

Stabilities of Carbonium Ions in Solution. 8. Heats of Ionization of Some Simple Alkyl Halides in Superacidic Media

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Abstract: Using the solution calorimeter described in the previous article, heats of formation of the following carbocations have been measured at low temperatures in four solvents (SO_2ClF , SO_2 , SO_2F_2 , CH_2Cl_2) by reaction of the alkyl chlorides and fluorides with SbF_5 : isopropyl, *sec*-butyl, *tert*-butyl, 2-norbornyl, 1-adamantyl, cyclopentyl, 1-methylcyclopentyl, 2-methylnorbornyl, cumyl, 2-phenylnorbornyl, phenyldichloromethyl, diphenylchloromethyl, and trityl. All attempts to observe or capture the cyclohexyl cation failed, immediate isomerization to 1-methylcyclopentyl cation occurring even at -110°C . A number of tests for internal consistency were used to authenticate the ionization process. Thus, the enthalpies for capturing the tertiary carbonium ions with $\text{Bu}_4\text{N}^+\text{Cl}^-$ in CH_2Cl_2 were inversely proportional to the corresponding enthalpies of ionization. Recovery of the alkyl halide from the capture reaction showed, by GLC analysis, that over 95% of the R-Cl had survived the ionization and capture cycle unscathed. The heat of isomerization for *sec*-butyl to *tert*-butyl cation was found to be -14.3 ± 0.5 kcal/mol, which confirms, within experimental error, the earlier value of -14.5 by Bittner, Arnett, and Saunders using an entirely different technique. Relative heats of formation for isomeric precursor halides may be determined when both produce the same carbonium ion. Thus, at -25°C *sec*-butyl chloride ($\Delta H_i = -30$ kcal/mol) and *tert*-butyl chloride (-25.4 kcal/mol) are both converted instantly to *tert*-butyl cation. The 4.6 kcal/mol greater stability of the tertiary chloride inferred from this experiment agrees within experimental error with the difference in their heats of formation. A similar difference between isomeric cyclohexyl chloride and methylcyclopentyl chloride shows that the secondary chloride is more stable by 4.9 kcal/mol. The 10 kcal/mol inversion of the secondary-tertiary difference underscores the importance of initial state stabilities when comparing ionization energies. This leads to a dilemma regarding the heat of ionization of cyclohexyl chloride to cyclohexyl ion and its heat of isomerization to 1-methylcyclopentyl ion. One or the other or both of these values must be abnormally small compared to other isomeric secondary-tertiary systems. The effect of the methyl group on the difference between ΔH_i for isopropyl chloride and *tert*-butyl chloride or between cyclopentyl and 1-methylcyclopentyl chloride is about 10 kcal/mol in SO_2ClF and SO_2F_2 . A slightly smaller value (7.5 kcal/mol) is found between ΔH_i for 2-norbornyl and 2-methylnorbornyl chloride. These and other comparisons of the data suggest a slightly larger driving force for ionization of the 2-norbornyl halides to the ion than for the other secondaries considered here, but the problem of initial state stabilities prevents a simple interpretation in terms of the ions. Solvent effects on the heat of ionization of *tert*-butyl chloride by SbF_5 in SO_2 , SO_2ClF , and SO_2F_2 are equal and opposite to the variation of the heat of solution of SbF_5 in these solvents. Also, heats of ionization of the other alkyl halides, relative to *tert*-butyl chloride, are mostly insensitive to solvent variation. These two facts provide strong independent support for other observations of the relative insensitivity of carbonium ion stabilities to differential electrostatic solvation. The 2-norbornyl ion appears to have a somewhat different means of balancing solvation energy vs. internal charge delocalization than do the other ions.

Introduction

The carbonium ion theory of organic reactions is one of the simplest and most powerful generalizations in chemistry. Thanks to it, a good undergraduate chemistry student can rationalize and also predict structure-reactivity relations for a tremendous range of reactions which were unexplainable 50 years ago. The theory has been established at one limit by the existence of resonance-stabilized ions, such as triarylmethyl cations, whose structures have been appreciated rather well since the early 1900s. At the other limit the relative stabilities of the simple and highly reactive aliphatic and alicyclic carbonium ions have been inferred only indirectly from gas-phase experiments (such as ionization potentials) or from kinetic data for substitution reactions (such as solvolysis). In neither of these cases can the carbocation be observed directly to confirm its structure. Furthermore, one may always have reservations about thermodynamic stabilities which have been deduced from reaction rates.

Direct evidence for the existence and structures of simple aliphatic and alicyclic carbonium ions became possible largely through the work of Olah,¹ who pioneered the use of superacids in solvents of very low nucleophilicity for generating the ions so that they could be studied by NMR spectroscopy. Thanks to subsequent work by Olah's group, Gillespie,² Saunders,³ Brouwer and Hogeveen,⁴ and many others a large body of information has been developed regarding the structures and the kinetics of interconversion for many secondary and tertiary carbocations in solution.⁵ There are, however, virtually no

corresponding thermodynamic data for these systems in solution.

We have described calorimetric procedures for determining the heats of formation of carbocations from alkyl halides in superacidic media.⁶ In this paper we shall present our results and discuss them briefly with regard to substituent and medium effects. Their relation to solvolysis mechanisms⁷ will be considered in a separate article.

Results

Tables I-IV present our results for reaction of a series of alkyl halides with SbF_5 in four solvents of low nucleophilicity (CH_2Cl_2 , SO_2 , SO_2ClF , and SO_2F_2) using the calorimetric procedures described in the preceding article.⁶ The heat of ionization is taken to be the difference between the molar heat of solution of the R-X substrate in a solution of excess SbF_5 in the solvent indicated, $-\Delta H_{\text{react}}(\text{SbF}_5/\text{solvent})$, and that of the substrate into pure solvent at the same conditions, $-\Delta H_s(\text{solvent})$.

