Stabilities of Carbonium Ions in Solution. 12. Heats of Formation of Alkyl Chlorides as an Entreé to Heats of Solvation of Aliphatic Carbonium Ions

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Abstract: Heats of formation (ΔH_f) of tertiary alkyl chlorides may be calculated from measurements of the heats of hydrochlorination of appropriate olefins at −50 °C in CH_2Cl_2. Since many good values for heats of formation of the olefins have been published, the heats of hydrochlorination lead directly to ΔH_f for the chlorides, for which few previous values are available. The new data, when combined with previously reported heats of ionization for the chlorides, provide heats of formation for the carbonium ions. Relative values for ΔH_f for the carbonium ions are remarkably similar in the gas phase and in SO_2ClF, thus supporting the proposal that differential solvation of carbonium ions is small in solvents such as SO_2ClF. Because solvation energies are nearly constant for carbonium ions, their relative energies as calculated from quantum theory should apply directly to nonnucleophilic condensed phase values—a situation which is drastically different from that for ammonium or oxonium ions. We have shown previously the close relationship between ionization energies for alkyl chlorides in SO_2ClF and their solvolysis rates in ethanol.[1] The present results complete the series of data which are necessary for rigorously relating theoretical calculations of carbonium ion stability to solvolysis reaction rates in solution. Thereby, they help to explain the great success of the carbonium ion theory of organic chemistry.

Introduction

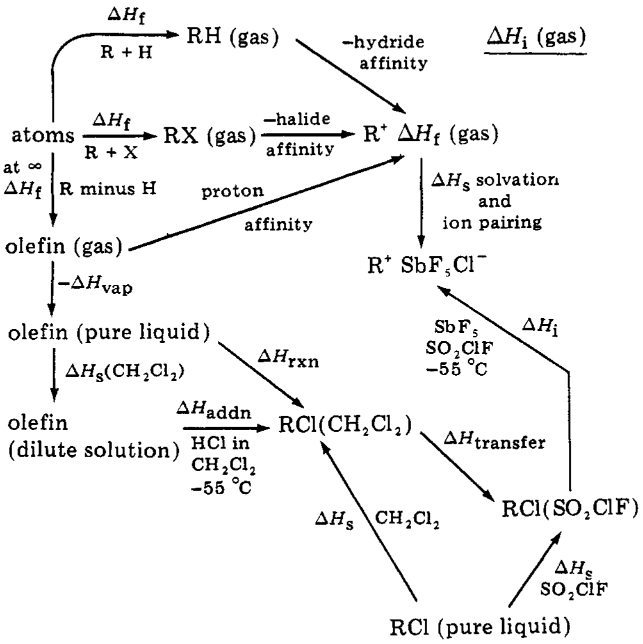
Thanks to several new mass spectrometric techniques. reliable thermodynamic data have become available for ionization of many organic molecules in the gas phase.[2-6] If the gas-phase heats of formation of the neutral precursors are known, the heats of formation of the ions can be calculated. Such heats of formation provide valuable tests for quantum-mechanical calculations of the factors which influence inherent ion stabilities.[7,8] They are also of interest for calculating solvation energies for cases where it is possible to determine energies of ion formation in solution by subtracting energies of formation of the solvated neutral precursor from the ionization energy. For example, we have recently described methods for measuring heats of ionization of alkyl halides, RX, to carbonium ions, R^+, in superacid solutions at low temperatures.[9-11] Although the state of aggregation of the final product $R^+SbF_5X^-$ is presently unknown, clear evidence against the formation of chloronium ions was provided.[9]

Unfortunately, few reliable heats of formation have been determined for alkyl halides so that calculations of carbonium stabilities have been limited severely. However, there is an abundance of good data for heats of formation of olefins and also their heats of vaporization, which are necessary to relate the gaseous and condensed states.[12]

Scheme I shows the various thermochemical quantities that are used to relate heats of formation of alkyl chlorides to olefins and to carbonium ions. The necessary enthalpy terms for transfer from one medium to another are also shown. Clearly, it would be possible to complete the entire sequence of steps if a reliable method could be found for determining the heat of hydrochlorination of olefins to the chlorides as shown in the lower left corner. Following a suggestion by Professor Paul Schleyer that such hydrochlorination might occur rapidly, even at low temperature, we set about finding conditions for their accomplishment. This article describes the method which we have developed for determining heats of hydrochlorination of branched olefins to tertiary chlorides. No comparably direct approach could be developed to produce primary or secondary chlorides under calorimetric conditions.

