35	2.740	0.965	−0.244	0.851	−0.827	4.271	1.384	1.177	0.918	1.382	0.686
1[d]	4.785	0.529	1.320	−0.244	0.851	−0.827	4.697	0.702	1.177	0.918	1.382	0.686
2		0.539										
3		0.000										
4								1.405				
5									0.897			
6				−0.268	0.936	−0.910				1.010	1.520	0.755
7				−0.122	0.426							
8		0.000		−0.122	0.426							
9		0.000		−0.122	0.426	−0.413						
10		0.705	1.026		0.851							

[a] Symmetry factored force constants, mdyn/Å. [b] All constants associated with redundant coordinate S_r assumed zero. [c] Force field for ground state from ref 20. [d] Reference force field; all other force fields identical except where entry noted.

however, using the previously reported ground state symmetry coordinates[20] to generate models for comparison with experimental KIE data. For the purpose of this study the experimental data are chlorine KIE values of 1.01087 at 10° and 1.00953 at 60° for a 0.05 *M* *tert*-butyl chloride reaction in methanol with 0.25 *M* lithium methoxide added.[8]

The correlation between the skeletal modes of *tert*-butyl chloride and *tert*-butyl cation is shown in Table II. Not only does the *tert*-butyl cation lack two vibrations present in *tert*-butyl chloride, but there are two distinct types of symmetry species in the cation nondegenerate modes, whereas all nondegenerate modes of *tert*-butyl chloride and the transition state are of the same symmetry species. This means that *tert*-butyl cation force constants are not easily transferred to the transition state. Faced with this obstacle, a slightly different approach was taken. It was assumed that transition state frequencies would lie not too far beyond the bounds of reactant and product frequencies and that they would resemble product frequencies somewhat more than reactant frequencies (again using the Hammond postulate[26]). It was further assumed that carbon–methyl stretch frequencies would increase somewhat from their ground state values, due to the developing positive charge on the central carbon.[22,23] All interaction constants were assumed to be unchanged initially from their ground state values, as was the CH_3–C–Cl bending constant. (Because the reaction coordinate is strongly coupled in the ground state, a particular effort was made to test this assumption; the results will be discussed in a later section.) The degenerate deformation constant, F_{55} (see Table III), was adjusted to give a frequency closer to the corresponding *tert*-butyl cation frequency. As the $(CH_3)_3C$ portion of the model becomes more planar, the symmetric methyl group deformation ν_3 is less well described by symmetry coordinate S_3 (see ref 20), due to the introduction of an additional redundancy condition; however, no additional coordinates were introduced, in order that all models might use the same symmetry coordinate and force fields. Due to this redundancy, small changes in $F_{33}^{\ddagger}$ did not strongly affect $\nu_3^{\ddagger}$ but did change the calculated KIE values somewhat. $F_{33}^{\ddagger}$ could, therefore, be used as a diagnostic parameter to bring the particular model KIE value at 10° closer to the experimental value.[8] The C–Cl stretch constant $F_{22}^{\ddagger}$ was chosen to generate a small imaginary value for ν_L. Additional force fields which varied one or two parameters from this configuration were then studied to determine the importance of the initial assumptions and are shown in Table III. Particular emphasis was placed on determining the importance of the off-diagonal force constants F_{12}, F_{13}, and F_{23}.

Kinetic Isotope Effect Calculations and Variations in the Force Field. Once the transition state force field was chosen, and a set of transition state frequencies calculated, the KIE, the temperature-independent factor (TIF), the temperature-dependent factor (TDF), and Wigner tunnel coefficients could be calculated using the partition function equations from the Teller–Redlich equivalent forms of ref 4, 15, and 29. The pertinent results for model 19 and force field 1 over the range of experimental interest are shown in Table IV using the terminology of Wolfsberg and Stern and are representative of all such output. Within the limits of computer error, the Teller–Redlich temperature-dependent factor (VP·EXC·ZPE) was identical with the equivalent partition function expression.[25] This feature was expected because a simple harmonic oscillator model was used.

