by forming such small amounts of iron(II) that our analytical methods cannot identify the oxygen derived from the equivalent amounts of hydrogen peroxide.

(d) The mechanism as developed here suggests that the oscillations could be followed potentiometrically. We made a number of experiments in which we recorded the potential between a platinum and a glass electrode. Tantalizing suggestions of oscillations could never be surely separated from noise due to bubbles on the electrode surface. We observed only small potential differences between sulfuric acid solutions prepared entirely with ferric or with ferrous salts. It appears that in this highly acidic medium the metal surface is so swamped by interaction with protons that small amounts of metal ions have no significant effect on the potential.

The above observations cause us a little concern as to whether we have yet identified all of the essential features of the mechanism. However, we have demonstrated unequivocally that oscillations do occur, that bursts of gas evolution do not result from nucleation of a supersaturated solution free of any gas phase, and that carbon monoxide therefore reacts chemically to promote its further formation. The mechanism we have developed does accommodate these facts, and we are unable to devise any alternative scheme that does not involve carbonyl complexes of transition metal ions. We hope that the essential features will stand up to further scrutiny, and we propose to undertake model calculations to test the mechanism further.

pointing out the large effect of carbonylation on   eduction potential of iron(III).

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Electronic Structure and Protonation of Alkyl Chlorides[1]

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Abstract: Trends and correlations for several properties of alkyl chlorides including ionization potentials, proton affinities and force constants are discussed using both experimental data and the results of MINDO/3 computations. The linear dependence of ionization potentials on Taft's σ^* constant appears to be valid only for simple, acyclic alkyl chlorides. However, a good, general correlation is discovered between proton affinities and the total charge on the ClH fragment in protonated alkyl chlorides. Thus, the ability of the alkyl group in RClH$^+$ to accommodate positive charge controls the proton affinities. This leads to the observation that there is a rough relationship between proton affinities and solvolysis rates. The utility of protonated chlorides as models for ion pairs is also considered. The stabilization of a carbonium ion by HCl in RClH$^+$ is found to be consistent with a simple charge transfer expression. Implications concerning the differential solvation of carbonium ions are discussed.

Alkyl halides are an important class of organic compounds owing to their widespread use as electrophilic substrates in carbon–carbon bond forming reactions, functional group interconversions, and solvolysis experiments.[3] Consequently, it is not surprising that some effort has been devoted to determining their physical characteristics, e.g., structural parameters,[4] ionization potentials,[5] electronic spectra,[6] dipole moments,[7] vibrational spectra and force constants,[8] dissociation energies,[9] conformational preferences,[10] and proton affinities.[11] The predominance of the data pertains to simple, acyclic compounds, which leaves a disappointing storage of quantitative information on the properties of cyclic alkyl halides.

Although understanding of these species could be enhanced, in principle, by studies employing nonempirical molecular orbital methods, such calculations have been generally restricted to simple fluorides owing to the large number of basis functions needed to describe the other halides.[12] Unfortunately, fluorides are less interesting from a traditional, experimental standpoint than chlorides, bromides, or iodides, since fluoride ion is both a relatively poor nucleophile and leaving group in protic solvents.[3]

An alternative for the study of these compounds is the semiempirical MO method, MINDO/3. Both Dewar[13] and we[2] have found the results to be in good agreement with ex-

Table I. LUMO Energies, Ionization Potentials, Proton Affinities, and HCl Affinities[a]

RCl	Calcd[b]				Exptl		
	ϵ_L	IP	PA	ΔE_s	IP[c]	PA	ΔE_s
HCl	0.86	12.11	148.1	148.1	12.74	141,[f] 138[j]	141,[c,f] 138[j]
MeCl	0.55	11.10	166.3	53.3	11.22	160[g]	51[g,i]
EtCl	0.44	10.91	180.4	33.0[d]	10.97	172[g,h]	27[g-i]
n-PrCl	0.44	10.80	183.4	34.0[e]	10.82		
i-PrCl	0.32	10.74	191.2	21.0	10.78		
t-BuCl	0.18	10.51	199.1	13.2	10.61		

[a] Orbital energies and IPs in eV; PAs and ΔE_s's in kcal/mol. [b] MINDO/3 results. [c] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, and K. Draxl, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 26 (1969). [d] $\angle$ClC2H fixed at 100° in reference ethyl cation. [e] $\angle$CCC fixed at 100° in refernce n-propyl cation. [f] M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969). [g] J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Patt, *J. Am. Chem. Soc.*, **94**, 2798 (1972). [h] J. L. Beauchamp, private communication. [i] F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970). [j] D. H. McDaniel, unpublished drift cell value.

Figure 1. The frontier orbitals of methyl chloride. The orbital energies are MINDO/3 values in eV.
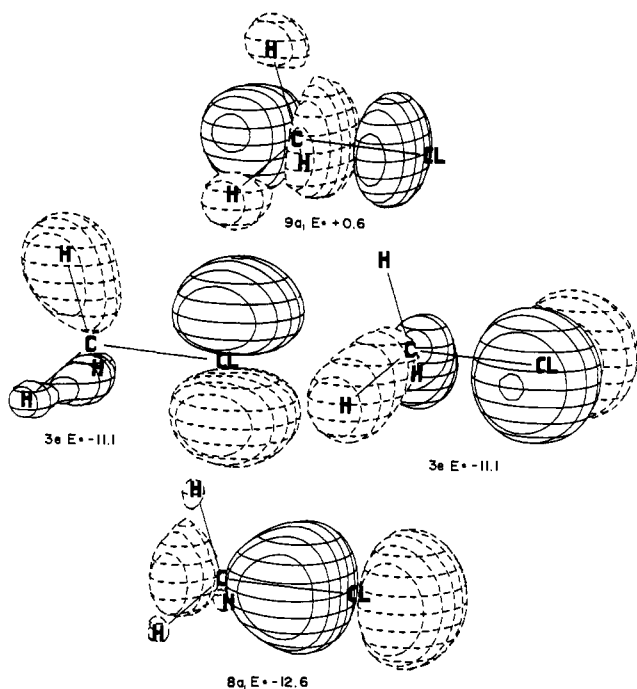

