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Alkylmethylchloronium Ions. Theoretical Model for Alkyl Carbocations and Methyl Substrates

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Structures and properties of several alkylmethylchloronium ions, RClCH$_3^+$, have been computed by employing the MINDO/3 method. Reaction equilibria have provided methyl cation affinities (MCAs) and methyl chloride stabilization energies (MCSEs). The calculated MCAs correlate linearly with calculated alkyl chloride proton affinities (PAs) and with the charge on the CH$_3$Cl portion of the alkylmethylchloronium ions, indicating that both PAs and MCAs are directly dependent on the ability of the alkyl group R to accommodate positive charge. A remarkable correlation is observed between calculated MCSEs and experimental heats of formation of alkyl cations. A method for accurately calculating alkyl cation heats of formation is suggested. Finally, a good correlation was found between experimental and calculated energies for gas-phase formation of oxonium and chloronium ions, and some predictions for unobserved reactions are discussed.

Carbocations and haloniums ions occupy such a prominent role in organic chemistry that few topics have been reviewed as often.[1] In fact, the extent of study given to these intermediates may, in part, be due to the inability to gain accurate insight from inexact experimental probes.[2] Nevertheless, a variety of experiments have revealed many factors which tend to obscure structural information, and, as a result, better methods have been developed for gaining information about these ions. Much revealing structural information has come from solvolytic studies in solvents of low nucleophilicity,[3] direct observation of ions in superacid media,[4,5] precise determination of heats of formation for cations in the gas phase[6] and in solution,[7] and study of various gas-phase[8] and solution[9] equilibria. The development of reliable theoretical methods[10–12] has paralleled and complemented the experimental methods. Thus, it is possible to make valid statements about the structures of some of these cationic intermediates and about the experimental and theoretical methods providing data.

For the past few years we have sought a suitable semiempirical theoretical method for studying various types of carbocations and halonium ions. The MINDO/3[11] and MNDO[12] methods developed by Dewar and his coworkers seemed to be the most appropriate for the variety of structural types of interest to us. Dewar[14] showed that there was reasonable agreement between the experimental and MINDO/3-calculated properties of alkyl chlorides. Simultaneously with our initial efforts,[13] Jorgensen[15,16] published a series of theoretical papers on alkyl chlorides, protonated alkyl chlorides, and carbocations solvated by HCl utilizing the MINDO/3 method as well as ab initio methods with the STO-3G basis set. He found general agreement between experiment and theory and concluded that MINDO/3 and STO-3G adequately modeled these compounds.[16] Our previous publications[13] indicated that MINDO/3 is adequate for describing the properties observed for chloronium ions.[17,18]

Harris and his co-workers[19] have recently published their extensive MINDO/3 study of carbocations. They found large errors between experimental and calculated ΔH_f values for several acyclic carbocations. However, isodesmic relationships provided reasonably good agreement between experiment and theory. They also determined that the MNDO method provided no advantage over the MINDO/3 method for calculating energies of carbocations.

We have utilized MINDO/3 and, to a lesser extent, MNDO to calculate the structures and properties of an extensive series of acyclic and cyclic hydrocarbons, alcohols, ethers, amines, thiols, thioethers, and alkyl chlorides in order to compare experimental and calculated properties.[20,21] These calculations have provided insight into the failures of the method (e.g., errors from branching, ring size, heteroatom incorporation, etc.) and have given us confidence in applying the MINDO/3 method to carbocations and chloronium ions.

Our earlier theoretical studies of chloronium ions[13] were aimed at modeling well-known unsubstituted and methyl-substituted tetra- and pentamethylenechloronium ions.

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[1] Reviews: Olah, G. A.; Schleyer, P. v. R. "Carbonium Ions"; Wiley-Interscience: New York, 1968–1976; Vol. 1–5. Olah, G. A. "Halonium Ions"; Wiley-Interscience: New York, 1975. Peterson, P. E. *Acc. Chem. Res.* 1971, *4*, 407. Bethell, D.; Gold, V. "Carbonium Ions, An Introduction"; Academic Press: New York, 1967. McManus, S. P.; Pittman, C. U., Jr. In "Organic Reactive Intermediates"; McManus, S. P., Ed.; Academic Press: New York, 1973; Chapter 4. Jones, M., Jr.; Moss, R. A., Eds. "Reactive Intermediates"; Wiley-Interscience: New York, 1981; Vol. 2. Knipe, A. C.; Watts, W. E., Eds. "Organic Reaction Mechanism"; Wiley-Interscience: London and New York, 1977; and previous volumes.

[2] E.g., see: Brown, H. C. "The Nonclassical Ion Problem"; Plenum: New York, 1977.

[3] Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* 1977, *14*, 1, and references therein.