Thus:

$$\Delta H_i(\text{solvent}/\text{SbF}_5) = \Delta H_{\text{react}}(\text{solvent}/\text{SbF}_5) - \Delta H_s(\text{solvent})$$

The latter term is necessary to correct for association, especially through lattice energies, of the R-X precursor under conditions of the reactions. Without this correction the observed heat of reaction obtained from dissolving a crystalline sample of R-X into a solution of SbF_5 might be several kilo-

Table I. Heats of Ionization of Chlorides in CH₂Cl₂

alkyl halide	$\Delta H_s(\text{CH}_2\text{Cl}_2)$	$\Delta H_{\text{react}}(\text{CH}_2\text{Cl}_2/\text{SbF}_5)$	$\Delta H_i(\text{CH}_2\text{Cl}_2/\text{SbF}_5)$	temp, °C
isopropyl chloride	0	-7.5 ± 1.5	-7.5 ± 1.5	-75
cyclopentyl chloride	0	-9.0 ± 1.0	-9.0 ± 1.0	-75
<i>exo</i> -norbornyl chloride	1.0 ± 0.1	-10.1 ± 0.3	-11.1 ± 0.4	-55
1-adamantyl chloride	1.2 ± 0.1	-9.9 ± 0.7	-11.1 ± 0.8	-55
<i>tert</i> -butyl chloride	0.6 ± 0.1	-14.9 ± 0.2	-15.5 ± 0.3	-55
trichlorophenylmethane	0.4 ± 0.05	-16.0 ± 0.6	-16.4 ± 0.7	0
1-methylcyclopentyl chloride	0.3 ± 0.1	-17.5 ± 0.4	-17.8 ± 0.5	-55
2-phenyl-2-propyl chloride	0 ^a	-19.0 ± 0.6	-19.0 ± 0.6	-55
2-methyl- <i>exo</i> -norbornyl chloride	0.8 ± 0.1	-18.8 ± 0.7	-19.6 ± 0.8	0
dichlorodiphenylmethane	0.6 ± 0.05	-23.1 ± 0.4	-23.7 ± 0.5	0
2-phenyl- <i>exo</i> -norbornyl chloride	5.7 ± 1.0	-20.2 ± 0.4	-25.9 ± 1.2	0
triphenylmethyl chloride	0.1 ± 0.05 ^a	-27.0 ± 0.2	-27.1 ± 0.3	-55
Bu ₄ N ⁺ Cl ⁻	0 ^a	-34.9 ± 1.0	-34.9 ± 1.0	-55

^a These values are for heat of dilution measurements; see previous article, Results.

Table II. Heats of Ionization in SO₂ClF (-55 °C)

RX	$\Delta H_s(\text{SO}_2\text{ClF})$	$\Delta H_{\text{react}}(\text{SO}_2\text{ClF}/\text{SbF}_5)$	$\Delta H_i(\text{SO}_2\text{ClF}/\text{SbF}_5)$
Chlorides			
isopropyl chloride	0	-15.3 ± 0.9	-15.3 ± 0.9
<i>sec</i> -butyl chloride	0.3 ± 0.1	-15.4 ± 0.7	-15.7 ± 0.8 (-75 °C)
	same	-29.7 ± 0.7	-30.0 ± 0.8 (-25 °C)
cyclopentyl chloride	0.3 ± 0.1	-17.0 ± 0.9	-17.3 ± 0.9
1-adamantyl chloride	3.0 ± 0.5	-18.6 ± 0.4	-21.6 ± 0.8
cyclohexyl chloride	1.0 ± 0.1	-21.5 ± 0.5	-22.5 ± 0.6 ^b
<i>exo</i> -norbornyl chloride	1.0 ± 0.2	-22.6 ± 0.6	-23.6 ± 0.8
<i>tert</i> -butyl chloride	1.0 ± 0.2	-24.4 ± 0.6	-25.4 ± 0.8
1-methylcyclopentyl chloride	0.5 ± 0.1	-26.6 ± 0.5	-27.1 ± 0.6
2-phenyl-2-propyl chloride	0 ^a	-30.3 ± 0.3	-30.3 ± 0.3
2-methyl- <i>exo</i> -norbornyl chloride	2.8 ± 1.0	-28.2 ± 0.9	-31.0 ± 1.5
2-phenyl- <i>exo</i> -norbornyl chloride	5.0 ± 0.4	-32.0 ± 0.9	-37.0 ± 1.2
Fluorides			
isopropyl fluoride	0	-16.8 ± 0.6	-16.8 ± 0.6
<i>sec</i> -butyl fluoride	0.3 ± 0.1	-17.1 ± 0.6	-17.4 ± 0.7 (-75 °C)
	same	-31.7 ± 0.7	-32.0 ± 0.8 (-25 °C)
1-adamantyl fluoride	3.0 ± 0.6	-19.9 ± 0.5	-22.9 ± 0.9
<i>exo</i> -norbornyl fluoride	1.0 ± 0.2	-24.8 ± 0.5	-25.8 ± 0.7
<i>tert</i> -butyl fluoride	0.7 ± 0.1	-26.6 ± 0.5	-27.3 ± 0.6

^a This is a heat of dilution measurement; see previous article, Results. ^b Ion rearranges; see text.

Table III. Heats of Ionization of Chlorides in SO₂ (-55 °C)

RCl	$\Delta H_s(\text{SO}_2)$	$\Delta H_{\text{react}}(\text{SO}_2/\text{SbF}_5)$	$\Delta H_i(\text{SO}_2/\text{SbF}_5)$
isopropyl chloride	0.3 ± 0.1	-3.7 ± 0.6	-4.0 ± 0.7
cyclopentyl chloride	0.5 ± 0.1	-4.7 ± 0.9	-5.2 ± 1.0
<i>exo</i> -norbornyl chloride	0 ^a	-11.7 ± 0.8	-11.7 ± 0.8
<i>tert</i> -butyl chloride	0 ^a	-12.0 ± 0.8	-12.0 ± 0.8
1-methylcyclopentyl chloride	0.6 ± 0.1	-14.3 ± 0.7	-14.8 ± 0.8
<i>sec</i> -butyl chloride	0.5 ± 0.1	-16.0 ± 0.3	-16.5 ± 0.4 ^b
2-phenyl-2-propyl chloride	0 ^a	-18.0 ± 0.4	-18.0 ± 0.4
2-methyl- <i>exo</i> -norbornyl chloride	0 ^a	-18.5 ± 0.8	-18.5 ± 0.8
2-phenyl- <i>exo</i> -norbornyl chloride	5.7 ± 1.1	-18.1 ± 0.2	-23.8 ± 1.2

^a These values are heat of dilution measurements; see previous article, Results. ^b Ion rearranges.

calories per mole too low because allowance had not been made for the heat absorbed in dissociating molecules from the crystal.