Figure 2. The frontier orbitals of isopropyl chloride. The orbital energies are MINDO/3 values in eV.

periment for alkyl chlorides, while the treatment of fluorides is less promising.[2a] In addition, we have recently performed ab initio calculations on the simple alkyl chlorides, HCl to t-BuCl, and their protonated analogues.[2e] The calculated properties using the STO-3G basis set were found to have similar reliability as MINDO/3 results, even though there are significant differences in the geometries of the protonated species predicted by the two methods. The general agreement between experimental, STO-3G, and MINDO/3 results for alkyl chlorides provides assurance that both theoretical procedures are suitable for modeling these compounds.[31]

In the present work, the results of our MINDO/3 studies of alkyl chlorides are summarized with emphasis on protonation and cyclic species. The accompanying paper focuses on the comparison of ab initio and MINDO/3 results for the acyclic compounds. Consequently, the description of the general aspects of the electronic structure and properties of alkyl chlorides is primarily contained in this work. Several interesting correlations are considered: ionization potentials and σ^*, proton affinities (PAs) and the charge on the ClH fragment in RClH[+], carbonium ion-HCl stabilization energies and a simple charge transfer expression, and proton affinities and solvolysis rates. Protonated alkyl chlorides are proposed
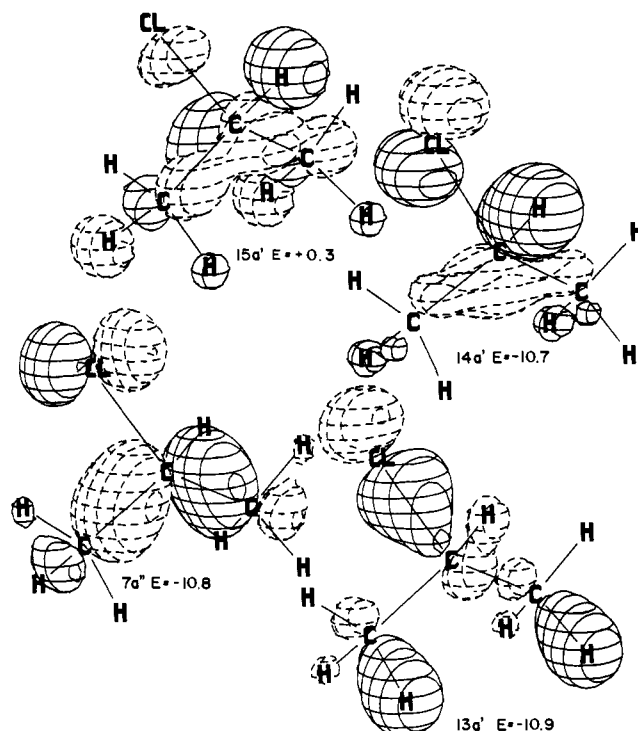
as a model for ion pairs occurring in solvolyses and also provide insight into the differential solvation of carbonium ions. Our position that more delocalized carbonium ions, e.g., nonclassical ions, should be relatively less well solvated in electron-donating solvents is reiterated.

Electronic Structure

Alkyl halides are characterized by three, high-lying, filled lone pair molecular orbitals and a low-lying, empty C-halide antibonding σ MO.[14] These orbitals are illustrated for methyl chloride and isopropyl chloride in Figures 1 and 2.[15,16] Using the standard notation,[17] the MOs for methyl chloride are designated n_σ, n_π, and σ^*_{CCl} where the n_π MOs are the degenerate HOMOs. The degeneracy is lifted slightly in isopropyl chloride owing to the reduction in symmetry. The n_σ MO for methyl chloride has σ_{CH_3} and σ_{CCl} as well as lone pair components, while the n_π MOs mix chlorine 3p and π_{CH_3} character in an antibonding manner, and σ^*_{CCl} reveals a contribution from $\sigma^*_{CH_3}$.[18]

Several investigators have noted correlations between the ionization potentials (IPs) for alkyl halides and Taft's σ^* constants for the alkyl groups.[5b,20] The correlation is illustrated
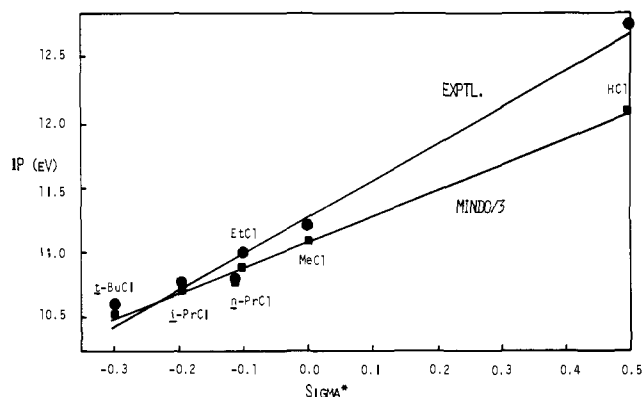
Figure 3. Linear relation between ionization potentials for alkyl chlorides and σ^* for the alkyl group.