[4] See: Olah, G. A.; Fung, A. P.; Rawdah, T. N.; Surya Prakash, G. K. *J. Am. Chem. Soc.* 1981, *103*, 4646 and previous papers in that series, and references therein.

[5] Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* 1980, *102* 6867. Saunders, M.; Siehl, H.-U. *Ibid.* 1981, *102*, 6869 and references therein.

[6] Traeger, J. C.; McLoughlin, R. G. *J. Am. Soc.* 1981, *103*, 3647 and references therein.

[7] Arnett, E. M.; Pienta, N. J. *J. Am. Chem. Soc.* 1980, *102*, 3329 and references therein.

[8] Bowers, M. T., Ed. "Gas-Phase Ion Chemistry"; Academic Press: New York, 1979; Vol. 2.

[9] Arnett, E. M.; Pienta, N.; Petro, C. *J. Am. Chem. Soc.* 1980, *102*, 398.

[10] Hehre, W. J.; Ditchfield, R.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* 1970, *52*, 2769. Ditchfield, R.; Hehre, W. J.; Pople, J. A. *Ibid* 1971, *54*, 724. Hehre, W. J.; Latham, W. A. *Ibid.* 1972, *56*, 5255.

[11] Dewar, M. J. S. *Chem. Br.* 1975, *11*, 97. Dewar M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* 1975, *97*, 1285.

[12] Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* 1977, *99*, 4899.

[13] McManus, S. P.; Worley, S. D. *Tetrahedron Lett.* 1977, 555. Beatty, S. D.; Worley, S. D. McManus, S. P. *J. Am. Chem. Soc.* 1978, *100*, 4254.

[14] Bingham, R. H.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* 1975, *97*, 1307.

[15] Jorgensen, W. L. *J. Am. Chem. Soc.* 1977, *99*, 280, 4272; 1978, *100*, 1057. Jorgensen, W. L.; Munroe, J. E. *Tetrahedron Lett.* 1977, 581.

[16] Jorgensen, W. L. *J. Am. Chem. Soc.* 1978, *100*, 1049.

[17] Corrections for branching errors were introduced (cf. ref 13).

[18] Lischka, H.; Kohler, H.-J. *J. Am. Chem. Soc.* 1978, *100*, 5297, concluded that the MINDO/3 does not give acceptable results with chloronium ions. Our more extensive studies and Jorgensen's suggest a different conclusion.

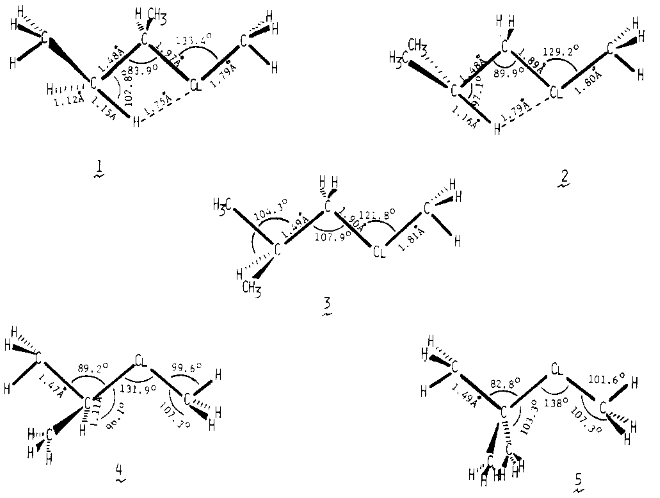
[19] Harris, J. M.; Shafer, S. G.; Worley, S. D. *Comput. Chem.* 1982, *3*, 0000.

[20] McManus, S. P.; Smith, M. R. *Tetrahedron Lett.* 1978, 1897. McManus, S. P.; Smith, M. R.; Smith, M. B.; Shafer, S. G. *J. Comput. Chem.* 1980, *1*, 233.

[21] McManus, S. P.; Smith, M. R.; Shafer, S. G. *J. Comput. Chem.* 1982, *3*, 0000.

0022-3263/82/1947-3070$01.25/0

Chart I



While our calculations seemed to adequately model these cations, there are no available gas-phase data for direct comparisons with the calculated energies of the cyclic ions. However, some acyclic dialkylchloronium ions have been studied in the gas phase by using ion–molecule chemistry and mass spectrometric detection.[22-25] Sharma and Kebarle[25] reported enthalpy of formation data which may be compared with theoretical calculations of the ionic equilibria. Therefore, for the purpose of evaluating our method, we have calculated the structures of the ionic and neutral species studied by Sharma and Kebarle. In addition to the above objective, an expanded list of chloronium ions was desired since alkyl methylchloronium ions may serve as theoretical models for both alkyl cations and methyl substrates. Thus we have calculated a variety of alkyl methylchloronium ions which provide methyl cation affinities (MCAs),[24] for comparisons with proton affinities (PAs)[16] and discussions of nucleophilicity, and methyl chloride stabilization energies (MCSEs), which are compared with recent experimental carbocation heats of formation.