However, if a primary or secondary halide will ionize rapidly and rearrange cleanly to an isomeric tertiary ion, then the difference in heats of ionization of the isomeric halides to the common carbonium ion is entirely assignable to the difference in heat of formation of the halides.[10] Therefore, if we can determine the heat of hydrochlorination of an olefin to a tertiary chloride and can determine the heat of ionization of the tertiary chloride to the tertiary ion, the heats of formation of the entire set of halides are available. The approach here is extremely simple and direct and yields values which are at least as good as most published heats of formation obtained from heats of combustion.[12]

Scheme I. Scheme for Relating Enthalpy Terms



In the following article the derived heats of formation of the carbonium ions in solution and in the gas phase will be used to approach the interesting problem of solvation energies for carbonium ions.

Experimental Section

All precursor olefins and chlorides were obtained from Chemical Samples Co. and were 99–99.9% pure, after distillation, as confirmed by GLC and NMR. Isobutylene (Matheson Gas Products, 99.8%) was used as obtained. Methylene chloride (Fisher) was purified by

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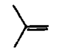
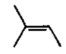
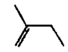
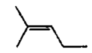
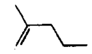
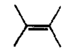
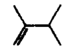
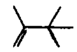
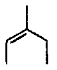
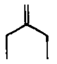
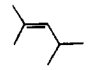
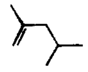
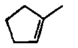
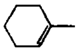
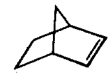
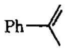
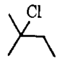
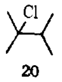
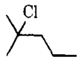
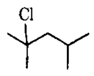
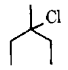
Table I. Derived Heats of Formation of Alkyl Chlorides from Heats of Hydrochlorination of Olefins at −55 °C and High Dilution in CH_2Cl_2

olefin		$\Delta H_f^\circ(\mathrm{l})$[a] olefin	ΔH_{rxn} −55 °C	$\Delta H_f(\mathrm{l})$[b] chloride
1		−9.18 ± 0.16	−15.08 ± 0.42	−50.4 ± 0.5
2		−16.6 ± 0.2	−14.12 ± 0.22	−56.2 ± 0.4
3		−14.7 ± 0.2	−15.23 ± 0.34	−55.5 ± 0.5
4		−23.6 ± 0.4	−14.10 ± 0.18	−63.2 ± 0.4
5		−21.5 ± 0.3	−15.46 ± 0.34	−62.5 ± 0.5
6		−24.2 ± 0.2	−12.91 ± 0.33	−62.6 ± 0.5
7		−22.2 ± 0.5	−14.86 ± 0.41	−62.5 ± 0.7
8		−28.1 ± 0.3	−14.33 ± 0.46	−69.3 ± 0.6
9		−22.6 ± 0.3	−14.08 ± 0.47	−62.2 ± 0.6
10		−20.8 ± 0.4	−16.06 ± 0.46	−62.4 ± 0.6
11		−29.4 ± 0.3	−11.38 ± 0.37	−66.3 ± 0.5
12		−28.0 ± 0.3	−12.91 ± 0.53	−66.4 ± 0.6
13		−8.66 ± 0.2	−12.92 ± 0.38	−47.4 ± 0.4
14		−19.4 ± 0.2	−13.41 ± 0.21	−58.9 ± 0.3
15		+12.1 ± 0.1[c] (+7.09)[d]	−16.94 ± 0.37	−31.4 ± 0.4 (−36.4)
16		+16.8 ± 0.3	−8.80 ± 0.45	−18.1 ± 0.6

[a] These are best published values from ref 12. [b] $\Delta H_f(\mathrm{RCl}) = \Delta H_f^\circ(\mathrm{olefin}) + \Delta H_{rxn} - \Delta H_s(\mathrm{RCl,CH_2Cl_2}) + \Delta H_f^\circ(\mathrm{HCl}) + \Delta H_s(\mathrm{HCl,CH_2Cl_2})$. The heat of solution of HCl in CH_2Cl_2 at −55 °C was determined as −3.45 ± 0.12 kcal/mol. The heat of formation of HCl is −22.05 kcal/mol.[12] [c] Reference 23a. [d] Reference 23b.