Because the evaluation of all models with all force fields produces voluminous data, some technique for

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Table IV. KIE Output for Model 19 Using Force Field 1[a]

Temp, °C	KIE	ZPE	EXC·ZPE	VP·EXC·ZPE	Tunnel coefficient	Tunnel × KIE
0.000	1.01140	1.01253	1.00912	1.00619	1.00002	1.01142
5.000	1.01120	1.01230	1.00893	1.00600	1.00002	1.01122
10.000	1.01101	1.01208	1.00874	1.00581	1.00002	1.01103
15.000	1.01083	1.01187	1.00856	1.00563	1.00002	1.01085
20.000	1.01066	1.01167	1.00839	1.00546	1.00002	1.01068
30.000	1.01034	1.01128	1.00806	1.00514	1.00001	1.01035
40.000	1.01004	1.01092	1.00777	1.00484	1.00001	1.01006
50.000	1.00977	1.01058	1.00750	1.00457	1.00001	1.00978
60.000	1.00952	1.01026	1.00725	1.00432	1.00001	1.00953

[a] Further output: calculated ν_{1L}/ν_{2L} = 1.0052; VP term 0.99710; the decomposition frequencies ν_{1L} and ν_{2L} are 38.444*i* and 38.246*i*; $\Delta\nu_L$ = 0.1980*i*.

are summarized as follows. The effect of including a small real ν_L in the partition function (force field 2) did not change the calculations markedly. Although both the excitation energy and zero-point energy terms associated with this mode change as functions of temperature, they change in *opposite* directions, and the net change of their product, which is the real ν_L contribution to the partition function, is slight. When ν_L is a large imaginary number (see Table VI, force field 3), the corrected KIE-10 and 10–60 difference values of 1.01358 and 18.6, respectively, are markedly different from the experimentally observed[8] values of 1.01087 and 13.4. The use of essentially a ground state force field for the degenerate modes did not change the KIE results appreciably. However, when the CH_3–C–Cl bending

Table V. Summary Data for Models 16–30 Using Force Field 1

Model	KIE[a]	10^4 × diff[b]	ν_{35L}/ν_{37L}	ZPE[a]	EXC·ZPE[a]	VP	VP·EXC·ZPE[a]
0	1.01960	14.6	1.0140	1.01566	1.01960	0.9862	1.00556
16	1.01138	14.3	1.0058	1.01171	1.00884	0.9968	1.00558
17	1.01183	15.5	1.0058	1.01313	1.01077	0.9953	1.00603
18	1.01062	14.9	1.0048	1.01185	1.00803	0.9978	1.00580
19	1.01101	14.9	1.0052	1.01208	1.00874	0.9971	1.00581
20	1.01162	15.0	1.0058	1.01245	1.00983	0.9960	1.00582
21	1.01211	15.0	1.0062	1.01275	1.01070	0.9952	1.00583
22	1.01146	14.9	1.0056	1.01224	1.00925	0.9966	1.00581
23	1.01663	15.1	1.0108	1.01433	1.01541	0.9905	1.00581
24	1.01909	15.2	1.0132	1.01575	1.01894	0.9871	1.00581
25	1.02004	15.2	1.0141	1.01658	1.02092	0.9852	1.00582
26	1.01077	14.3	1.0052	1.01130	1.00770	0.9979	1.00556
27	1.01123	15.5	1.0052	1.01278	1.00969	0.9964	1.00602
28	1.01158	16.4	1.0052	1.01395	1.01137	0.9951	1.00637
29	1.01223	18.0	1.0052	1.01630	1.01506	0.9921	1.00702
30	1.01296	19.9	1.0052	1.01922	1.02042	0.9876	1.00774

[a] Values calculated at 10°. The experimental value is 1.01087.[8] [b] [(KIE at 10°) − (KIE at 60°).] The experimental value is 13.4 × 10^{-4}.[8]