Figure 4. Variation of the energy of the n_σ and average of the n_π MOs with σ^*. MINDO/3 results.

Table II. Bond Lengths and Force Constants[a]

	Calcd[b]		Exptl	
RCl	r_{XCl}	f_{XCl}	$r_{XCl}{}^c$	f_{XCl}
HCl	1.230	4.94	1.274	4.81[e]
MeCl	1.745	3.77[d]	1.781	3.50[f]
EtCl	1.775	3.49	1.779	
n-PrCl	1.774	3.47	1.775	
i-PrCl	1.809	3.16	(1.795)[i]	3.34[g]
t-BuCl	1.847	2.83[d]	1.80	2.86[h]

[a] Bond lengths in Å; force constants in mdyn/Å. [b] MINDO/3 results with complete geometry optimization. [c] L. E. Sutton, *Chem. Soc., Spec. Publ.*, No. 11 (1958); No. 18 (1965). [d] D. G. Graczyk, R. L. Julian, J. W. Taylor, and S. D. Worley, *J. Am. Chem. Soc.*, **97**, 7380 (1975). [e] T. L. Cottrell, "The Strength of Chemical Bonds", Butterworth, London, 1958. [f] J. Bron, *Can. J. Chem.*, **52**, 3078 (1974). [g] C. G. Opaskar and S. Krimm, *Spectrochim. Acta, Part A*, **23**, 2261 (1967). [h] R. C. Williams and J. W. Taylor, *J. Am. Chem. Soc.*, **95**, 1710 (1973). [i] Estimated.[g]

Table III. Calculated Properties for Cyclic Chlorides[a,b]

Chloride	ϵ_L	IP	PA	ΔE_s	r_{CCl}	f_{CCl}
Cyclopropyl	0.38	9.95	179.8	28.0	1.768	3.74
Cyclobutyl	0.36	10.23	186.2	24.2	1.787	3.56
endo-2-Norbornyl	0.35	10.29	189.3	14.7	1.796	3.65
Cyclopentyl	0.34	10.48	191.1	20.9	1.797	3.00
exo-2-Norbornyl	0.34	10.22	193.2	18.9	1.795	3.49
2-Methyl-*endo*-2-norbornyl	0.23	10.16	198.5	4.5	1.841	
2-Methyl-*exo*-2-norbornyl	0.24	10.05	203.1	8.8	1.844	

[a] See footnote a of Tables I and II for units. [b] MINDO/3 results.

in Figure 3 using the IP data for simple alkyl halides summarized in Table I. As shown, the agreement between MINDO/3 and experimental IPs is very good except for HCl. Interestingly the correlation of the MINDO/3 values with σ^* is better than for the experimental ones. The equation

$$IP(eV) = 2.819\sigma^* + 11.291 \qquad (1)$$

gives the relation for the experimental data determined by a least-squares fit. The correspondence is clearly not general. For example, the experimental IPs of CCl_4, $CHCl_3$, and CH_2Cl_2 are 11.5, 11.5, and 11.3 eV,[5] while eq 1 predicts 18.8, 16.8, and 14.2 eV, respectively.[21] Furthermore, the MINDO/3 IP for cyclopentyl chloride (Table III) and eq 1 may be used to predict a σ^* for cyclopentyl of -0.29, which does not compare well with Taft's value of -0.20.[21]

The progressive lowering of the IPs (raising of the HOMO energies) with increasing size of the alkyl chloride and lowering of σ^*_{CCl} (ϵ_L in Table I) is easily rationalized and is manifested in increasing λ_{max} values.[6] First, the C–Cl bond lengthens with greater substitution (Table II) which reflects greater R^+Cl^- character as R^+ becomes more stable. This decreases the C–Cl antibonding in σ^*_{CCl}. In addition, branching provides increased bonding interactions in the LUMO as illustrated by comparing Figures 1 and 2. This is analogous to the situation in conjugated hydrocarbons.[22] For the HOMOs, the C–Cl bond lengthening reduces the antibonding. However, this is more than offset by two factors: (1) The π_{CH_3} components in the HOMOs of methyl chloride are progressively replaced by contributions from (higher energy) π-type CC bonding combinations. (2)
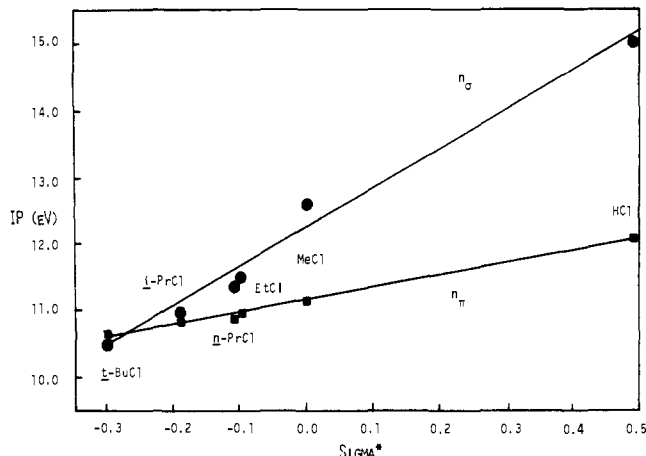
The number of antibonding interactions (nodes) increases as in conjugated systems.