Results and Discussion

Structures and Properties. The structures of the neutral compounds and cations listed in Tables I and II were computed by using the QCPE version of Dewar's MINDO/3 method.[13] Details of some structural features and properties of the alkylmethylchloronium ions are also given in Table I.

All structures were computed with no symmetry conditions imposed and with independent optimization of bonds and angles. By use of this procedure, two methylchloronium ions gave unusual results. The *sec*-butylmethylchloronium ion (1, Chart I) and the isobutylmethylchloronium ion(2) favored bridged structures. Jorgensen[16] previously commented on the tendency of an α- or β-hydrogen to bridge to chlorine in some protonated alkyl chlorides. The bridging was suggested to be an artifact of MINDO/3.[16]

When the dihedral HCCCl angle in 1 or 2 was changed from the calculated value (~0°) to 180° and minimization continued, energy minima different from those in 1 and 2 were found. In the case of the *sec*-butylmethyl-

Table I. MINDO/3 Calculated Energies (kcal/mol) and Properties

R	ΔH_f (gas phase, 25 °C)				RCl affinities		R^+	$RClCH_3^+$ properties						
										bond lengths, Å		angles, deg		
	RCl[a]	$RClCH_3^+$ [b]	$RClH^+$ [a]	R^+ [g]	PA[a]	MCA	MCSE	IP, eV	charge $q(ClCH_3^+)$	CH_3-Cl	R-Cl	C-C-Cl	C-Cl-C	C-C-Cl-C
H	−21.6	185.4	197.3	367	148.1	53.0	166.3	18.7	0.700	1.84	1.26			
Me	−15.3	180.7	185.4[b]	260.3	166.3	64.0	64.3	17.3	0.540	1.83	1.83		120	
Et	−28.3	159.7	158.3	212.9	180.4	72.0	37.9	16.4	0.429	1.82	1.89	100.3	124	180
n-Pr	−34.8	151.7	153.3[e] (148.8)[d]	204.4	(183.4)[d]	73.5	37.4	16.0	0.412	1.81	1.89	99.7	124	182
i-Pr	−34.2	146.8	141.6	184.2	191.2	79.0	22.1	15.9	0.300	1.80	1.97	89.2	132	172
n-Bu	−41.1[b]	144.2	145.4[e] (141.0)[d]	194.9	180.5[b] (184.9)[b,d]	74.7	35.4	15.2	0.400	1.81	1.89	99.1	124	182
i-Bu	−32.8[b]	152.7 (150.1)[d]	*f*	202.3	*f*	74.5	34.3	15.5	0.404	1.80	1.90	99.7	122	182
sec-Bu	−39.2[b]	(136.3)[c,d]	*f*	175.5	*f*	(84.5)[d]	23.9	(15.3)[d]	(0.265)[d]	(1.80)[d]	(1.98)[d]	(83.9)[d]	(134)[d]	(182)[d]
t-Bu	−31.9	142.9	136.0	170.8	199.1	85.2	12.6	15.5	0.199	1.80	2.09	82.8[h]	139	182

[a] Except as noted, from ref 16. [b] Calculated for this work. [c] Two minima were calculated; both were bridged (i.e., they had strong bonding between chlorine and an eclipsed hydrogen on the β-carbon). The lower energy minimum is given here. [d] Energies of bridged structures are shown in parentheses (see footnote *c* above). [e] The structure reported in ref 16 is bridged. Two similar nonbridged minima were found in our work (ΔH_f = 153.27 and 153.96 kcal/mol, respectively). [f] Not calculated. [g] Reference 19. [h] The other two *t*-Bu methyl groups have ∠CCCl = 103° (see 5).

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(22) Tiernan, T. O.; Hughes, B. M. *Adv. Chem. Ser.* **1968**, *No. 82*, 412.
(23) McAskil, N. A. *Aust. J. Chem.* **1969**, *72*, 2275.
(24) Beauchamp, J. L.; Holtz, D.; Woodgate, S. D.; Patt, S. L. *J. Am. Chem. Soc.* **1972**, *94*, 2798. Beauchamp, J. L. In "Interactions Between Ions and Molecules"; Ausloos, P., Ed.; Plenum Press: New York, 1975.
(25) Sharma, D. K. S.; Kebarle, P. *J. Am. Chem. Soc.* **1978**, *100*, 5826.