Most measurements were made at -55 °C. However, sometimes experimental problems required working at temperatures well above or below this value. Thus, in some cases the carbocations were only stable at very low temperatures. In other cases R-X was not soluble except at temperatures well above -55 °C. Again, since SO₂F₂ boils at -55.4 °C all measurements in this solvent were done at -65 °C. Not all of the alkyl halides listed in Tables I-III will dissolve in SO₂F₂ or SO₂F₂/SbF₅ at this temperature. Note also that because of low solubility of the halides in this solvent we have used heats of solution in SO₂ClF to derive the ΔH_i values in Table IV. For these reasons we are forced to make some comparisons between ionization processes at different temperatures. As was shown previously⁶ this is not apt to lead to significant errors.

Table V lists the enthalpies of reaction for capturing the carbocations in CH₂Cl₂ with Bu₄N⁺Cl⁻ in the absence of excess SbF₅. This procedure has also been described.⁶ Unfortunately, insolubility of the tetralkylammonium salt and some other difficulties prevented us from applying this confirmatory test in the other three solvents.

Discussion

In this section we will consider the data we have gathered for the presumed ionization of a series of simple secondary and

Table IV. Heats of Ionization in SO_2F_2 (-65°C)^a

alkyl halide	$\Delta H_s(\text{SO}_2\text{ClF})^b$	$\Delta H_{\text{react}}(\text{SO}_2\text{F}_2/\text{SbF}_5)$	$\Delta H_i(\text{SO}_2\text{F}_2/\text{SbF}_5)$
Chlorides			
isopropyl chloride	0	-17.9 ± 0.8	-17.9 ± 0.8
sec-butyl chloride	0.3 ± 0.1	-20.1 ± 0.8	-20.4 ± 0.9
cyclopentyl chloride	0.3 ± 0.05	-21.0 ± 0.6	-21.3 ± 0.7
tert-butyl chloride	1.0 ± 0.2	-28.0 ± 0.6	-29.0 ± 0.6
1-methylcyclopentyl chloride	0.5 ± 0.1	-30.9 ± 0.7	-31.4 ± 0.8
Fluorides			
isopropyl fluoride	0	-19.8 ± 0.9	-19.8 ± 0.9
sec-butyl fluoride	0.3 ± 0.1	-20.9 ± 0.7	-21.2 ± 0.8
exo-norbornyl fluoride	1.0 ± 0.2	-29.0 ± 1.0	-30.0 ± 1.0
tert-butyl fluoride	0.7 ± 0.1	-29.8 ± 0.6	-30.5 ± 0.7

^a These measurements were made at -65°C because the boiling point of SO_2F_2 is -55.4°C . ^b Owing to insolubility of RX into pure SO_2F_2 these values are used as the reference state for un-ionized RX .

Table V. Heats for Capturing Carbonium Ions in CH_2Cl_2 with $\text{Bu}_4\text{N}^+\text{Cl}^-$ (-55°C)

RCl	$\Delta H_i(\text{CH}_2\text{Cl}_2/\text{SbF}_5)$	$\Delta H_{\text{SbF}_5}(\text{CH}_2\text{Cl}_2/\text{RCl})^a$	$\Delta H_{\text{cap}}(\text{CH}_2\text{Cl}_2/\text{R}^+)^b$
exo-norbornyl chloride	-11.1 ± 0.4	-11.5 ± 0.3	-23.9 ± 0.8
1-adamantyl chloride	-11.1 ± 0.8	-12.8 ± 1.0	-21.0 ± 0.8
tert-butyl chloride	-15.5 ± 0.3	-16.2 ± 0.2	-18.1 ± 0.5
trichlorophenylmethane	-16.4 ± 0.7 (0°C)		-18.5 ± 0.5
1-methylcyclopentyl chloride	-17.8 ± 0.5	-19.2 ± 1.5	-15.4 ± 1.3
2-methyl-exo-norbornyl chloride	-19.6 ± 0.8	-17.9 ± 0.8	-16.3 ± 0.6
dichlorodiphenylmethane	-23.7 ± 0.5 (0°C)		-12.5 ± 0.4
2-phenyl-exo-norbornyl chloride	-25.9 ± 1.2	-23.6 ± 0.7	-10.3 ± 0.6
triphenylmethyl chloride	-27.1 ± 0.3	-26.8 ± 0.6	-6.0 ± 0.3
$\text{Bu}_4\text{N}^+\text{Cl}^-$	-34.9 ± 1.0	-33.6 ± 1.3	

^a See previous paper for details of measuring these values. It was not possible to measure $\Delta H_s(\text{SbF}_5)$ into CH_2Cl_2 precisely owing to a slow reaction between SbF_5 and CH_2Cl_2 ; thus these values are not corrected for this term. Since the reaction of SbF_5 with excess RX was immediate and complete in this solvent, correction for reaction of SbF_5 with CH_2Cl_2 was also considered to be irrelevant. ^b $\Delta H_s(\text{Bu}_4\text{N}^+\text{Cl}^-)$ into CH_2Cl_2 = -2.2 kcal/mol and the reported values have been corrected for this term.

tertiary alkyl chlorides in several solvents both as they relate among themselves and to gas-phase ionization work by others. Such comparisons of numbers are without value unless the processes to which they refer are authenticated thoroughly. For this reason, and because of the importance which we attach to these results, we have gone to unusual lengths to check them. Regrettably, none of these checks could be applied with equal rigor to all of the systems which were studied. However, the degree of self-consistency of the results is sufficiently high that we believe that considerable confidence can be placed in them (within our rather large experimental error limits).

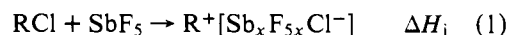
The ^1H NMR spectra of all ions in all solvents agreed reasonably well with published ones both in terms of chemical shifts and line shapes.⁶ However, in several cases such as the sec-butyl^{3a} or the 2-norbornyl^{5a} ions, which undergo very rapid degenerate rearrangements at low temperature, the ^1H NMR spectra are really of little value for structural proof or analytical determination because the lines are so broad. Thus, the price which is paid for gaining valuable kinetic information in these cases is the loss of resolution for structural proof.

Of much stronger inference for proving that ions were formed cleanly was our ability to capture them by addition of excess tetrabutylammonium chloride to solutions in which the ions had presumably been generated by the addition of SbF_5 to RCl in CH_2Cl_2 at low temperature.