Table VI. Comparison of Results for Model 19 with Force Fields 1–10

Force field no.	KIE[a]	10^4 × diff[b]	ν_{35L}	ν_{35L}/ν_{37L}	ZPE[a]	EXC·ZPE[a]	VP·EXC·ZPE[a]	Corrected[c] KIE[a]	Corrected[c] 10^4 × diff
1	1.01101	14.9	38.44*i*	1.0052	1.01208	1.00874	1.00581	1.01103	15.0
2	1.01095	14.9	19.55	1.0051	1.01205	1.00867	1.00580	1.00579	14.8
3	1.01233	15.3	317.68*i*	1.0063	1.01282	1.01005	1.00595	1.01358	18.6
4	1.01099	14.8	38.44*i*	1.0052	1.01177	1.00872	1.00579	1.01101	14.9
5	1.01170	16.8	38.44*i*	1.0052	1.01484	1.01052	1.00650	1.01172	16.9
6	1.00980	14.9	147.26*i*	1.0040	1.01197	1.00753	1.00574	1.00999	15.4
7	1.01206	15.0	36.92	1.0062	1.01244	1.00978	1.00584	1.00582	14.9
8	1.01263	15.2	314.41*i*	1.0067	1.01276	1.01035	1.00590	1.01392	18.6
9	1.02051	17.7	140.14*i*	1.0137	1.01702	1.01821	1.00673	1.02107	19.1
10	1.00603	13.6	34.27*i*	1.0007	1.00950	1.00376	1.00533	1.00606	13.6

[a] Values calculated at 10°. [b] [(KIE at 10°) − (KIE at 60°).] [c] Correction is from the contribution of Wigner tunnel coefficient for imaginary frequencies or from including ν_L in the partition function for real frequencies.

comparing the computed KIE and the experimental KIE was needed. Practically, it is convenient to report the KIE data at 10° (KIE-10) and the difference between that value and the 60° KIE value (10–60 difference). Because both experimental[8] and calculated data vary linearily with $1/T$ over this range, these two parameters are equivalent to the intercept and slope of the linear function and completely define it. The results of the variations of all the force fields on all the models are available[25] but only those for force field 1 on models 16–30 and for model 19 with force fields 1–10 are shown in Tables V and VI, respectively. The conclusions derived from model 19 under the variations shown in Table VI are similar to those from other models and mode was decreased (force field 5), the 10–60 difference is significantly greater than when using force field 1. When all off-diagonal constants were increased by 10 per cent (force field 6), the effects were relatively minor. For the a_1 symmetry block interaction constants, it was necessary to study the effects of three separate force fields (7–9) to isolate the effects due only to changes in these constants. Because the ground state is strongly coupled large changes in these force constants generate large changes in ν_L and large tunnel coefficients which in turn cause additional changes in the calculated KIE. When only $F_{12}^{\pm}$ and $F_{13}^{\pm}$ were reduced by 50%, there were appreciable changes in the KIE-10 (1.01206 *vs.* 1.01101), but only slight changes in the 10–60 difference.

When 50% values were used for all three interaction constants, while $F_{22}^{\ddagger}$ was held at zero, it became apparent that the choice of $F_{23}^{\ddagger}$ is critical and introduces appreciable changes in the KIE temperature dependence.

Variation of the degenerate diagonal constants shows that the calculated KIE data remains virtually the same, unless the CH_3–C–Cl bending mode is decreased appreciably. This finding implies that the choice of these constants is not crucial, except for $F_{66}^{\ddagger}$, which clearly plays a sizable role in determining the calculated temperature dependence. The reason for this is that of the three degenerate modes, only ν_6 shows any appreciable (calculated) isotopic splitting in the ground state. Because we have also observed that isotopic splittings generally decrease when frequencies are lowered, lowering $F_{66}^{\ddagger}$ decreases $\nu_6^{\ddagger}$ and $\Delta\nu_6^{\ddagger}$, again generating a smaller transition state shift sum and a larger zero-point energy difference and temperature dependence. Conversely, slightly changing $\nu_4^{\ddagger}$ and $\nu_5^{\ddagger}$ will have essentially no effect, since calculated isotopic shifts in these frequencies are only very small portions of the total sum. Here, too, the data indicate that the bending motion associated with ν_L is essentially unperturbed until the bond is broken.