Table II. Comparison of MINDO/3 Calculated and Experimental Energies (kcal/mol) for Chloronium and Oxonium Ion Formation

$R^+ + B \rightleftarrows RB^+$	$\Delta H_f(RB^+)$ calcd[a]	$\Delta H_f(RB^+)$ obsd[b]	ΔH_{reac} calcd[a]	ΔH_{reac} obsd[b]
$CH_3^+ + H_2O \rightleftarrows CH_3OH_2^+$	136.6	137	-70.1	-66.2
$CH_3^+ + HCl \rightleftarrows CH_3ClH^+$	185.4	189.7	-53.3	-49.2
$CH_3^+ + CH_3OH \rightleftarrows CH_3OHCH_3^+$	137.6	133.2[c]	-72.1	-80[c]
$CH_3^+ + CH_3Cl \rightleftarrows CH_3ClCH_3^+$	180.7	(187.1)[d] (185.4)[f]	-64.3	(-56.6)[e] (-54.9)[g]
$C_2H_5^+ + CH_3OH \rightleftarrows C_2H_5OHCH_3^+$	119.4	120.9	-42.9	-50.1
$C_2H_5^+ + CH_3Cl \rightleftarrows C_2H_5ClCH_3^+$	159.7	169	-37.9	-30.7
$i\text{-}C_3H_7^+ + CH_3OH \rightleftarrows i\text{-}C_3H_7OHCH_3^+$	111.8[h]	110.8	-21.8	-33.2
$i\text{-}C_3H_7^+ + CH_3Cl \rightleftarrows i\text{-}C_3H_7ClCH_3^+$	146.8	149.8	-22.1	-22.9
$t\text{-}C_4H_9 + CH_3OH \rightleftarrows t\text{-}C_4H_9OHCH_3^+$	113.0[h]	97[i]	-7.2	-21[i]
$t\text{-}C_4H_9 + CH_3Cl \rightleftarrows t\text{-}C_4H_9ClCH_3^+$	142.9	(145.7)[d] (133.8)[f]	-12.6	(-13.1)[e] (-1.2)[g]

[a] Using RB^+ from Table I or calculated for this work (oxonium ions) with no symmetry constraints. Cation ΔH_f values are from ref 19, and ΔH_f values for neutrals are from ref 21. [b] From ref 25 unless otherwise noted. [c] No direct measurement was made. Value was deduced from the PA given by: Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445. [d] No direct measurement was made for this reaction. Extrapolated from the plot of the calculated and observed ΔH_f values of RB^+ (Figure 4). [e] Extrapolated from the correlation of calculated and observed ΔH_{reac} (Figure 5). [f] Calculated by using the extrapolated ΔH_{reac} (footnote *e*) and experimental ΔH_f values of R^+[6] and B.[21] [g] Calculated by using the extrapolated ΔH_f of RB^+ (footnote *d*) and the experimental ΔH_f values of R^+[6] and B.[21] [h] For structures of these calculated ions, see ref 44. [i] No direct measurement was made. The value was deduced from the PA predicted from a measured IP. Cf.: Benoit, F. M.; Harrison, A. G. *J. Am. Chem. Soc.* **1977**, *99*, 3980.

chloronium ion, a similar but different bridged structure was found. However, an unbridged structure, **3**, was calculated for the isobutylmethylchloronium ion. While the ΔH_f of structures **2** and **3** are similar (Table I), some of the calculated properties are quite different. For example, the sum of the positive charge (q) on the $ClCH_3$ fragment in **2** is 0.352 while that in **3** is 0.404.

Jorgensen[16] commented on the similarities between the structures of the protonated alkyl chlorides and the respective carbocations. The CCCl angles in the methylchloronium ions (Table I) show the tendency toward planarity of the alkyl carbon bonded to carbon in these ions as well.

Two additional structures deserve some discussion. Protonated isopropyl chloride had some bonding between either an α- or a β-hydrogen in the two structures calculated.[16] The minimum-energy structure that we calculated for the isopropylmethylchloronium ion (**4**) has no Cl to H bridging. However, its bond angles show that it is geometrically different from the ions involving Cl bonding only to primary carbon (Table I). The *tert*-butyl group in the structure of the *tert*-butylmethylchloronium ion (**5**) is also interesting because of the greatly different CCCl angles present in structure **5**. The CCCl angles are probably distorted by steric repulsion between the chlorine-bound methyl and the two methyls of the *tert*-butyl group.