Table II. Heats of Formation of Pure Liquid Alkyl Chlorides from Isomeric Olefins (kcal/mol)

olefins	chloride	$\Delta H_f(\mathrm{l})$ chloride
2	 **18**	−56.2 ± 0.4
3		−55.5 ± 0.5
6	 **20**	−62.6 ± 0.5
7		−62.5 ± 0.7
4	 **19**	−63.2 ± 0.4
5		−62.5 ± 0.5
11	 **23**	−66.3 ± 0.5
12		−66.4 ± 0.6
9	 **22**	−62.2 ± 0.6
10		−62.4 ± 0.6

prolonged stirring with concentrated sulfuric acid, washing with aqueous sodium bicarbonate and water, and fractional distillation from P_2O_5. Hydrogen chloride (Matheson, electronic grade, 99.99%) was dissolved in cold (<25 °C) methylene chloride to a concentration of approximately 0.15–0.70 M and then thermally equilibrated to −55 °C in a solution calorimeter previously described.[7] Sealed ampules of olefin (10–50 mg) were thermally equilibrated and broken into this solution. The heat of reaction (ΔH_{rxn}) is the heat evolved from addition of a small increment of olefin to the HCl solution and represents the sum of the heat of solution of the olefin in pure CH_2Cl_2 and the heat of addition of HCl to dissolved olefin, ΔH_{addn}, as can be seen in Scheme I. Since we are only concerned here with the change in heat content on going from the pure olefin to a dilute solution of the alkyl chloride, we have not measured the heats of solution of the olefins in CH_2Cl_2. These values would be needed to derive accurate values for ΔH_{addn}. They would probably be very small.

To determine that these reactions went to completion and to a simple product, replicas of the calorimetric runs were conducted in NMR tubes, spectra taken, and the solution then analyzed by GLC. All reactions were quantitative.

Heats of ionization, ΔH_i, of the chlorides at −55 °C were measured as described previously.[9] All of these chlorides have been shown to go cleanly to the corresponding carbocations by the ^{13}C NMR studies of Olah and Donovan[13] and we have confirmed this by low-temperature ^1H NMR in our laboratory. The three hexyl isomers (dimethylisopropyl, dimethyl-*n*-propyl, and diethylmethyl carbonium ions) were shown by Brouwer[14] to be formed in a statistical equilibrium mixture, irrespective of the olefin from which they were formed, by HF/SbF_5 addition at temperatures above 40 °C. Subsequently, Saunders and co-workers showed that the individual carbonium ions could be isolated by ionization of the corresponding chlorides at much lower temperatures.[15]

Results

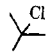
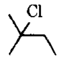
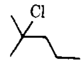
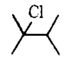
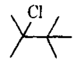
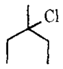
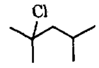
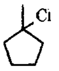
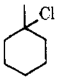
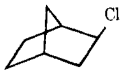
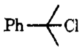
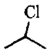
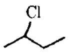
Table I presents our values for heats of reaction, ΔH_{rxn}, for a number of olefins with HCl in CH_2Cl_2 at −55 °C. The best published values[12] for the heats of formation of the liquid olefins are also listed and also the derived heats of formation, $\Delta H_f(\mathrm{l})$, for the chlorides with proper accounting for the heat of formation and solution of HCl.

In a few cases published determinations of $\Delta H_f(\mathrm{RCl})$ may be compared with our values. Thus the heats of formation of 2-chloro-2-methylpropane (**17**) and 2-chloro-2-methylbutane (**18**) are reported here as −50.4 ± 0.5 and −56.5 ± 0.3 kcal/mol, respectively (see Table I). The values for the same chlorides reported previously[12] are −50.6 ± 0.6 and −56.4 ± 0.8 kcal/mol, respectively.

In order to demonstrate that ΔH_{rxn} values were not sensitive to temperature the following comparisons were made. For 2-methyl-2-butene ΔH_{rxn} values of −13.88 ± 0.40 and −14.12 ± 0.22 kcal/mol were obtained at −25 and −55 °C. For 2-methyl-2-pentene values of −13.90 ± 0.32 and −14.10 ± 0.18 kcal/mol were found at the same pair of temperatures. The heats of ionization, ΔH_i, of two of the hexyl systems were measured at −55 and −100 °C to confirm that no isomerization had occurred at the higher temperature. Thus, 2-chloro-2-methylpentane gave ΔH_i values of −27.1 ± 0.7 and −26.8 ± 0.5 kcal/mol at −55 and −100 °C, and 3-chloro-3-methylpentane gave −27.9 ± 0.5 and −27.4 ± 0.5 kcal/mol, respectively, at those temperatures. We have never observed a temperature coefficient for any heat of reaction or heat of solution in such systems unless molecular rearrangement occurs.