From these observations it became evident that for the planar model 19, the value used for $F_{33}^{\ddagger}$ seemed rather high and $\nu_3^{\ddagger}$ and $\nu_4^{\ddagger}$ were somewhat further from the *tert*-butyl cation values than might reasonably be predicted. In addition, the calculated temperature dependence varied from the experimental one by over 10%. Because the C–Cl bond length calculations indicated that the transition state might be somewhat less product like than previously expected, the slightly nonplanar model 23 was chosen as a central model for the force field variation. The best fit to the experimental data occurred with force field 10 and model 23 (as shown in Table VIII). The detailed evaluation of other force fields and models is reported elsewhere.[25]

Discussion

One of the objectives of this work was to evaluate the transition state in terms of transition state geometry and to limit the large number of possible models by comparison of the assumed models with experimentally determined KIE values from solvolysis data. This approach was used implicitly in Table VII and is used in choosing the most likely transition state models for closer scrutiny. The two criteria used to evaluate the models were the KIE-10 value and the 10–60 temperature difference. In contrast to other models based on different solvents and different systems,[4,15,30] the transition state geometry of this model has a rather large influence on calculated results. The three geometric parameters which describe the model (C–Cl distance, C–CH_3 distance, and methyl Z coordinate) are discussed in order of decreasing influence on KIE calculations. Unless noted otherwise, results are cited for models using force field 10; however, these results are representative of the results from other force fields also.

Table VII. Comparison of Experimental KIE with Calculated Results Using Force Field 10 and Model 23

T, °C	Exptl[a,b]	Calcd
10	1.01087 ± 0.00002	1.01087
20	1.01058 ± 0.00007	1.01055
30		1.01026
40	1.00994 ± 0.00002	1.00999
50		1.00974
60	1.00953 ± 0.00006	1.00951

[a] Reference 8. [b] Average deviation from the mean; estimated precision better than ±0.00015.

C–Cl Distance. The 10–60 difference increases linearly with the C–Cl bond length over the first 10–20% increase in C–Cl length; beyond 20% the relationship is nonlinear, and eventually the 10–60 difference approaches an asymptotic limit.[25] This pattern is repeated, without exception, for all calculations made. It is interesting to note that due to the symmetry of the molecule changes in C–Cl bond length scarcely affect any of the symmetric vibrations. The principal effect of increasing this bond seems to be a lowering of the CH_3–C–Cl bending mode; the 10–60 differences were also high in force field 5 (see Table III) when this bending frequency was decreased. These results suggest that it is possible to adjust the 10–60 temperature dependence by varying the C–Cl bond length.

Methyl Group Z Coordinate. The degree of planarity of the $C(CH_3)_3$ carbons appears to have an appreciable effect on the calculated KIE values. Decreasing the planarity of the model increases primarily the KIE-10 value and the correlation is approximately linear from $Z = 0$ to $Z = -0.24$ Å.[25] (The KIE-10 value for $Z = 0$ was 1.00603, whereas it rose to 1.01670 at $Z = -0.24$ Å.) It might have been considered that the changes in KIE-10 were purely functions of the changes in moments of inertia, but Table I reveals that the trend of changes in the MMI term would alter the KIE-10 values in the *opposite* direction. Vibrational data reveal that the principal change in the calculated transition state vibrations is an increasing C–Cl isotopic splitting as the model becomes more nonplanar. This is confirmed by the fact that the temperature-dependent factor (VP·EXC·ZPE) is 1.00532 ± 0.00001 for all these cases, while the temperature-independent factor (ν_{35L}/ν_{37L}) varies from 1.0007 to 1.0113. Thus it also appears possible to adjust the temperature-independent factor by varying the degree of planarity. When it is possible experimentally to measure the TIF, this effect may then be used to estimate the transition state degree of planarity.