Methyl Cation Affinities and Proton Affinities. Continuing with our original interest[13] in the relationship between the stability of halonium ions and related carbocations, we have calculated the structures and properties of a series of methyl-substituted chloronium ions (Table I). From eq 1, we can derive MCAs. Jorgensen[16] has

$$RCl + CH_3^+ \rightleftarrows RClCH_3^+ \qquad MCA \equiv \Delta H_{reac} \qquad (1)$$

previously calculated proton affinities (PAs) for alkyl chlorides and found that calculated PAs correlated with σ^*. We find an excellent correlation between the calculated PAs and MCAs (Figure 1). Jorgensen also correlated the PAs with the sum of the calculated charges on the ClH fragment of $RClH^+$. Similarly, an inverse relationship between calculated MCAs and the sum of charges on the $ClCH_3$ fragment of $RClCH_3^+$ is found (Figure 2). Therefore, it is obvious that *both the proton affinities and methyl cation affinities of alkyl chlorides are directly dependent on the ability of the alkyl group R to accommodate positive charge.*

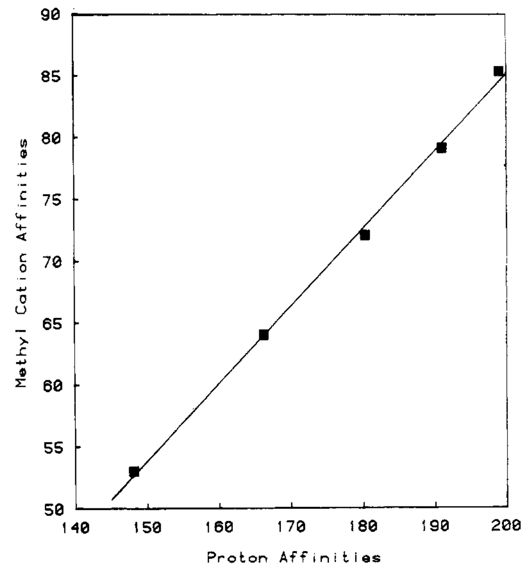

Figure 1. Comparison of calculated relative methyl cation affinities (MCAs) and relative proton affinities (PAs) of alkyl chlorides ($r = 0.999$) which give unbridged ions when their structures are computed by using MINDO/3.

The above correlations are relevant to dicussions of basicity and nucleophilicity.[26-28] Experimental PAs have been correlated with ionization potentials (IPs),[28,29] alkyl substituent constants σ^{*16} and, over a limited range, with solution basicity and nucleophilicity.[28] Therefore, one might expect that methyl cation affinities would also correlate with nucleophilicity to the extent that complicating factors[27] would allow. Relative to this point, Beauchamp et al.[24,26] have measured PAs and MCAs for some neutral donor bases. While the same base order is

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(26) Holtz, D.; Beauchamp, J. L.; Woodgate, S. D. *J. Am. Chem. Soc.* **1970**, *92*, 7484.

(27) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219.

(28) McManus, S. P. *J. Org. Chem.* **1981**, *46*, 635 and references therein.

(29) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1972**, *94*, 4726. Dougherty, R. C. *Tetrahedron Lett.* **1975**, 385.

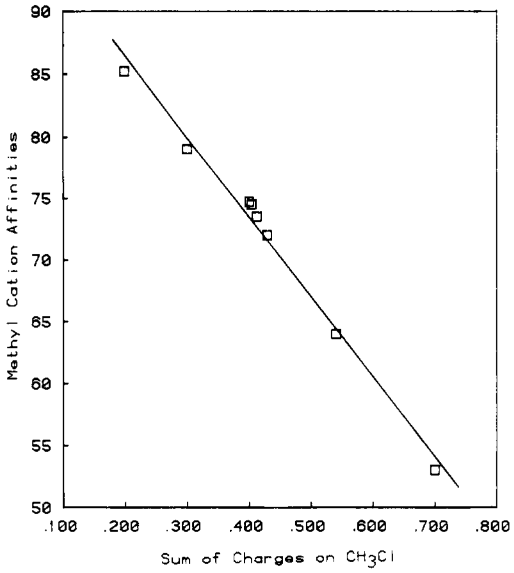
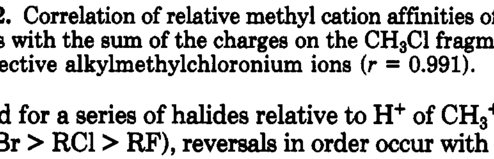


Figure 2. Correlation of relative methyl cation affinities of alkyl chlorides with the sum of the charges on the CH_3Cl fragment of the respective alkylmethylchloronium ions ($r = 0.991$).

observed for a series of halides relative to H^+ of CH_3^+ (i.e., RI > RBr > RCl > RF), reversals in order occur with other neutral bases when the acid is changed. For example, the MCAs of a series of bases were found to be CO > HI > H_2O > HCl > CH_3F > N_2 > HF while the PAs for the same bases are in the order H_2O > CH_3F > HI > CO > HCl > HF > N_2.