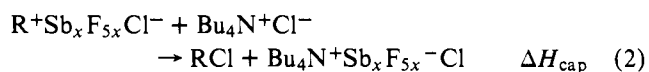
Analytical GLC experiments, which duplicated the conditions of the calorimetric ones, showed that in all cases over 95% of the RCl which had been exposed to the ionization and capture cycle could be recovered. Furthermore, in no case were extra GLC peaks found which were due to other products from rearrangement or elimination. Thus, we believe that conversion

to carbocation was essentially quantitative and that the incursion of significant side reactions could be ruled out.

The reaction which generates carbonium ions (or ion pairs) in solution is written for the sake of simplicity¹¹



The capture reaction is



Adding these as written gives



ΔH_i measures the enthalpy for heterolysis of the $\text{R}-\text{Cl}$ bond and generating " $\text{Sb}_x\text{F}_{5x}\text{Cl}^-$ " anion¹¹ in the solvent concerned. ΔH_{cap} measures the heat of forming the $\text{R}-\text{Cl}$ bond plus whatever electrostatic effects arise from transferring the complex anion from R^+ to Bu_4N^+ . Since such electrostatic terms are probably small, one should obtain a straight line of slope -1.00 and intercept ΔH_3 from a plot of ΔH_i vs. ΔH_{cap} ; i.e., the effects of substituents on ΔH_i , for breaking the $\text{R}-\text{X}$ bond, should be exactly inversely proportional to their effects on ΔH_{cap} , which measures the enthalpy of $\text{R}-\text{X}$ bond formation. Figure 1 confirms the validity of this treatment for reactions in CH_2Cl_2 at -55°C .

The Question of Chloronium Ions. Examination of the concentration dependence of the ^1H NMR spectra of several ions showed a gradual shift to lower field as the SbF_5/RCl ratio was increased. The thermodynamically more stable ions such as tert-butyl, adamantyl, 2-norbornyl, methylcyclopentyl, etc.,

reached a constant shift value of SbF_5/RCl ratios slightly greater than 1:1 in CH_2Cl_2 and SO_2ClF . However, the species produced from isopropyl chloride and cyclopentyl chloride only reached constant shifts after SbF_5/RCl ratios had exceeded 4/1. Furthermore, in CH_2Cl_2 and SO_2 the downfield shift never reached that obtained in SO_2ClF (the solvent of choice for carbonium ion generation) even when the ratio reached 20/1.

This behavior raised the possibility that the true species which were being made from isopropyl and cyclopentyl chlorides might include the chloronium ions $(\text{R}-\text{Cl}-\text{R})^+$ as proposed by Olah⁸ and Peterson⁹ even though our concentrations are far lower than those where they might be expected. This difficulty could not have been detected by the capture experiment since attack of $\text{Bu}_4\text{N}^+\text{Cl}^-$ on $\text{R}-\text{Cl}-\text{R}^+$ would presumably regenerate RCl exactly as it would from R^+ , with the same inverse relationship of ΔH_{cap} to the apparent ΔH_i .

The involvement of chloronium ions, as such, in the ΔH_i experiments was ruled out simply by repeating them with the corresponding alkyl fluorides. No evidence has yet been reported for the successful generation of aliphatic fluoronium ions, despite several attempts.⁸ We therefore consider that the constant difference of 1.5 ± 0.5 kcal/mol between ΔH_i for $\text{R}-\text{F}$ and $\text{R}-\text{Cl}$ for generation of the five cations (isopropyl, *tert*-butyl, *sec*-butyl, 2-norbornyl, and adamantyl) eliminates chloronium ion formation as a thermochemical problem in SO_2ClF . Chloronium ions can only be formed from quite unstable secondary ions. It therefore seems out of the question that a constant difference between ΔH_i for generating carbocations of greatly differing stabilities from RF and RCl could be found unless they all formed chloronium ions to the same extent or did not form them at all. The latter possibility seems far more likely. We recognize the possibility of chloronium ions being present in CH_2Cl_2 where no checks against fluorides were done.

Both isopropyl and cyclopentyl cations showed the same limiting downfield shifts when generated from 5/1 SbF_5/RF as from 5/1 SbF_5/RCl . For the former this corresponded to that obtained for isopropyl fluoride in neat SbF_5 .¹⁰ We take this to mean that these species and all of the other carbonium ions are fully formed (although not necessarily dissociated from their counterions) at low ratios and at all higher ones. The changing downfield ^1H NMR shifts at lower ratios might be due to loosening of the ion pair interaction between the carbonium ion and the complex antimony halide¹¹ ions as the fluoride content of the latter increases. The degree of dissociation of unstable carbonium ion pairs is at present entirely unknown. However, by analogy to alkylammonium, -phosphonium, and -sulfonium salts in weakly ionizing solvents^{12,13} there is no reason why ionization of $\text{R}-\text{X}$ by SbF_5 to the $\text{R}^+\text{SbF}_5\text{X}^-$ salt could not be complete even when there is virtually no dissociation to "free" ions such as could be detected by conductance experiments. We are unable to provide a thoroughly satisfying interpretation for the variable NMR shifts for these unstable ions but note that they are not accompanied by parallel thermochemical behavior.

Checks Based on Ionization of Isomeric Halides to a Common Ion. Most secondary ions which can rearrange to tertiary ions do so very rapidly.⁴ Under conditions where the same ion is produced as the final state from isomeric secondary and tertiary chlorides as initial states, the difference between the heats of ionization of the alkyl chlorides is simply the difference in their heats of formation, ΔH_f . Some relevant ΔH_f values have been measured or calculated with high precision by additivity schemes and molecular mechanics.¹⁴ A powerful external check on our results is therefore possible in cases where reliable ΔH_f values for $\text{R}-\text{X}$ are available. Unfortunately, these are very few.