The reliability of our method may be tested through the comparison of ΔH_{rxn} for pairs of isomeric olefins of known ΔH_f which yield the same tertiary chloride. In this case the differences in heat of reaction, ΔH_{rxn}, should correspond exactly to the differences in heats of formation of the initial olefins. Table II demonstrates the internal consistency of the data for several such pairs of compounds. Considering the accumulated errors in determining the heats of formation of the olefins and heats of hydrochlorination the agreement is good.

Table III. Heats of Solution of Alkyl Chlorides in CH_2Cl_2 and SO_2ClF, Improved Heats of Ionization (ΔH_i) in SO_2ClF, and Gas-Phase Hydride Affinities of Carbonium Ions

	RCl	$\Delta H_s(CH_2Cl_2)$	$\Delta H_s(SO_2ClF)$	ΔH_i[a]	$D(R^+H^-)$[b]
17		0.60 ± 0.10	1.00 ± 0.20	−24.8 ± 0.3	235.9
18		0.33 ± 0.09	0.62 ± 0.10	−27.1 ± 0.5	232.5
19		0.56 ± 0.06	1.30 ± 0.29	−27.1 ± 0.7	232.7
20		0.98 ± 0.10	1.15 ± 0.10	−27.6 ± 0.5	230.5
21		1.34 ± 0.22	3.02 ± 0.24	−26.9 ± 0.6	228.1
22		0.48 ± 0.05	0.51 ± 0.10	−27.9 ± 0.5	231.1
23		0.76 ± 0.07	0.65 ± 0.07	−28.5 ± 0.4	231.2
24		0.33 ± 0.10	0.50 ± 0.10	−27.1 ± 0.6	
25		0.60 ± 0.10	0.98 ± 0.08	−26.9 ± 0.3	229.5
26		1.00 ± 0.10	1.00 ± 0.20	−23.2 ± 0.4	234.4
27		0.65 ± 0.20	0.85 ± 0.20	−30.3 ± 0.3	
28			0.30 ± 0.10	−15.3 ± 0.9	
29			0	−15.9 ± 0.4	

[a] Some ΔH_i values were reported previously.[9] The values presented here are considerably improved through the use of a rebuilt calorimeter.
[b] Gas-phase hydride affinities from ref 26.

Table III presents heats of solution of the chlorides in SO_2ClF and CH_2Cl_2. Heats of ionization in SO_2ClF (ΔH_i) are the difference between the heats of reaction of the chlorides with a solution of SbF_5 in SO_2ClF and their heats of solution in that solvent.[9] Also listed in Table III are the gas-phase hydride affinities for the carbonium ions corresponding to the ones which would be generated in SO_2ClF by ionization of each chloride. The two ionization properties are plotted against each other in Figure 1.

Table IV lists heats of formation of the carbonium ions shown in SO_2ClF and in the gas phase, all values being taken relative to the *tert*-butyl cation in order to emphasize structural differences. The heat of formation of each ion is simply the sum of ΔH_f, ΔH_i, and ΔH_s for the corresponding alkyl chloride. Relative heats of solvation, $\delta \Delta H_s(R^+)$, are the difference between heats of formation in solution and in the gas phase.

Table V demonstrates that heats of formation of primary and secondary chlorides can be evaluated if they are converted rapidly and completely to the carbonium ion derived from their isomeric tertiary chloride.