Olmstead and Brauman[27] have also discussed MCAs[30-32] in gas-phase nucleophilic displacement reactions. Their studies of common anions reacting with a variety of neutral methyl substrates are of a different charge type than that of Beauchamps. Nevertheless, using the affinity for a single substrate, they found that a comparison of PAs and MCAs revealed some inversions in order. They accounted for the order reversals in terms of charge-concentration differences.

Angelini and Speranza[33] have recently studied some gas-phase reactions which may be compared with solution nucleophilicity data. They studied the efficiency of neighboring-group participation[34] by the internal nucleophile X (eq 2), where X is Cl, Br, and OH. The participation (nucleophilic) order found is OH ≫ Br ≥ Cl which parallels the MCA order of CH_3OH, CH_3Br, and CH_3Cl.[24,25] The order of participation in solution, however, is Br > OH > Cl.[34,35] Solvation of the hydroxyl group probably accounts for the reversal of order of Br and OH in solution.



(2)

X = Cl, Br, or OH; Y = F, Cl, or Br; R = H, CH_3, or C_2H_5

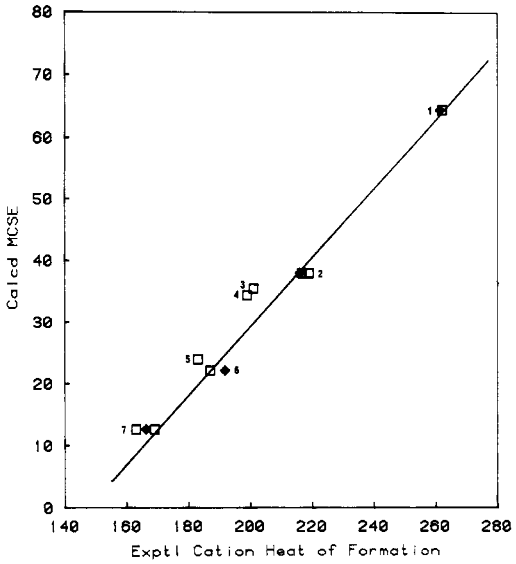


Figure 3. Comparison of calculated methyl chloride stabilization energies (MCSEs) for alkyl cations and experimental heats of formation of the respective carbocation. The cations are as follows: 1, Me; 2, Et; 3, *n*-Bu; 4, *i*-Bu; 5, *sec*-Bu; 6, *i*-Pr; 7, *t*-Bu. The solid line represents the best fit for the four solid diamonds, which are one set of data for the nonrearranging cations, where, ΔH_f = 1.783(MSCE) + 147.8 ($r = 0.996$).

In summary, there seem to be some reversals in order on comparing PAs and MCAs of widely varying neutral and ionic substances and on comparing gas-phase and solution nucleophilicities. However, the relative order of gas-phase MCAs of CH_3OH, CH_3Br, and CH_3Cl is the same as the nucleophilic order (alkyl cation affinity) of the OH, Br, and Cl groups in examples involving ring closure (eq 2). Our calculations predict that the PAs of alkyl chlorides will follow the same order as their MCAs; however, there is insufficient experimental data to allow verification.

Methyl Chloride Stabilization Energies and Carbocation Heats of Formation. From the above conclusion that MCAs are controlled by the ability of the alkyl groups to accomodate positive charge, there should be a relationship between the stability of alkyl chloronium ions and the respective carbocations. As stated above, Harris and co-workers[19] found that isodesmic relationships reduced errors in comparisons of calculated and observed cation energies. Apparently, the computational errors[20,21] are minimized. Computational errors should also be largely minimal with the relationship shown in eq 3, which

$$R^+ + CH_3Cl \rightleftarrows RClCH_3^+ \qquad MCSE \equiv -\Delta H_{reac} \quad (3)$$

provides methyl chloride stabilization energies (MCSE) for carbocations (Table I). These calculated MCSEs should correlate with experimental MCSEs or gas-phase heats of formation for simple alkyl cations if the MINDO/3 method adequately treats these ions. As shown in Figure 3, a comparison of calculated MCSEs and experimental carbocation ΔH_fs for simple alkyl cations gives a remarkable correlation. Although the correlation for all included

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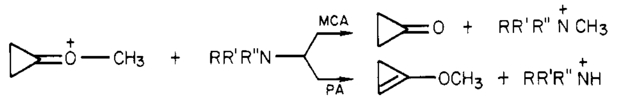
[30] Because of differences in charge types employed, MCA as defined by Olmstead and Brauman[27]—the ΔH_{reac} of $X^- + CH_3^+ \rightarrow CH_3X$ but with a neutral molecule such as CH_3Cl as the CH_3^+ donor—may not be equivalent to MCA as defined by Beauchamp[24] and used here—the $-\Delta H_{reac}$ of $M + CH_3^+ \rightarrow MCH_3^+$, where M is a neutral substrate.