The important example considered here is the formation of

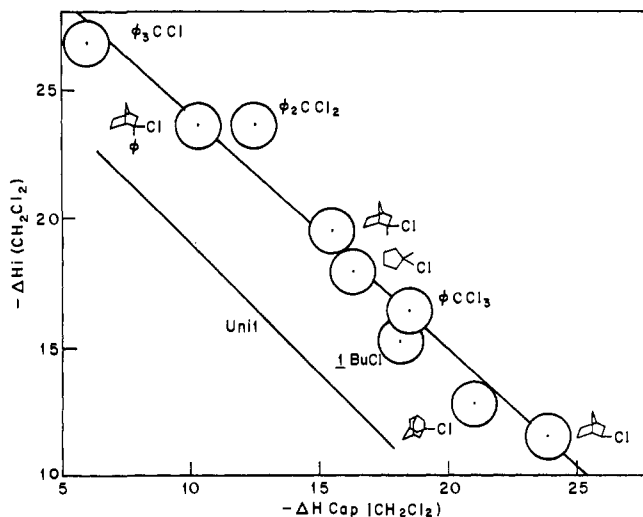


Figure 1. Inverse correlation of enthalpy of forming and capturing carbonium ions in dichloromethane.

the *tert*-butyl carbonium ion from *sec*-butyl chloride and *tert*-butyl chloride. At -25 °C in $\text{SO}_2\text{ClF}/\text{SbF}_5$ both chlorides are converted instantly to the *tert*-butyl cation. This is a clean reaction as shown by the presence of a single, sharp peak at 4.23 ppm in the ^1H NMR spectra of both solutions. The difference in ΔH_i (Table II) is 4.7 ± 0.7 kcal/mol for the fluorides and 4.6 ± 0.7 kcal/mol for the chlorides—the tertiary chlorides being more stable than their secondary isomers. The corresponding difference in heat of formation for the chlorides¹⁵ is reported to be 5.1–5.2 kcal/mol. In view of the problems of measuring heats of formation, the approach described here is probably the simplest and most precise available for comparing appropriate isomeric halides. Thus, for 1-methylcyclopentyl chloride and cyclohexyl chloride, both of which go to the methylcyclopentyl ion, we find cyclohexyl chloride to be *less stable* by 4.6 kcal/mol. Here the relative stabilization of secondary halide compared to tertiary chloride is reversed compared to the pair of butyl chlorides. The inversion of 10 kcal/mol for the secondary–tertiary difference serves to emphasize strongly the important contribution that initial state stabilities can make to energies of ionization.

Enthalpy of Rearrangement of *sec*-Butyl to *tert*-Butyl Cations. This rearrangement occurs at a conveniently measurable rate between about -60 and -40 °C. *sec*-Butyl carbonium ion can be prepared at -75 °C or lower temperatures and held without rearrangement for 1 h or more in pure SO_2ClF .^{3,16}

In a previous report¹⁶ the enthalpy of the rearrangement was determined using scanning calorimetry by measuring the integrated heat liberated from a 0.5 M solution of *sec*-butyl cation as it warmed from -80 to -20 °C. In the present study we have measured ΔH_i for generating the *sec*-butyl cation at -75 °C, from *sec*-butyl chloride and fluoride. The same measurements were repeated at -25 °C where both halides go to the *tert*-butyl cation. The difference between ΔH_i obtained at the two temperatures (-14.3 ± 0.7 for the chloride and -14.6 ± 0.7 for the fluoride) corresponds closely to our previous value of -14.5 ± 0.5 kcal/mol¹⁶ and to the gas-phase difference of -14 kcal/mol.¹⁷ The agreement of the two results obtained by quite different calorimetric techniques is encouraging. Furthermore, the fact that the present values were obtained at much lower concentrations, ca. 10^{-3} M, supports the claim that concentration effects are negligible within our limits of error. A complete accounting of the enthalpy differences between ionization of *sec*-butyl and *tert*-butyl halides is represented in Figure 2.

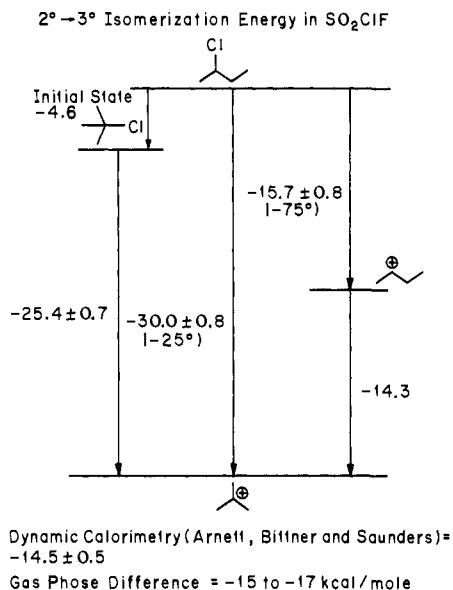


Figure 2. Dissection of contributing terms to enthalpy of formation of *tert*-butyl carbonium ion from *sec*-butyl chloride and *tert*-butyl chloride in SO₂ClF/SbF₅.

Rearrangement of Cyclohexyl to Methylcyclopentyl Cation.

Numerous attempts were made to generate the cyclohexyl carbonium ion at temperatures down to -110 °C. They all failed in our hands as they have for others.¹⁸ Apparently, the conversion of this ion to the methylcyclopentyl cation occurs instantly, even in the gas phase.^{18b}

As noted above, the fact that cyclohexyl chloride ionizes *less exothermically* to methylcyclopentyl cation than does methylcyclopentyl chloride means that cyclohexyl chloride is stabler by 4.6 kcal/mol than is methylcyclopentyl chloride. This difference corresponds well to the difference between cyclohexane and methylcyclopentane¹⁵ or between methylcyclohexane and 1,1-dimethylcyclopentane, which may be considered as models for cyclohexyl chloride and 1-methylcyclopentyl chloride, and presumably reflects the smaller strain and nonbonded repulsion factors in the cyclohexyl ring.

Comparison of Figure 3 with Figure 2 clarifies the differences between the cyclohexyl and the *sec*-butyl chloride ionizations and isomerizations. The dotted lines on the right show two hypothetical ways of apportioning the -22.5 kcal/mol heat of ionization for cyclohexyl chloride to methylcyclopentyl ion. One approach is to consider that the heat of ionization of cyclohexyl chloride to cyclohexyl ion is in the "normal" range for secondary chlorides (Table II) and is close to that for cyclopentyl chloride to cyclopentyl cation, i.e., about -17 kcal/mol. This option leaves only -5.5 kcal/mol for the heat of isomerization of cyclohexyl ion to methylcyclopentyl ion.

This approach has independent support from the correlation of ΔH_i 's and free energies of activation for solvolysis which we have reported previously.¹⁹ One may estimate a ΔH_i for cyclohexyl chloride to the cyclohexyl cation of -16.1 kcal/mol. This leaves only -6.4 kcal/mol for the isomerization energy of cyclohexyl to 1-methylcyclopentyl cation, which even on the face of it seems abnormally low compared to other secondary-tertiary differences.⁴ However, if the methylcyclopentyl cation had 5 kcal/mol more ring strain than the cyclohexyl cation, as is true for the chlorides, the discrepancy is understandable.