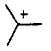
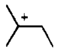
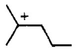
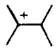
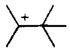
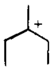
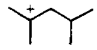
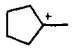
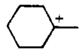
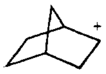
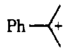
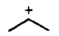
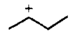
Discussion

Heats of Hydrochlorination and Heats of Formation of Chlorides. The heats of hydrochlorination (ΔH_{rxn}) listed in Table I show a nearly constant value of about −14.5 kcal/mol for the first six entries—there is very little effect of elaborating alkyl groups at positions either α or β to the double bond under attack. We take this to imply that there is negligible variation in steric or electronic factors associated with the C–Cl bond in these chlorides. The relatively low value for hydrochlorinating α-methylstyrene probably reflects the loss of conjugation to the olefin. Since there is little variation in ΔH_{rxn}, the heats of formation of the olefins produce a pattern which is followed closely by the heats of formation of the chlorides. A major factor here is simply the added increment of −5 to −7 kcal/mol for each replacement of a hydrogen by a methyl group. The small heat of formation of norbornene is probably due to its high degree of strain.[16]

Heats of Ionization and Heats of Formation of Carbonium Ions. Figure 1 compares heats of ionization by hydride ion abstraction in the gas phase with heats of ionization of the chlorides in SO_2ClF probably to produce an undissociated $R^+SbF_5Cl^-$ ion pair. This updates a similar plot in a previous article[10] with new data reported here in Table IV and in a recent review of gas-phase data.[2]

Comparison of Figures 1 and 2 illustrates the confusion which can arise when ionization processes (such as solvolysis rates, hydride affinities, or heats of ionization) are interpreted directly in terms of the stabilities of the ions or transition states formed in the process. The stability of the ion is most properly presented in terms of its heat of formation from its separated atoms at infinity, $\Delta H_f(R^+)$. To chemists the ionization processes, such as ΔH_i, are probably more relevant since they represent relative reactivity for conversion of a neutral species to an organic ion. Heats of formation depend on such factors as the number of atoms and bonds in the molecule or ion, conjugation, strain, etc. When simple ionizations occur, most of these contributions are present in both the neutral initial state and in the ion, although to a varying degree. A high reactivity, therefore, can be caused by relief of strain in the initial

Table IV. Relative Heats of Formation of Carbonium Ions in SO_2ClF and the Gas Phase and the Derived Heats of Solvation (kcal/mol)

R^+	$\delta\Delta H_f$ SO_2ClF[a]	$\delta\Delta H_f$ gas (Aue)[b]	$\delta\Delta H_f$ gas (Kebarle)[c]	$\delta\Delta H_s$ R^+ [a,d]
	0 (−74.2)	0 (+165)[e]	0	0, 0 (−239)
	−8.8 ± 0.8	−6.1	−8.0	−2.7, −0.8
	−15.3 ± 1.0	−12.3	−17.6	−3.0, +2.3
	−15.7 ± 1.0	−14.7	−15.9	−1.0, +0.2
	−18.9 ± 1.1	−23.4	−24.6	+4.5, +5.7
	−15.9 ± 1.0	−12.6	−13.8	−3.3, −2.1
	−20.8 ± 0.9	−19.6	−20.4	−1.2, −0.4
	+0.2 ± 0.9	+2.4	+0.2	−2.7, 0
	−10.6 ± 0.7	−8.1		−2.5, —
	+20.6 (+15.4)	+25.2	+18.2	−4.6, +2.4
	+26.7 ± 0.9	+22.9		+3.8, —
	+19.1 ± 1.5	+22.1		−3.0, —
	+12.2 ± 2.1	+13.9		−1.7, —

[a] Although there is strong evidence[9,10] for complete ionization of RCl by SbF_5 under these conditions, the final state of the carbocation is probably an undissociated ion pair. These values therefore include a factor of solvation of the complex counterion and probably a small nearly constant term for the ion-pairing enthalpy. [b] Reference 2. The absolute values for ΔH_f (kcal/mol) are listed in parentheses in the row for *tert*-butyl cation. [c] Reference 3. [d] $\delta\Delta H_s(R^+) = \delta\Delta H_f(SO_2ClF) - \delta\Delta H_f(\text{gas})$ using the $\delta\Delta H_f(\text{gas})$ values of Aue[2] and Kebarle,[3] respectively. [e] See ref 26 for a recent extensive discussion of the proper value for this reference ion and a recommended alternative of 162.1 ± 0.8 kcal/mol.