[31] Another report[32] involved study of the reaction schemes i and ii, where both H^+ and CH_3^+ transfer are observed to occur. The preliminary report, however, did not report relative efficiencies. Such data would, of course, provide a measure of PAs and MCAs for the series of amines using the same donor.



(i)

(ii)

[32] Van Tilborg, M. W. E. M.; van Doorn, R.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1979**, *101*, 7617.

[33] Angelini, G.; Speranza, M. *J. Am. Chem. Soc.* **1981**, *103*, 3800.

[34] Capon, B.; McManus, S. P. "Neighboring Group Participation"; Plenum: New York, 1976; Vol 1.

[35] Winstein, S.; Grunwald, E.; Ingraham, L. L. *J. Am. Chem. Soc.* **1948**, *70*, 821 see also footnote 27 of ref 32.

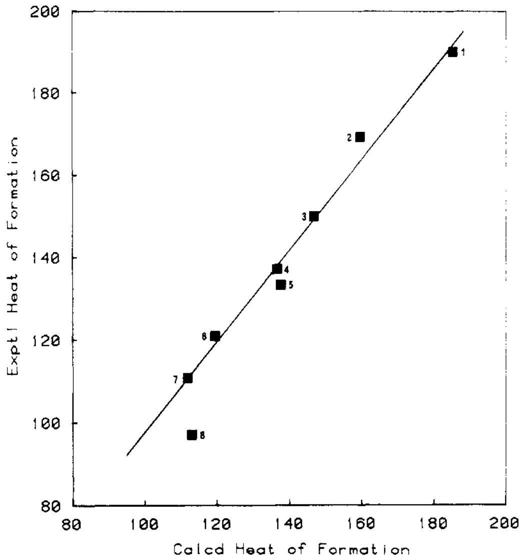


Figure 4. Comparison of experimental and calculated heats of formation of some chloronium and oxonium ions from Table II ($r = 0.992$). The ions are as follows: 1, $MeClH^+$; 2, $EtClMe^+$; 3, *i*-$PrClMe^+$; 4, $MeOH_2^+$; 5, Me_2OH^+; 6, $EtOHMe^+$; 7, *i*-$PrOHMe^+$; 8, *t*-$BuOHMe^+$. The last point is not included in the least-squares treatment.

cations is good ($r = 0.982$), there is concern about the actual structure of some carbocations that have been studied.[19,36] For example, since it is known that certain primary and secondary carbocations rearrange, the measured energy may be of a rearranged or partially rearranged structure. Since our plot could reveal rearranged ions by their noncorrelation, a plot of MCSE versus experimental ΔH_f values of non-rearranging cations is the proper approach. In Figure 3, the solid diamonds represent calculated MCSEs plotted vs. ΔH_fs for the nonrearranging methyl, ethyl, isopropyl and *tert*-butyl cations. The experimental data are from the most recent study by Traeger and McLoughlin.[6] The open squares for the same cations are other experimental measurements we believe to be state of the art.[37] The solid line results from least-squares treatment for only the solid diamonds ($r = 0.996$). The other butyl cation isomers rearrange under certain conditions although the experimental data selected for this study are for structures not previously questioned.[37] Furthermore, their correlation in Figure 3 indicates that their structures are properly assigned.

Chloronium Ion–Carbocation Equilibria. Kebarle and his co-workers[25] have measured the gas-phase equilibria of some simple alkyl cations with water, hydrogen chloride, methanol, and methyl chloride. Such data provide a dramatic test of the theoretical method and provide a basis for calculating the heats of reaction of other equilibria. Their derived heats of formation of the oxonium and chloronium ions are in remarkable agreement with MINDO/3 calculated values (Table II and Figure 4). The ΔH_f of $(CH_3)_2OH^+$, derived from an observed PA (Table II) of the respective ether, correlates well with the least-squares line for the other points in Figure 4. Not unexpectedly, however, the ΔH_f of *t*-$BuOHCH_3^+$, derived from the ether PA which, in turn, was estimated from a measured IP (Table II), correlates poorly with the least-squares line of the other data (Figure 4). Branching errors are most likely the cause of the poor correlation.[13,20,21]

Since a comparison method where computational errors cancel is preferred to direct energy comparisons, we have plotted MINDO/3 calculated heats against experimental heats (Figure 5). The oxonium ion equilibria gives an excellent correlation ($r = 0.984$ for all five points and $r = 0.998$ for the three measured equilibria; Table II, Figure 5b). The correlation of the chloronium ion equilibria (Figure 5a) is not as good ($r = 0.972$), with probable experimental and computational errors contributing to the uncertainty.[38] Extensive previous comparisons of various funtionalized aliphatics would strongly suggest that the two correlations in Figure 5 should have the same slope.[21] Since the slopes are nearly the same, predictions from either correlation should be valid.