The most pronounced effect of branching is on the n_σ level. The energy of this MO also correlates with σ^* as shown in Figure 4, but with a steeper slope than for n_π. This may be attributed to decreased C–Cl bonding in n_σ with increased branching and to replacing the σ_{CH_3} character in the MO with σ_{CC}. The absolute energies of the n_σ levels appear to be overestimated by MINDO/3 based on the PES value of 14.4 eV for the second band in CH_3Cl as compared to the MINDO/3 prediction of 12.6 eV.[23] A consequence is the apparently incorrect finding of MINDO/3 that the HOMO of *tert*-butyl chloride is n_σ rather than n_π by a slim margin. Both STO-3G[2e] and EH[24] calculations yield the opposite order with gaps of 1.6 and 0.9 eV, respectively.

The IPs for the simple cyclic alkyl chlorides (Table III) decrease from cyclopentyl to cyclopropyl. For the smallest compounds, the low IPs result from strong mixings of the lone pair orbitals with the high-lying, filled Walsh MOs of cyclopropane and cyclobutane.[25] For cyclopropyl chloride the HOMO is predicted to be e_a-n_π and for cyclobutyl chloride e_s''-n_σ. The lowering of the σ^*_{CCl} energy (Table III) with in-
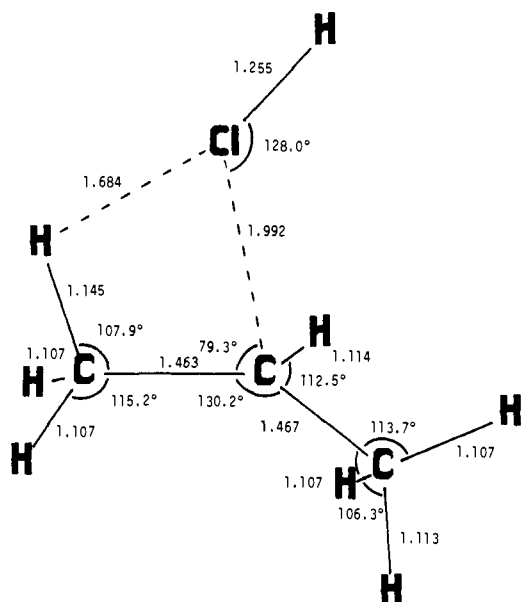

$e_a - n_\pi$

$e_s^* - n_\sigma$
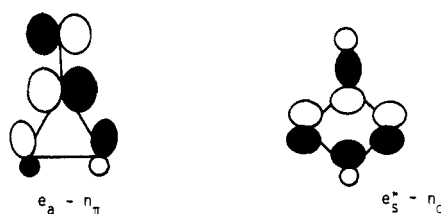
Figure 5. Important structural parameters computed for protonated isopropyl chloride in C_1 symmetry.
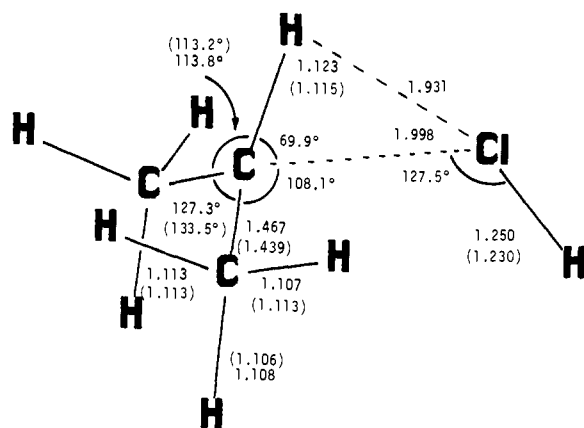

Figure 6. Important structural parameters computed for protonated isopropyl chloride in C_s symmetry. Values for separated isopropyl cation and HCl in parentheses.

Figure 7. Important structural parameters computed for protonated 1,3-dimethylallyl chloride. Values for separated 1,3-dimethylallyl cation and HCl in parentheses.

creasing ring size parallels the increase in C-Cl distance that is generally attributed to enhanced "s character" in the bonds exo to small rings.[26] The results for the norbornyl chlorides are discussed in a forthcoming paper.[27]

Tables II and III also contain computed C-Cl stretching force constants.[28] The agreement with the "experimental" values determined by normal mode analyses is impressive, as noted previously by Taylor et al.[29] This is auspicious for the study of reactions with alkyl chlorides using MINDO/3. As usual, the force constants vary inversely with bond length, though the results for the norbornyl chlorides are out of line.[27] The lower force constant for the exo isomer is, of course, provocative.[27]