Alternatively if we consider that the cyclohexyl-methylcyclopentyl ion difference lies in the normal secondary-tertiary carbonium ion range our estimate from the generally accepted best numbers would make it -16 kcal/mol.²⁰ If this were so it leaves a very modest -6.5 kcal/mol for ΔH_i , the heat of

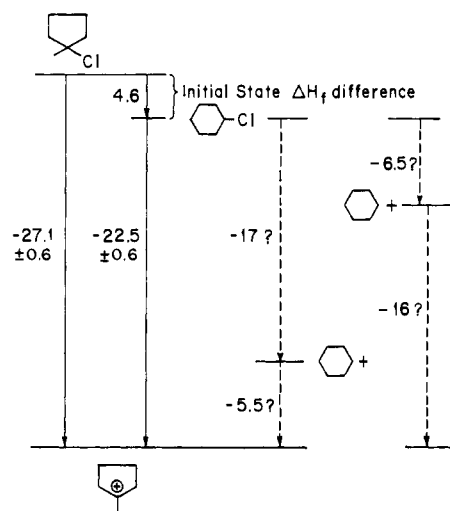


Figure 3. Isomerization of cyclohexyl ion to methylcyclopentyl ion.

formation of the cyclohexyl ion from cyclohexyl chloride in SO₂ClF, which raises the question of why its solvolysis rate should be so close to that of cyclopentyl chloride if its heat of ionization is smaller by 10 kcal/mol.

There remains an intriguing dilemma whose limits seem to be set by the -22.5 kcal/mol heat of conversion of cyclohexyl chloride to 1-methylcyclopentyl ion, a value which seems very solidly based. Either the heat of formation of the cyclohexyl ion is abnormally (10 kcal/mol) small or its heat of isomerization to the 1-methylcyclopentyl cation is abnormally small (10 kcal/mol). "Splitting the difference" makes both of them abnormal by 5 kcal/mol. In view of the present dearth of information about related systems we can only pose the problem rather than present a rigorous explanation. We prefer to consider that the isomerization energy is small because of strain in the methylcyclopentyl cation ring (a proposal advanced by a referee).

Substituent Effects on ΔH_i . Having presented the evidence for the reliability of our ΔH_i values, we will now consider the effect of changing carbonium ion structure on the ionization process. The principal point of reference will be the values listed in Table II, which were determined, unless stated otherwise, at -55 °C in carefully purified SO₂ClF with a large excess (10- to 20-fold) of SbF₅. All systems, except those derived from the phenylchloromethanes, were soluble in this medium and gave clear solutions which were water white or light yellow at the end of each run following seven or eight successive additions of R-X to generate the R⁺ cation in the calorimeter. This was the best system both in terms of quality and quantity of results and fortunately is the one which has been used for many related NMR studies.⁶ In Table VI we have referenced all results to ΔH_i for the *tert*-butyl cation since we have high confidence in our ability to generate it cleanly under all conditions considered here.

Descending the column under ΔH_i in Table II, it is clear that the exothermicity of the reaction increases over a wide range from formation of the thermodynamically least stable isopropyl cation to the most stable 2-phenyl-2-norbornyl one. ΔH_i is calculated as the difference between the heat of solution of R-X into pure SO₂ClF [$\Delta H_s(\text{SO}_2\text{ClF})$] and that of RX in SO₂ClF/SbF₅ solution [$\Delta H_{\text{react}}(\text{SO}_2\text{ClF}/\text{SbF}_5)$]. Since the partial molar volume of the R⁺Sb_xF_{5x}X⁻ salt should be nearly the same as that of the corresponding amount of RX + SbF₅, we do not expect relative enthalpy contributions due merely to cavity effects to be significant.²¹ Therefore, ΔH_i should represent the heat release from transferring the halide moiety from R-X to solvated SbF₅ in solution. The magnitude of ΔH_i

Table VI. $\delta\Delta H_i(R^+)$ Relative to *tert*-Butyl Chloride

RX	$\delta\Delta H_i(\text{soln RCl})$					$\delta\Delta H_i(\text{gas, RH})^a$
	CH ₂ Cl ₂	SO ₂	SO ₂ ClF	SO ₂ F ₂		
isopropyl chloride	+8.0 ± 1.5	+8.0 ± 1.1	+10.1 ± 1.0	+11.1 ± 1.0	+15.8 ± 1.4	
isopropyl fluoride			+8.6 ± 1.2 (-75 °C)	+9.2 ± 1.1		
<i>sec</i> -butyl chloride			+9.7 ± 1.1 (-25 °C)	+8.6 ± 1.1		
<i>sec</i> -butyl fluoride			-4.6 ± 1.1 (-75 °C)	+7.8 ± 1.0	+12.0 ^b ± 2.8	
cyclopentyl chloride	+6.5 ± 1.0	+6.8 ± 1.3	+8.1 ± 1.1	+7.7 ± 0.9	+9.9 ± 1.4	
1-adamantyl chloride	+4.4 ± 0.9		+3.8 ± 1.1		-10.8 ^b ± 10.0	
1-adamantyl fluoride			+2.5 ± 1.2			
cyclohexyl chloride			+2.9 ± 1.0			
<i>exo</i> -2-norbornyl fluoride			-0.4 ± 1.1	-1.0 ± 1.2		
<i>exo</i> -2-norbornyl chloride	+4.4 ± 0.5	+0.3 ± 1.1	+1.8 ± 1.1		-1.5 ± 1.4	
<i>tert</i> -butyl chloride	0(-15.5) ± 0.3	0(-12.0 ± 0.8)	0(-25.4) ± 0.8	0(-29.0) ± 0.6	0 ± 1.0	
<i>tert</i> -butyl fluoride			-1.9 ± 1.0	-1.5 ± 0.9		
1-methylcyclopentyl chloride	-2.3 ± 0.6	-2.8 ± 1.1	-1.7 ± 1.0	-2.4 ± 1.0	-6.4 ± 1.4	
cumyl chloride	-3.5 ± 0.7	-6.0 ± 0.9	-4.9 ± 0.9			
2-methyl- <i>exo</i> -norbornyl chloride	-4.1 ± 1.0	-6.5 ± 1.1	-5.6 ± 1.6		-7.5 ± 1.4	
2-phenyl- <i>exo</i> -norbornyl chloride	-10.4 ± 1.2	-11.8 ± 1.4	-11.6 ± 1.4			
phenyltrichloromethane	-0.9 ± 0.8					
diphenyldichloromethane	-8.2 ± 0.6					
triphenylchloromethane	-11.6 ± 0.4					
tetrabutylammonium chloride	-19.4 ± 1.0					
SbF ₅ ^c	-1.8 ± 0.8	-11.5 ± 1.30	0.0	5.6 ± 1.0		

^a These data are from J. J. Solomon and F. H. Field, *J. Am. Chem. Soc.*, **98**, 1567 (1976). ^b $\delta\Delta H_i(\text{gas})$ from R-Br data: J. L. Beauchamp, private communication. ^c These values are for the heats of solution of SbF₅ in the solvent shown.