Table V. Heats of Formation of Primary and Secondary Alkyl Chlorides Derived from Heats of Isomerization to the Isomeric Tertiary Carbonium Ion[a]

chloride	this report	lit.[b]
30 1-chloropropane	*c*	−37.9 ± 0.3
28	*c*	−40.1 ± 1.0
31 1-chlorobutane	−41.8 ± 0.9[d]	−43.0 ± 2.0
29	−45.8 ± 0.8[e]	−46.1 ± 2.0
17	−50.4 ± 0.5	−50.6 ± 0.6
18	−56.5 ± 0.3	−56.6 ± 2.0
24	−47.5 ± 0.4	
32 cyclohexyl chloride	−51.3 ± 0.8[f]	−49.5 ± 0.3

[a] Heats of formation for primary and secondary chlorides were determined by measuring the heat of ionization differences of that chloride and the isomeric tertiary (or secondary in the case of propyl) chloride to a common tertiary (or secondary in the case of propyl) carbonium ion. [b] Reference 12. [c] The difference in heats of ionization for *n*-propyl chloride to isopropyl chloride is $\delta\Delta H_i = -1.2 \pm 1.2$ kcal/mol. However, the heat of formation of neither isomer was measured. [d] **31** → **17**, $\delta\Delta H_i = -8.6 \pm 0.7$ kcal/mol. [e] **29** → **17**, $\delta\Delta H_i = -5.0 \pm 0.6$ kcal/mol. [f] **32** → **24**, $\delta\Delta H_i = +4.6 \pm 0.7$ kcal/mol.

state or by a higher degree of charge delocalization in a large conjugated ion relative to its neutral when compared to a smaller, less stabilized ion and its neutral. Thus, for ionization processes some contributions due simply to the number of atoms and bonds are not apparent since they are also present in the neutral. Dramatic examples of the differences between ΔH_i and ΔH_f as measures of ion stability are revealed by comparing the relative positions of cumyl, norbornyl, isopropyl, and cyclopentyl ions on the two plots. The order in Figure 1 should be quite familiar to those well schooled in reactivity patterns of organic compounds. However, the sequence of actual heats of formation of the ions in Figure 2 would be puzzling unless it is understood that ring-strain and size factors are present which have little to do with resonance delocalization.

Solvation Energies. Although the $\Delta H_f(R^+)$ values are not of direct value for discussing reactivity, they are just what is needed for comparison with theoretical calculations and for the estimation for solvation energies. Figure 2 and Table IV provide abundant support for the useful conclusion[1,10,17] that in solvents of sufficiently low nucleophilicity there is very little differential solvation of carbonium ions or their ion pairs. With one or two noteworthy exceptions (see below) the same heat of formation (relative to *tert*-butyl cation) is found for each ion in solution and in the gas phase, even though there is an enormous absolute difference between ΔH_f for each ion in the two media. In SO_2ClF the carbonium ion is probably electrostatically paired to a complex antimony hexahalide anion as well as being stabilized by Born charging of the solvent. A small discrepancy may be noted between the relative ΔH_f for *sec*-butyl ion as derived by the present method and that reported previously from the isomerization energy of the *sec*-butyl ion to *tert*-butyl ion.[18] This discrepancy probably arises because the values listed in Table IV contain an accumulation of errors that is absent from the directly measured ionization energy.

If all of the carbonium ions treated here had exactly the same solvation energies for transfer from the gas phase to the same final state, the slope of Figure 2 would be exactly unity and all relative solvation energies in Table IV would be displaced by their cumulative standard deviations from 0.0. However, some deviations are apparent which are probably significant.