C–CH_3 Distance. If the variation of the KIE-10 is plotted[25] *vs.* C–CH_3 bond length for planar models 18–21, or nonplanar models 23, 35, or 36 ($Z = -0.16$ Å), the 10–60 differences and the temperature-dependent factors (VP·EXC·ZPE) are essentially unchanged, but the KIE-10 values increase for decreasing C–CH_3 bond lengths, again in contrast to the trend of MMI changes. Thus, the carbon–methyl bond distance can also be used to change the temperature-independent factor, without appreciably changing the TDF, but because the changes are smaller, it is apparent that the carbon–methyl distance is a considerably less sensitive parameter than the degree of planarity. The data also indicate that this parameter is slightly more sensitive for nonplanar than for planar configurations.

Decomposition Frequency. Considerable discussion

(30) M. J. Stern and M. Wolfsberg, *J. Pharm. Sci.*, **54**, 849 (1965).

has evolved concerning the choice of a value for ν_L. Results have been presented where ν_L was a large imaginary number, and the tunnel coefficient was used to bring calculated values into correspondence with observed data.[7] Other workers have included the contribution of a small real ν_L in the KIE partition function expression.[14] As was noted earlier, the contribution of a small real ν_L to the partition function is a constant near room temperature, for reasonably small $\Delta\nu_L$. This contribution will change the KIE-10 but should not change the temperature dependence (slope) of a ln (KIE) *vs.* T^{-1} plot. Moreover, if the real ν_L is factored out just as if it were imaginary, results essentially identical to those calculated for a small imaginary ν_L are achieved. Because the inclusion of small real ν_L modes does change the KIE-10, it is probably not valid to include them in the partition function expressions. When large tunnel coefficients are used to achieve considerably higher KIE values, the KIE 10–60 value is altered appreciably, because the tunnel coefficients are temperature dependent. For these *tert*-butyl chloride transition state models, those corrections which appreciably increased the calculated KIE values also elevated temperature dependences far above the corresponding experimentally measured values. This indicates that models requiring large imaginary ν_L values and involving large tunnel corrections are not realistic descriptions of the transition state structures.

Evaluation of the Final Model and Calculations Involving Fewer Frequencies. As can be seen from Table VII the use of force field 10 with model 23 adequately reproduces both the experimentally observed KIE-10 and the experimentally observed temperature dependence, within the limits of the experimental uncertainty. Because neither the model nor the force field is uniquely determined, however, the agreement must be interpreted qualitatively rather than quantitatively. Thus, the transition state carbon–chlorine bond length is probably closer to 1.89 Å than to 1.98 or 1.80 Å, and the carbon–methyl distance is probably closer to 1.50 Å than to 1.53 or 1.46 Å, while the methyl Z coordinate is more nearly −0.16 Å than −0.24 or −0.08 Å. These limits permit allowance for the various assumptions made in generating the model and force field. If model 23 can be taken as a reasonable representation of the transition state geometry, however, it is possible to use it to evaluate other approaches for calculation of the kinetic isotope effects.

The individual Bigeleisen G factor calculations[31,32] were performed on the various models and the data are reproduced elsewhere.[25] Because the full G factor calculations gave essentially identical results when compared with partition function calculations, these data may be used to estimate the error involved in deleting the contribution of various frequencies. For instance, for model 23 in force field 10, neglecting all three degenerate frequencies in ground and transition state would generate a TDF of 1.00501, rather than 1.00531. In this case, the difference between the $G(u)\Delta u$ sum including the degenerate vibrations and that excluding the degenerate vibrations is only about 6% because there is not much change from the ground state. This error becomes greater if a greatly elongated C–Cl bond is used, and it also becomes greater as more frequencies are deleted from the summation. Perhaps the greatest surprise was the size of the term contributed by ν_1, which is 15% of the a_1 mode sum. Clearly calculations attempting to reproduce experimental data must take this term into account, or find some way of compensating for it.