Protonation

The structures computed by MINDO/3 for the protonated alkyl chlorides are intriguing, but appear to suffer somewhat from the overestimation of nonbonded attractions with chlorine.[2e] Thus, MINDO/3 finds the eclipsed form of protonated ethyl chloride to be favored over the staggered by 3.5 kcal/mol and predicts a barrier of only 1.0 kcal/mol for ethyl chloride.
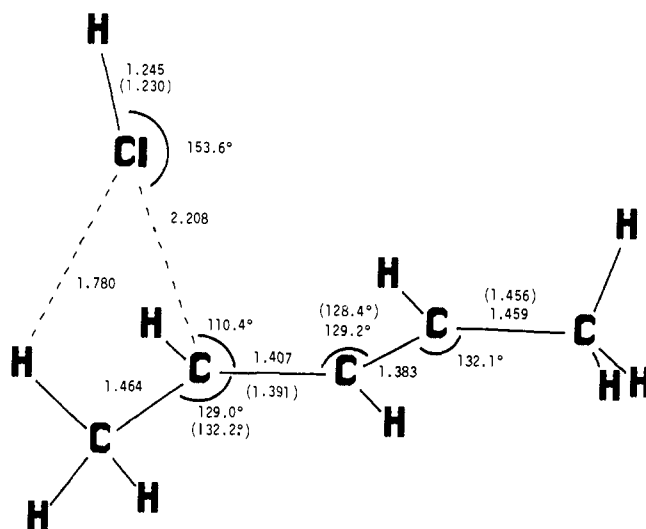
STO-3G calculations[2e] nearly reproduce the experimental barrier of 3.7 kcal/mol for ethyl chloride and find the staggered form of the protonated species more stable by 3.0 kcal/mol. MINDO/3 geometries have been illustrated previously for protonated ethyl and homocubyl derivatives.[2b,c] Many of the compounds possess multiple minima.[2a-c] For example, the two lowest energy minima for protonated isopropyl chloride have the structures of C_1 and C_s symmetry illustrated in Figures 5 and 6. The C_1 form, which was overlooked in the preliminary report,[2a] is more stable by 5.4 kcal/mol. Both isomers reveal coordination of chlorine with both the carbonium carbon and hydrogen in what may be regarded formally as the carbonium ion fragment of the complex. On the basis of the ab initio studies,[2e] the coordination of chlorine with the eclipsing hydrogens is probably an artifact of MINDO/3. The energetic impact of the effect is not great (ca. 3–5 kcal/mol), so the computed PAs are still reasonable. The C-Cl separation in *i*-PrCl is calculated to expand by about 0.2 Å upon protonation. Additional, higher energy minima are essentially hydrogen bonded forms of HCl and isopropyl cation.[2a-c] Another type of isomerism is revealed by protonated 1,3-dimethylallyl chloride. There is an unsymmetric form shown in Figure 7 and a 6 kcal/mol more stable alternative with the chlorine symmetrically bridged between C1 and C3.

Proton Affinities

The results for proton affinities are compiled in Tables I and III. In each case, the calculations involve determining the heats of formation of the chloride and its protonated derivative. The PAs are then given by ΔH_f (RCl) + ΔH_f (H$^+$) − ΔH_f (RClH$^+$). For reference, the calculated heats of formation are reported in Table IV. The limited experimental data (Table I) indicate that the MINDO/3 PAs are uniformly overestimated by ca. 7 kcal/mol. PAs calculated by MINDO/3 for amines and alcohols are also in good agreement with experiment (ca. ±5 kcal/mol).[32] Substantial absolute errors occur for unsaturated species, e.g., carbonyl compounds, imines, and nitriles; however, relative values for closely related series are still reasonable.[32]

Correlations of PAs with various σ constants have been noted in the past.[33] Experimental PAs for alcohols[34,35] and primary amines[35] are plotted against σ^* in Figure 8 along with the MINDO/3 values for chlorides reduced by 7 kcal/mol. Reasonable linearity is observed except for HCl. One notable

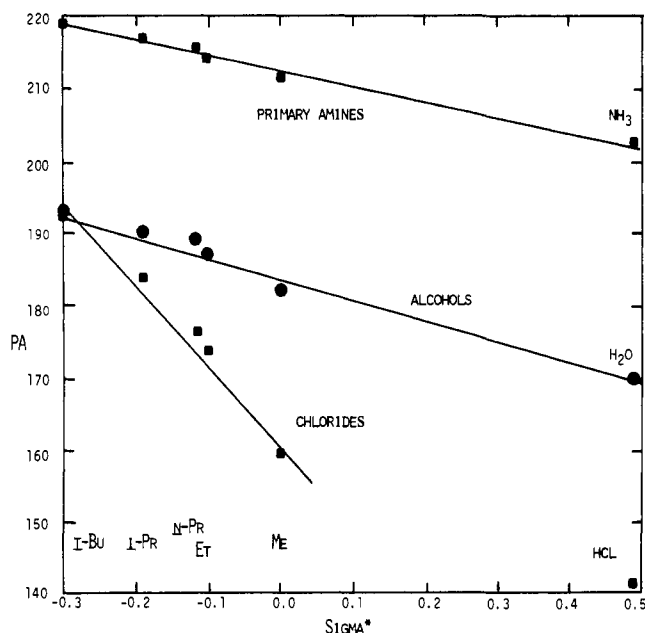Figure 8. Correlation of experimental PAs (kcal/mol) for alcohols and amines, and of corrected MINDO/3 PAs for chlorides with σ^*.

Table IV. Calculated (MINDO/3) Heats of Formation[a]

R	ΔH_f (RH)	ΔH_f (RCl)	ΔH_f (R$^+$)	ΔH_f (RClH$^+$)
Hydrogen		−21.6	367[c]	197.3
Methyl	−6.3	−15.3	260.3	185.4
Ethyl	−19.9	−28.3	212.9[b]	158.3
n-Propyl	−26.5	−34.8	204.4[b]	148.8
Isopropyl	−26.5	−34.2	184.2	141.6
tert-Butyl		−31.9	170.8	136.0
Cyclopropyl	8.5	1.0	237.7	188.1
Cyclobutyl	−8.1	−16.0	210.6	164.8
Cyclopentyl	−28.1	−35.3	183.1	140.7
exo-2-Norbornyl	7.2	0.0	214.2	173.8
endo-2-Norbornyl	7.2	0.2	214.2	177.9
2-Methyl-*exo*-2-norbornyl		1.7	196.0	165.6
2-Methyl-*endo*-2-norbornyl		1.5	196.0	170.0
Bicyclo[3.1.0]-hex-2-yl	4.6		198.0	167.1
9-Homocubyl	113.5		314.3	277.9
1,3-Dimethyl-1-allyl			176.9	147.5[d]

[a] MINDO/3 results with complete geometry optimization: ΔH_f's in kcal/mol. [b] ∠HC2Cl in C$_2$H$_5^+$ and ∠CCC in *n*-C$_3$H$_7^+$ fixed at 100°. [c] Experimental value. [d] Unsymmetric form. ΔH_f for symmetric (C_s) is 141.5.

feature is the much greater sensitivity of the chlorides to substitution. This results from the fact that the bonding of the ClH fragment to the alkyl group in RClH$^+$ is weaker than the corresponding interactions in ROH$_2^+$ or RNH$_3^+$ (vide infra). Therefore, the protonated chlorides have more carbonium ion character (R$^+$···ClH) and the increased sensitivity reflects the response of the carbonium ion to substitution. A consequence is the predicted similarity of PAs for tertiary alkyl chlorides and tertiary alcohols.