The first five ions in Table IV are interesting with respect

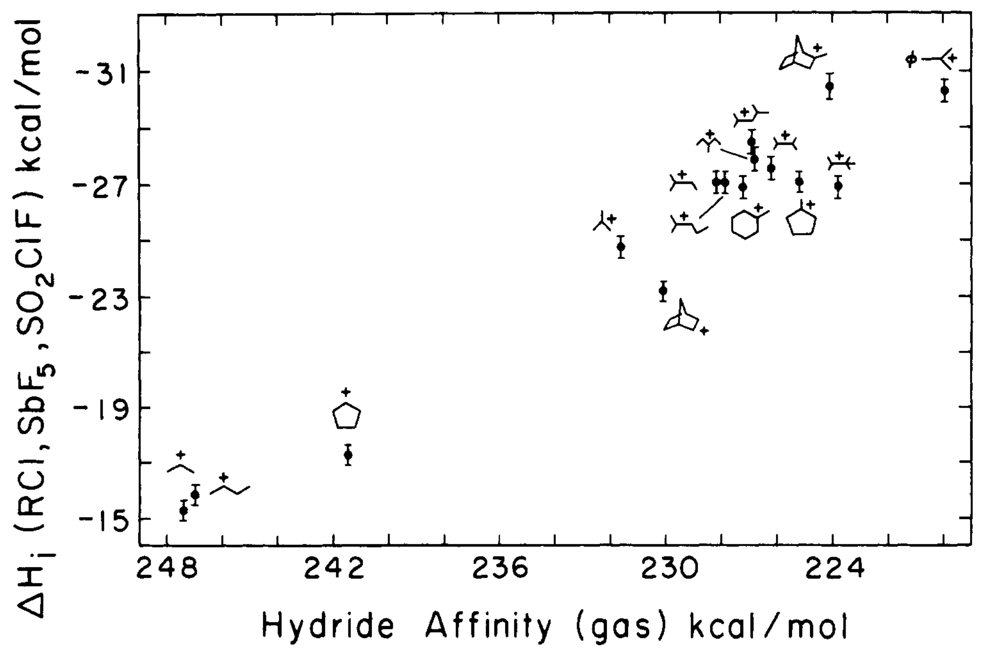


Figure 1. Comparison of ionization data for generating alkyl and alicyclic cations (or ion pairs) in SO_2ClF solution from chloride precursors and from hydride transfer in the gas phase,[2] slope 1.63, coefficient of correlation 0.973.

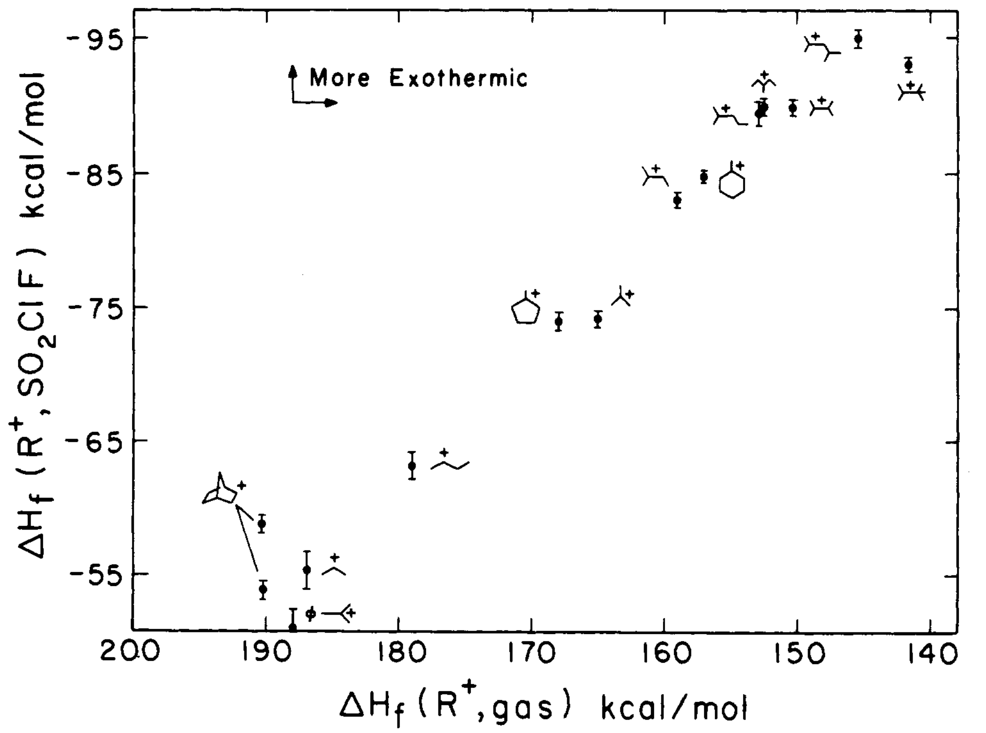


Figure 2. Comparison of heats of formation of carbocations in solution and in the gas phase.[2] The final state of the ion is probably an $R^+SbF_5Cl^-$ ion pair. Note the large differences in relative orders for some ions when compared to Figure 1. Such discrepancies are attributable to initial state contributions, slope 0.973, coefficient of correlation 0.986 (not including point for the norbornyl cation).