In Table VIII, data are presented which enable a comparison to be made between the two calculation methods and the number of vibrational frequencies which are used in simplified G factor calculations. In each case, the complete calculation factor of 5.31×10^{-3} for model 23 and force field 10 is assumed to be correct to provide a point of reference and because of the previous arguments. Thus, the use of ν_2 and ν_3 without any attempt to estimate $\nu_3^{\ddagger}$ is accurate to about 11%. The last calculation in the table is equivalent to estimating $G(u_3^{\ddagger})\Delta u_3^{\ddagger} \simeq 0.20G(u_3)\Delta u_3$. Since $G(u_3^{\ddagger})\Delta u_3^{\ddagger}$ was actually closer to 60% $G(u_3)\Delta u_3$ for model 23, one way of compensating for a missing u_1 contribution is to underestimate the $G(u_3^{\ddagger})\Delta u_3^{\ddagger}$ term. Whether this procedure will work for less symmetric molecules is unclear at this time, but what is clear is that frequencies other than the nominal C–Cl stretch ν_2 must be examined for appreciable contributions to the KIE terms.

Table VIII. Calculated TDF Using Various Combinations of Frequencies

Freq used in calculation	$10^3 \times [\Sigma G(u)\Delta u - \Sigma G(u^{\ddagger})\Delta u^{\ddagger}]$	% error[a]	TDF
$\nu_1 - \nu_6$; $\nu_1^{\ddagger}$, $\nu_3^{\ddagger} - \nu_6^{\ddagger}$	5.31	0	1.00531
$\nu_1 - \nu_3$; $\nu_1^{\ddagger}$, $\nu_3^{\ddagger}$	5.01	−6	1.00501
ν_2, ν_3; $\nu_3^{\ddagger}$	3.98	−25	1.00398
ν_2	2.78	−48	1.00278
$\nu_1 - \nu_3$	6.95	+31	1.00695
ν_2, ν_3	5.89	+11	1.00589
ν_2, ν_3; $\nu_3^{\ddagger} = \nu_3$, $\Delta\nu_3^{\ddagger} = 0.2\nu_3$	5.27	−1	1.00527

[a] Calculated assuming that the 5.31×10^{-3} value for model 23 force field 10 is current.

Conclusions

The reported data clearly show that the TIF/TDF and heavy-atom approximations give equivalent results to the more rigorous partition function calculations, when all ground state and transition state *skeletal* frequencies are evaluated. Ignoring all frequencies associated with atoms further than two bonds away from the leaving group (*i.e.*, assuming identical hydrogen modes for both chlorine isotopes) appears to be successful in this instance. The practice of using large imaginary ν_L values, and their commensurate temperature-dependent tunnel coefficients, to bring calculated values into correspondence with experimental values will probably have to be discarded in systems that show appreciable temperature dependence.

The data indicate that essentially the same results are observed for small real or small imaginary vibrations and that variation of the geometry of the transition state appears to be a more reasonable way of fitting the data. It is also found that the practice of using only the nominal carbon–chlorine stretching frequency and isotopic shift must be discarded. It does appear, however, that

(31) J. Bigeleisen and M. Goeppert-Mayer, *J. Chem. Phys.*, 15, 261 (1947).

(32) M. Dole, "Introduction to Statistical Thermodynamics," Prentice Hall, Englewood Cliffs, N. J., 1954, pp 240–241.

reasonably reliable calculations may be made by selectively excluding noncrucial degenerate modes. Furthermore, the kinetic isotope effect temperature dependence appears to be more reliable than the KIE measured at any one value, as a diagnostic tool for transition state models. Similarly, it should provide a more reliable experimental probe, since relative and reproducible errors tend to cancel in the slope determination.