We have sought general correlations of all the computed PAs with many combinations of calculated atomic charges in the chlorides and protonated species.[2d] An excellent correlation was discovered with the sum of the charges on the ClH fragment in RClH$^+$.[2d] The generality of the relation is illustrated in Figure 9 which includes all the PAs from Tables I and III
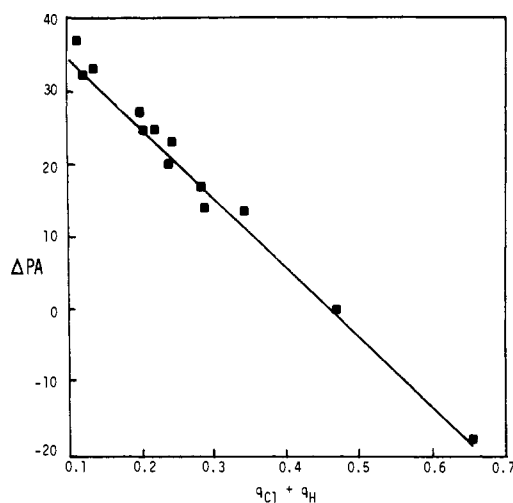

Figure 9. Correlation of PAs (kcal/mol) for alkyl chlorides relative to CH$_3$Cl with the sum of the charges on the ClH fragment in RClH$^+$.

recorded relative to methyl chloride. A least-squares fit yields

$$\Delta PA = -96.66(q_{Cl} + q_H) + 45.00 \qquad (2)$$

and a mean error of 1.3 kcal/mol for the 13 points covering a 50 kcal/mol range. Similar correlations are found between the PAs for alcohols[32] and primary amines[32,36] and the charge on the OH$_2^+$ and NH$_3^+$ groups in the protonated species. Adding another term to eq 2 proportional to the charge on chlorine in the neutral chlorides renders only token improvement to the fit. The calculated charges are tabulated elsewhere.[2d]

The interpretation of eq 2 is gratifyingly simple: *the proton affinities of alkyl chlorides are controlled by the ability of the alkyl group to accommodate positive charge.* In order to gauge whether the correspondence results from charge transfer and/or polarization effects, correlations involving a simple charge transfer expression
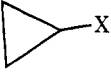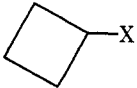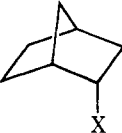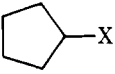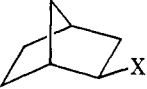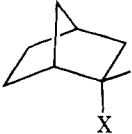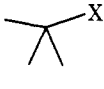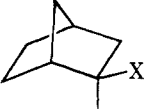
$$PA = \frac{aQ_H}{\epsilon_L(H^+) - \epsilon_H(RCl)} + b \qquad (3)$$

were also evaluated. The relation represents the frontier interaction between the HOMO of the alkyl chloride and the empty 1s orbital on the proton expressed in a simple perturbation theory format.[2a,17] Thus, Q_H is the electron density on chlorine in the HOMO of the alkyl chloride, $-\epsilon_H$ (RCl) is the ionization potential for the chloride, and $\epsilon_L(H^+)$ is the energy of the 1s orbital of H$^+$ which may be treated as an adjustable parameter along with a and b. Equation 3 turns out to be useless for estimating the PAs for the alkyl chlorides recorded in Tables I and III. For the simple alkyl chlorides, methyl to *tert*-butyl, eq 3 yields a respectable fit. This observation is obviously not general and does not argue for the importance of charge transfer effects in determining PAs. The result also warns against drawing global conclusions from correlations for short and/or closely related series of compounds.

The preceding discussion is interesting in view of the difference of opinion concerning the controlling factor in relative amine basicity. Morokuma[38] and Pullman[39] have both applied energy component analysis to the problem and reached different conclusions. Morokuma determined polarization to be the key term, while Pullman found charge transfer effects to dominate. The discrepancy may arise from differences in the basis sets for the ab initio calculations and from differences in the procedures for the energy decomposition. Without further support, the value of such analyses appears diminished.

Ion Pairs and Solvolysis Rates

Since Figure 9 and eq 2 indicate that the PAs provide a measure of the electron-donating ability of the alkyl groups, the PAs should also reflect the relative stabilities of the corresponding alkyl cations. The computed data support this notion as the PAs increase in proceeding from primary to tertiary alkyl groups. The observation is not purely a size effect because cyclopentyl and *tert*-butyl fall between the endo and exo, secondary and tertiary norbornyl compounds, respectively. Naively, one might then expect a relation between the proton affinities and rates for solvolytic reactions that generate the carbonium ions. The obvious complicating factors are anchimeric and solvent assistance, and the significant fact that solvolyses of simple, secondary alkyl substrates yield ion pairs and not free carbonium ions.[40] Nevertheless, when the PAs and relative acetolysis rates are compiled for the secondary and tertiary substrates, only cyclobutyl and isopropyl are out of sequence.[41] The former error is attributable to anchimeric assistance,[42a] while the origin of the latter discrepancy may be an overly high MINDO/3 PA for isopropyl chloride owing to the conformational flexibility in the protonated form (Figure 5).