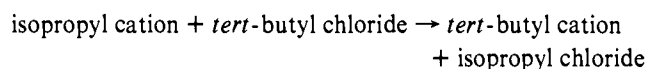
Table VII. Stabilization Energies Resulting from Exchange Reactions $R^+ + R'Cl \rightarrow RCl + R'^+$, $\delta\Delta H_i$ (kcal/mol)

R ⁺ to R' ⁺	CH ₂ Cl ₂	SO ₂	SO ₂ ClF	SO ₂ F ₂	gas ²⁸
Methyl Effect					
isopropyl to <i>tert</i> -butyl	-8.0	-8.0	-10.1	-11.1	-16
cyclopentyl to 1-methylcyclopentyl	-8.8	-9.0	-9.8	-10.1	-16
2-norbornyl to 2-methyl-2-norbornyl	-8.5	-6.8	-7.4	not soluble	-6
Phenyl Effect					
isopropyl to cumyl	-12.5	-14	-15.0	insoluble	no data
2-norbornyl to 2-phenyl-2-norbornyl	-14.8	-12.1	-13.4	insoluble	no data

will depend on the ability of the cation and anion to stabilize charge by internal delocalization through hyperconjugation, polarization, etc., and by interaction with the medium. It will also depend (see below) on the strength of the interaction of SbF₅ with the solvent.

According to electrostatic theory, the solvation enthalpy of an ion depends inversely on its size. There should therefore be some cancellation of the increasing ability of carbonium ions to delocalize charge within their structures as their size increases and the corresponding decrease in their electrostatic solvation energy. The general trend of increasing stability with the increasing size is in complete conformity with predictions of the carbonium ion theory even at its most primitive level. Thus, for the secondary ions we find the order of increasing stability: isopropyl < *sec*-butyl < cyclopentyl << 2-norbornyl. For the tertiaries: *tert*-butyl < methylcyclopentyl << 2-methylnorbornyl.

The effect of substituents of stabilizing the charge of carbonium ions is a matter of perennial interest,²² especially in view of arguments concerning the secondary bicyclic systems.²³ The data in Table VI allow us to explore this question by setting up hypothetical exchange reactions by adding pairs of ionization reactions, e.g.:



The result of such a transfer of chloride ion to a secondary carbonium ion from a homologous tertiary chloride is about -10 kcal/mol both for the isopropyl → *tert*-butyl cation conversion and for the cyclopentyl → 1-methylcyclopentyl cation conversion. Conversion of the 2-norbornyl to 2-methylnorbornyl cation is somewhat less exothermic, the methyl effect being about -7.4 kcal/mol (see Table VII). This corresponds closely to Brown's estimate^{23c} (-6.5 kcal/mol) based on the difference in free energies of activation for solvolysis of 2-norbornyl and 2-methyl-2-norbornyl chloride.

We draw attention to the fact that ΔH_i values for the 2-norbornyl and the 2-methyl-2-norbornyl systems are somewhat larger than for the other secondary and tertiary systems. However, the exothermic increase on going from the 2-norbornyl to the 2-methylnorbornyl system is somewhat smaller than for the isopropyl → *tert*-butyl or the cyclopentyl → 1-methylcyclopentyl cases.

The effect of replacing the methine hydrogen by a phenyl group is greater by 5-6 kcal/mol than is that for a methyl

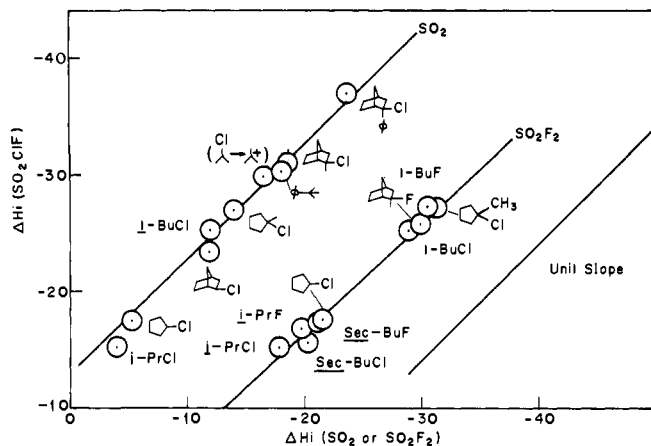


Figure 6. Correlation of heats of ionization of alkyl halides in SO_2ClF vs. corresponding values in SO_2 and SO_2F_2 .

isopropyl one. The effect of replacing chlorine by phenyl in the phenylchloromethanes is considerable (Table VI).

Figures 5 and 6 compare the ΔH_i values obtained in SO_2ClF with those in other solvents— CH_2Cl_2 , SO_2 , SO_2F_2 , and magic acid. Although complete data sets were not obtained in any solvent, the nearly unit slope for correlations of comparable data imply that similar processes are occurring in each case, namely, carbonium ion formation.

Comparison with Gas-Phase Results. Carbonium ion formation has been compared in the gas phase by hydride ion transfer,²⁸ by bromide transfer,²⁹ and by protonation of olefins.²² The results are correlated with ours in Figure 7. Conformity of the gas-phase data for the norbornyl ion to the correlation line of Figure 6 implies that the gas-phase ionization process for this ion is nearly equivalent to that in solution and that it is probably not suffering rearrangement to an isomeric ion in the gas phase.²⁸

The slope of the line in Figure 6 is roughly 1.5 for $\Delta H_i(\text{gas})$ vs. $\Delta H_i(\text{SO}_2\text{ClF})$ which is comparable to that of 1.23 which Wolf, Abboud, and Taft³⁰ have found for a corresponding free-energy plot of a series of resonance-stabilized carbonium ions in the gas phase and in water. This provides strong support for the notion that relative orders of carbonium ion stability are usually (though not invariably)³¹ almost insensitive to electrostatic solvent effects.³² Such a result is surprising enough for highly delocalized cations. It is more extraordinary to see such close correspondence between the transfer behavior of very stable ions from the gas phase to water³⁰ and of very unstable ones to SO_2ClF (Figure 7). We recognize, of course, that unless carbonium ions enjoy unusual resonance stabilization they will be captured by nucleophilic solvents. However, unlike ammonium or oxonium ions, which are strongly hydrogen bonded to basic solvents,^{33,34} carbonium ions are denied this type of specific mode of solvation. A fascinating example of the difference in such interactions was reported recently by Hiraoka and Kebarle³⁵ for the gas-phase hydration of the *tert*-butyl cation. They found that the addition of the first water molecule, to produce the *tert*-butyl alcohol oxonium ion ($\text{C}_4\text{H}_9\text{OH}_2^+$), was considerably less exothermic than were the following steps whereby water molecules were hydrogen bonded to the oxonium ion to produce a gas-phase cluster.