A study of the force field variations also indicates certain assumptions which may be used for transition state calculations. (1) If ν_L is of the same symmetry as any other transition state vibration, and if the ground state interaction with that vibration is strong, the transition state interaction remains strong until the bond is broken. (2) Similarly, until the departing fragment actually ceases to be bound, there is little indication that the associated bending mode must be changed. Inordinately large 10–60 differences were observed whenever ν_6 decreased appreciably, whether from force constant adjustment (force field 5) or changes in geometry (models 27–30). (3) Slight changes in the other off-diagonal and degenerate force constants are not crucial. This is especially true of interaction constants which link modes of similar ground state but dissimilar transition state symmetry. It is also true of degenerate modes, which usually have higher energies and appreciably smaller isotopic shifts than their corresponding nondegenerate modes. In either case, the ground state constants may generally be used.

Although these conclusions have been drawn specifically for *tert*-butyl chloride, they should hold for other molecules with C_{3v} symmetry, or pseudo-C_{3v} symmetry. Thus, the conclusion should be applicable to methyl chloride, triphenylmethyl chloride, and similar molecules, as well as for analogous bromides. The (nominal) C–Cl stretch mode interactions with other modes are expected to be less in molecules of lower symmetry such as ethyl and isopropyl chloride, and more geometric parameters are required to describe the transition state configuration; thus the conclusions reported here are not immediately applicable to molecules of lower symmetry. However, it is expected that other work will extend these conclusions to models of lower symmetry. In such an extension, it is expected that the temperature dependence will continue to be dependent on the transition state C–Cl distance, the temperature-independent factor will be dependent on a combination of other geometrical parameters, and the use of these additional pieces of kinetic isotope effect information may help to unravel the complexity of transition state model choices.

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Kinetics, Equilibrium, and Negative Temperature Dependence in the Bimolecular Reaction t-$C_4H_9^+$ (i-C_5H_{12}, i-C_4H_{10}) t-$C_5H_{11}^+$ between 190 and 570°K

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Abstract: The approach to equilibrium and the values of the equilibrium constant were investigated in the reaction system (k_f) t-$C_4H_9^+ + i$-$C_5H_{12} \rightleftharpoons t$-$C_5H_{11}^+ + i$-$C_4H_{10}$ (k_r) by pulsed high-pressure mass spectrometry. The equilibrium constants measured and the resultant thermodynamic values, $\Delta H = -3.3$ kcal/mol, $\Delta G_{300} = -2.5$ kcal/mol, $\Delta S_{300} = -2.7$ eu, showed good agreement with values obtained previously using a continuous ion source technique. The value of k_f was measured as 1.6×10^{-11} cm^3/(mol sec) at 328°K. The rate constant for this slow exothermic bimolecular reaction exhibits a temperature dependence between 190 and 570°K best expressed as $k_f \approx CT^{-8}$. The meaning of this temperature dependence in the present reaction system, involving a highly complex reaction intermediate with $3N - 6 = 84$ internal degrees of freedom, is discussed in the context of transition state theory concepts.

The thermodynamics of the hydride-transfer equilibria occurring in the t-$C_4H_9^+$ (i-C_5H_{12}, i-C_4H_{10}) t-$C_5H_{11}^+$ system between 323 and 548°K was previously investigated in this laboratory[1] by high-pressure mass spectrometry applied in the continuous mode of ion production and extraction. The kinetics of the hydride-transfer reactions of *tert*-butyl ion with 22 C_5–C_8 alkanes at 298°K was studied by Ausloos and Lias[2] using the techniques of radiation chemistry. They found the rates of these reactions to be uncharacteristically slow for exothermic ion–molecule reactions, with rate constants generally between 10^{-10} and 10^{-11} cm^3/(mol sec), although hydride abstraction is the only reaction channel. An activation energy (≤ 3.5 kcal/mol) inversely related to the exothermicity of the reaction was postulated.

In the present study, the temperature dependence of

(1) J. J. Solomon and F. H. Field, *J. Amer. Chem. Soc.*, **95**, 4483 (1973).

(2) P. Ausloos and S. G. Lias, *J. Amer. Chem. Soc.*, **92**, 5037 (1970).