PA	179.8	186.2	189.3
log k_{rel}	-5.5	0.8	0.0

PA	191.1	191.2	193.2
log k_{rel}	1.4	0.0	2.6

PA	198.5	199.1	203.1
log k_{rel}	6.7	7.6	9.7

Under these circumstances, it seems reasonable that the factors that govern relative solvolysis rates might be illuminated by studying the reasons for differences in the PAs of corresponding alkyl chlorides. The analogy for the secondary derivatives is enhanced by the idea that the protonated alkyl chlorides may represent a viable model for ion pairs.[40] The interaction energies between the secondary carbonium ions and ClH and RClH$^+$ are ca. 15-20 kcal/mol (vide infra), which seems like an acceptable number for a tight ion pair, though experimental information is lacking on this point.[40] Thus, investigation of the source of the lower PAs for the *endo*-2-norbornyl chlorides as compared with the exo isomers may help explain the origin of the faster solvolysis rates for the exo species.[27,42b] In addition, the occurrence of isomeric ion pairs and protonated chlorides as in the case of 1,3-dimethylallyl chloride is worthy of further study.[45]

Carbonium Ion-HCl Interactions

The stabilization energy for the carbonium ions by ClH in the protonated chlorides is defined by[2a]

$$\Delta E_s \equiv \Delta H_f (R^+) + \Delta H_f (HCl) - \Delta H_f (RClH^+) \quad (4)$$

Table V. Carbonium Ion-Base Interaction Energies[a]

R$^+$	NH$_3$ Expt[b]	NH$_3$ MINDO/3	H$_2$O Expt[c]	H$_2$O MINDO/3	HCl Expt[d]	HCl MINDO/3
Me	103	98	66	70	51	53
Et	70	66	37	41	27	33
i-Pr	52	44	23	25		21
t-Bu	40	27	11	13		13

[a] ΔH for the reaction RBH$^+$ → R$^+$ + :BH, in kcal/mol. Experimental ΔH_f's for carbonium ions from ref 5d and F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970). [b] PAs from ref 35. [c] PAs from ref 34. [d] See ref 2a.

Thus, ΔE_s is the enthalpy required to separate RClH$^+$ to R$^+$ and HCl. The computed values are given in Tables I and III using the data in Table IV. The general pattern is that the interaction energies are less for the more stable carbonium ions, so ΔE_s declines from ca. 35 kcal/mol for primary species to 20 for simple secondary compounds and to 13 for *tert*-butyl, though the MINDO/3 values are again overestimated. A comparison is made with experimental data and with the ΔE_s values for simple alcohols and primary amines in Table V. The statement above that the interaction of HCl with the alkyl group in RClH$^+$ is relatively weak is clearly supported. In fact, STO-3G results indicate that *t*-BuClH$^+$ is no more than marginally stable with respect to loss of HCl.[2e] HCl is clearly a weaker base than H$_2$O or NH$_3$.

The ΔE_s values for secondary ions vary over a 20 kcal/mol range as indicated in Table III and from the ΔE_s's that can be computed from Table IV for 1,3-dimethylallyl (7.8 kcal/mol) and for *syn*-bicyclo[3.1.0]hex-2-yl (9.4 kcal/mol). The diminished interactions for the latter species are due to π and σ conjugation, respectively, in the corresponding carbonium ions.

As we have discussed previously,[2a-c] the important stabilizing interaction between the carbonium ions and ClH in RClH$^+$ involves the LUMO of the cation and the lone pair HOMO of HCl. The interaction energies are then anticipated via PMO-theory to fit the equation

$$\Delta E_s^{est} = \frac{aQ_L}{\epsilon_L(R^+) - \epsilon_H(HCl)} + b \quad (5)$$

In the expression, Q_L is the electron density on the carbonium carbon in the LUMO of the cation, if it were occupied by one electron; $\epsilon_L(R^+)$ is the energy of the LUMO of the carbonium ion; and $\epsilon_H(HCl)$ is the energy of the HOMO of HCl which may be treated as an adjustable parameter along with a and b. The Q_L and ϵ_L values are determined by MINDO/3 calculations on the carbonium ions. The majority of these have been tabulated.[2a,b]

Correlation using eq 5 is good for the eight secondary species listed in Table IV.[43] A least-squares treatment yields $\epsilon_H = -10.1$ eV, $a = 99.61$, and $b = -2.888$ and a mean error of 1.05 kcal/mol over the 20 kcal/mol range. The fit is illustrated in Figure 10. The agreement emphasizes the importance of the two factors in determining the stabilization energies: (1) the delocalization parameter, Q_L, which implies that more delocalized cations are less stabilized by HCl; and, (2) the energy of the carbocation's LUMO, ϵ_L, which measures the electron affinity of the ion. These key terms also control the sensitivity of solvolysis rates to substituents as measured by ρ^+.[44]