In previous papers^{33,34} we have used a Born cycle³⁶ to calculate relative solvation energies for ammonium and oxonium ions from the gas phase to fluorosulfuric acid. Staley, Wieting, and Beauchamp²⁹ have applied the same approach to solvation of a few carbocations (mostly bromonium ions). We regret that there do not exist at this time a sufficient number of reliable heats of formation of the neutral halide precursors to make such an exercise meaningful for the carbonium ions studied

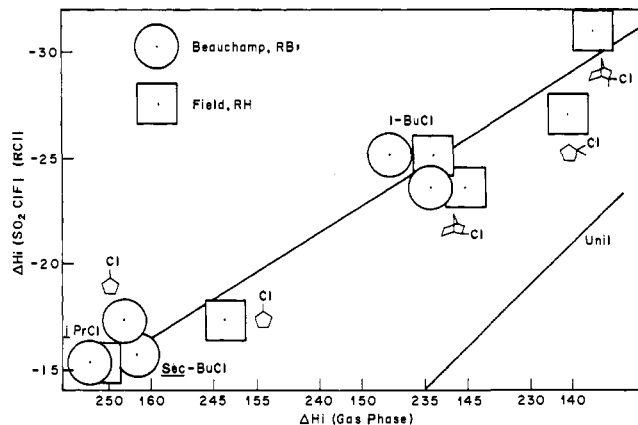


Figure 7. Correlation of heats of ionization of alkyl chlorides in SO_2ClF vs. gas phase: O, Beauchamp's²⁹ values for RB; □, Field's²⁸ values for hydride exchange.

by us. Gas-phase stabilities of carbonium ions are becoming increasingly well established.^{17,22,29,37} We hope that the corresponding information regarding the neutrals will soon be forthcoming.

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Reactivity of Arylcarbenium Ions with Alkylamines and Ammonia in Solutions. Kinetic Effect of Cyclopropyl Substitution. Solvent Effect¹

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Abstract: Rate constants have been determined for some selected reactions of arylcarbenium ions with trialkylamines and ammonia in three chlorinated hydrocarbon solvents. They were obtained by pulse radiolysis which permits the direct optical observation of the transient and its reactions in real time. Included among these are the reactions of α -cyclopropyl- and α,α -dicyclopropylphenylcarbenium ion. Cyclopropyl substitution is found to produce only a very small kinetic effect. A significant solvent effect is found for only small changes in solvent properties. The results are considered with regard to the relationship between the reactivity of a carbocation and its solvolytic rate.

We have recently reported² pulse radiolysis studies of arylcarbenium ions in 1,2-dichloroethane solution in which absolute rate constants for a number of electrophilic reactions of these carbocations were presented. Among these were the reactions with trialkylamines. This work on the amine reactions has been extended to obtain new information on the following: (a) the reactivity of α -cyclopropylphenylcarbenium ions toward the alkylamines, allowing us to compare our data on the kinetic effect of cyclopropyl substitution with observations from a different type of experiment, namely, with solvolysis data;³⁻⁷ (b) the reactivity in different solvents, which demonstrates that even a small difference in solvent properties can result in a significant change in reactivity of the carbocations; (c) the reactivity of the arylcarbenium ions with ammonia, which will be seen to have a direct bearing on the consideration of mechanism.

Experimental Section

As previously described,^{8,9} the source of the electron pulse was a Varian V-7715A electron linear accelerator, delivering 3-4 MeV electrons at a pulse current of about 300 mA for pulses of 100-1400-ns duration and about 600 mA for pulses of less than 80-ns duration. Electron pulses ranging from 60 to 800 ns were used in this work. The concentration of transients produced was on the order of 10^{-66} - 10^{-7} M. All the runs were done at 24 ± 1 °C. Transient absorptions were determined using an RCA 1P28 or RCA 7200 photomultiplier as detector. The time resolution of the detection system is about 5 ns, so

that it was possible to observe the kinetics on a submicrosecond time scale. A Bausch and Lomb grating monochromator, type 33-86-25, f/3.4, was used with grating parameters and exit slit widths such that the band-pass was 3 nm or less. Appropriate Corning filters were used.

Our standard 20-mm reaction cells with high-purity silica windows were used in all experiments. Generally, a double pass of the analyzing light beam was used. A detailed description of the optical arrangement and the detection system has been presented elsewhere.^{8,9}

1,2-Dichloroethane (DCE), methylene chloride (MC), and 1,1,2-trichloroethane (TCE) were used as solvents. The DCE was obtained from Matheson Coleman and Bell, the MC from Fisher, and the TCE from Aldrich. The purification has been described.¹⁰ Solvent was transferred into the reaction cell by distillation *in vacuo*, the quantity being determined by weight difference. All liquids were degassed by a series of freeze-evacuation-thaw cycles.

The purification of dibenzylmercury (Alfa Inorganics), bromodiphenylmethane (Chemical Samples Co.), and triphenylmethanol (Aldrich) has been described.² Cyclopropylphenylcarbinol and dicyclopropylphenylcarbinol (both from Aldrich) were purified by fractional distillation at about 18 Torr. Triethylamine, tripropylamine, and tri-*n*-butylamine (all from Aldrich) were purified as described previously.² The quantity of amine transferred into the reaction cell was determined by weight difference. Ammonia (Matheson) solutions in DCE were made up from amounts of ammonia determined by *P-V* measurement of the gas. The concentration of ammonia in solution was determined from the solubility in DCE (8 mol %) for a cell with 80% liquid volume, and assuming Henry's law; the calculation showed that only 1% of the measured amount of ammonia remained in the gas phase.