to the Baker-Nathan effect for alkyl groups of increasing carbon number and branching. Although attributed originally to electronic factors,[19] it was shown to be a solvation phenomenon[20,21] and subsequently was shown to be rather general for formation of positive and negative ions in a variety of solvents.[22] In the present case, a steady increase in ΔH_f is found for tertiary cations **1-5** as one of the methyl hydrogens is replaced by methyl, ethyl, isopropyl, and *tert*-butyl groups in the gas phase. In SO_2ClF, however, a reversal is observed in the ΔH_f of the last two members of the series. This *must be* a solvation effect, but there is no way of determining at present whether its source is electrostatic or due to a solvent cavity effect arising from differences in cohesive energy densities.[22]

Finally we should refer to the two points listed for ΔH_f of the norbornyl ion. These arise simply from the various sets of values for ΔH_f of norbornene.[23] At the present moment these results shed no light on the controversial matter of whether the norbornyl ion is or is not abnormally stable. When a reliable ΔH_f for 2-methylnorbornene is determined, this question can be tested yet again. However, our previous publications[11,24] supply strong evidence of 5-8 kcal/mol of "extra stability" relative to a standard aliphatic case. Since we[10] and Jorgensen[27] have argued that this ion should have a lower solvation energy if it is in fact stabilized internally there is reason to favor the more endothermic value (+2.4 kcal/mol) for $\delta\Delta H_s$.

Conclusion

We have developed a simple, accurate, and precise method for determining heats of formation of alkyl chlorides. When combined with other readily available data this allows determination of the heats of formation of the derived carbonium ions in SO_2ClF and in the gas phase. The close correspondence of relative heats of formation in the two media supports our earlier claim that differential solvation energies of carbonium ions are small in superacid media.

We have reported a close correlation between energies of activation for solvolysis rates and heats of ionization in superacid and those in the gas phase.[1] Heats of formation of carbonium ions are now accessible to ab initio calculations.[7,8] Since we have shown that differential solvation energies for carbonium ions in nonnucleophilic solvents are small or negligible, theoretical values for ΔH_f should apply approximately to SO_2ClF solution and hence be translatable into solvolysis rates. This would be the achievement of a long-sought goal of organic chemistry—the prediction of relative reaction rates in solution from quantum-mechanical calculations. Its success here cannot be generalized but is a good step in the right direction.

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Heats of Formation of Gaseous Free Radicals via Ion Cyclotron Double Resonance Spectroscopy

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Abstract: An ion cyclotron double resonance bracketing experiment combined with the previously determined gas-phase basicity scale has been employed to determine heats of formation (kcal mol^{-1}) for eight free radicals: phenoxy, 11.6 ± 2.3; benzyl, 48.0 ± 2.2; cycloheptatrienyl, 69.0 ± 3.1; cyclopentadienyl, 63.2 ± 2.2; cyclopropenyl, 105.1 ± 4.1; allyl, 43.7 ± 2.2; cyclopropyl, 66.5 ± 2.7; vinyl, 71.5 ± 2.2.

Introduction

It has recently been demonstrated that pulsed ion cyclotron double resonance bracketing techniques[1] used in conjunction with the quantitative gas-phase basicity scale[2] are capable of determining the enthalpies of formation of a wide variety of transient neutral molecules.[3] This paper reports the application of these techniques to the determination of the thermochemical stabilities of eight free radicals. Since most of the systems studied have published heats of formation, this work serves as a critical test of the double resonance bracketing techniques. It also represents the exposition of an experimental technique which could prove to be an important source of thermochemical data for molecules which are too short lived to be amenable to other experimental probes.

Experimental Section

Experiments were performed with a pulsed ion cyclotron resonance (ICR) spectrometer having a one-region trapped ion cell and a capacitance bridge detector.[4,5] Gaseous positive ions were formed by low-energy electron impact (ca. 12 eV) and efficiently trapped for many tenths of a second by static electric and magnetic fields. In the pulsed mode of operation, the electron beam is gated on for 10 ms, and the ions thus formed are trapped and allowed to react for a set delay time of typically 200 ms. This is followed by an 8-ms detection period during which time ions of a given mass-to-charge ratio are accelerated at their cyclotron frequency, $\omega_c = qB/m$, by a radio-frequency pulse from the capacitance bridge detector in order to measure their abundance in the ICR cell. Finally, all ions are removed from the cell by a quench pulse which neutralizes them by collison with the side plates of the cell.

0002-7863/80/1502-3334$01.00/0