The same fit provides acceptable predictions for the ΔE_s of ethyl (32.8) and *n*-propyl (26.4); however, the stabilization of tertiary ions, e.g., *tert*-butyl (18.8), is overestimated, since steric effects probably become influential. Overall, the significance of the charge transfer expression (eq 5) for determining carbonium ion-HCl interaction energies is established.
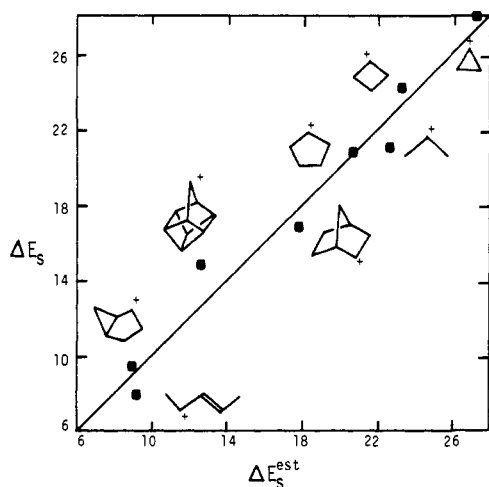
Figure 10. Comparison of carbonium ion–HCl stabilization energies calculated by MINDO/3 and estimated from eq 5.

Implications for the Solvation of Carbonium Ions

The weaker interaction of HCl with the delocalized ions, 1,3-dimethylallyl and bicyclo[3.1.0]hex-2-yl, is curious because inasmuch as HCl may be considered a solvent molecule, the observation makes one wonder whether the solvation energies for such ions might be less than for more localized isomers. The difference becomes extreme in comparing isomeric ions such as 1–3,[2a] 4 and 5,[2b] bisected and bridged ethyl.[2c] For 3 and 5
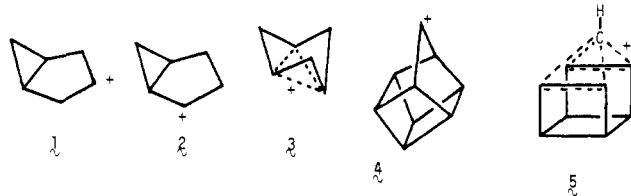
interacting with HCl, no minima could be found with chlorine coordinated with a carbon.[2a,b] In both cases, the only minima are for nearly linear C–H···Cl–H hydrogen bonded forms. The hydrogen bond energies are all around 7 kcal/mol so there is little preference between different hydrogens in 3 and 5.[46] Using eq 5 the predicted stabilization for 3–ClH$^+$ can be calculated as 5.5 kcal/mol, which falls below the hydrogen bond energy. Thus, this analysis agrees that coordination of chlorine with carbon should be forsaken. The low stabilization energies for nonclassical ions like 3 and 5 are largely due to the ions' high LUMO energies (low electron affinities) and to the delocalization of their LUMOs.[2a–c] This fact is simply illustrated by comparing the LUMOs of bisected and bridged ethyl cation in Figure 11. The LUMO for the bisected form is essentially nonbonding and has a computed energy of −7.8 eV, while the LUMO for the bridged species is reminiscent of a π^* antibonding MO and is 1.8 eV higher in energy.[2c]

Several more issues must be considered before any conclusions can be reached about differential solvation. First, perhaps the weaker interactions between solvent and carbons in the more delocalized ions might be offset by increased hydrogen bonding. This appears not to be true because hydrogen bond energies have been computed for a variety of ions and are similar.[2a,b] The regularity is consistent with the observation that the total charge on hydrogens remains nearly constant for isomers like 1–3, and 4 and 5.[2a–c] Secondly, perhaps bulk polarizability may eliminate the initial discrepancy in solvation when more solvent molecules are added. To test this notion, calculations were performed on the ethyl cations with up to five surrounding HCls.[2c] The results showed a slight increase in
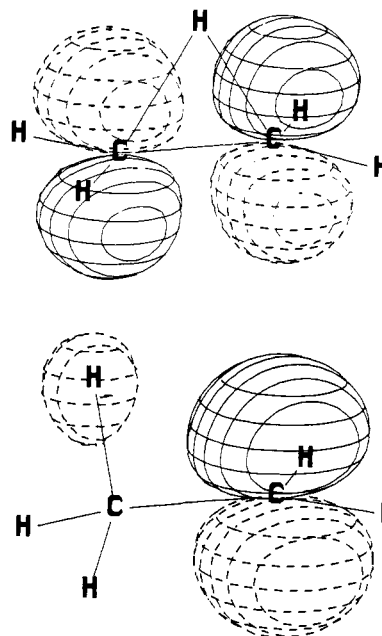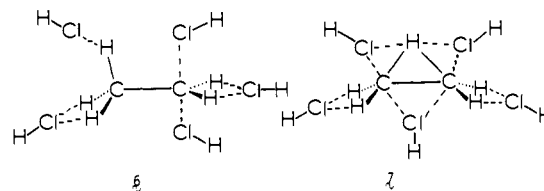

Figure 11. The LUMOs of the bridged and bisected ethyl cations. The MINDO/3 orbital energies are −6.0 and −7.8 eV, respectively.

the preference for the bisected form over the bridged species from 13.6 kcal/mol for one HCl to 16.1 kcal/mol for five HCls (6 and 7). Some remaining doubts concern the influence of

outer solvent layers and entropy on aggregates such as 6 and 7. Though these problems may be approached using statistical mechanics techniques in the future, for now the computational evidence summarized here suggests that the relative energies of isomeric carbonium ions in the gas phase and in a solution of moderate solvating ability like HCl are not necessarily the same.

Change in the electron-donating ability of the solvent is reflected in eq 5 by ϵ_H. Electron donors with low ionization potentials are the most stabilizing, while less labile alternatives compress the range of ΔE_s. Thus, in solutions that lack good electron-donating species such as superacid the effects of differential solvation should be minimized.[47] However, the relative viability of nonclassical ions compared to classical isomers under conditions such as acetolysis appears diminished.

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