Sharma and Kebarle[25] also attempted to measure the reaction heat represented by eq 4. However, the reaction

$$t\text{-}C_4H_9^+ + CH_3Cl \rightleftarrows t\text{-}C_4H_9ClCH_3^+ \qquad (4)$$

was found to favor *tert*-butyl cation and methyl chloride to the extent that no useful quantitative data was gathered. Using the correlation that we derived (Figure 5a) and the theoretical ΔH_{reac} calculated from the reaction in eq 4 (Table II), we estimate an experimental ΔH_{reac} of −13.1 kcal/mol. When combined with experimental ΔH_f values for the *tert*-butyl cation and methyl chloride, the ΔH_{reac} of −13.1 and eq 4 give an estimated ΔH_f for *t*-$C_4H_9ClCH_3^+$ of 133.8 kcal/mol. A ΔH_f for *t*-$C_4H_9ClCH_3^+$ (145.7 kcal/mol) may be extrapolated from the correlation in Figure 4. This alternative ΔH_f and eq 4 provide an estimate of the ΔH_{reac} in eq 4 of −1.2 kcal/mol. These data are shown in Table II. The estimates of ΔH_f for *t*-$C_4H_9ClCH_3^+$, (133.8 and 145.7 kcal/mol) and ΔH_{reac} for eq 4, −13.1 and −1.2 kcal/mol, include the errors inherent in the several experimental measurements and in the theoretical method.

As mentioned in the discussion above, cations with tertiary carbons would not be expected to correlate in Figure 4. This is because the MINDO/3-calculated ΔH_f would be too high.[11,13,20] This would give an extrapolated "observed" ΔH_f value which is too high and an estimated ΔH_{reac} value which is too low. Therefore, for estimation of the most reasonable values for eq 4, the ΔH_{reac} obtained from the alternate treatment of Figure 5 is preferred. Thus, the actual values of ΔH_{reac} and ΔH_f (RB^+) are expected to lie closer to −13.1 and 133.8 kcal/mol, repsectively. Given the expected highly positive ΔS for eq 4, the projected ΔH_{reac} confirms that there might be experimental difficulty in measuring equilibrium constants for this process under conditions similar to those used for measuring the other equilibria.

By use of the same procedure as above, estimated ΔH_f values based on observed values of similar molecules may be obtained for the dimethylchloronium ion (Table II). Also, the range for ΔH_{reac} for the production of this ion from methyl chloride and the methyl cation is estimated and included in Table II. It is readily observed that the range of the values for the CH_3^+ reaction is considerably less than that for the *t*-$C_4H_9^+$ reaction. This, of course, again reflects the contribution of MINDO/3 branching errors in the tertiary system. Even with greater ranges of the tertiary systems, these predictions for ΔH_f and ΔH_{reac}

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(36) E.g., see: Attina, A.; Cacace, F.; Giacomello, P. *J. Am. Chem. Soc.* **1981**, *103*, 4711.

(37) The experimental ΔH_f values of carbocations other than those from ref. 6 are those selected by Harris et al.[19] for their comparisons; see also Bohme, D. K.; Makay, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 2173 for recent PA measurements which affect the previous accepted value for $C_2H_5^+$.

(38) Angelini and Speranza[33] give the relative hardness scale (their footnote 34) as $CH_3^+ < C_2H_5^+ < H^+$. Since the reactions under question involve transfer of *i*-$C_3H_7^+$ and H^+, a tendency toward an anomolous hardness order may produce the deviations from linearity noted in Figure 5b.

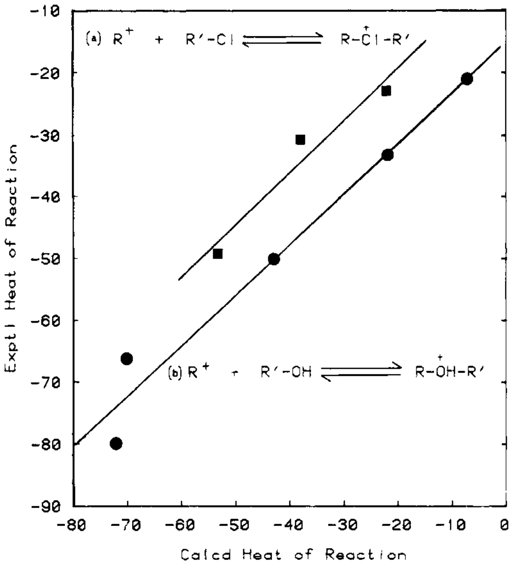

Figure 5. Comparison of experimental and calculated heats of reaction for the gas-phase equilibria involving some chloronium (■) ions and oxonium (●) ions.

provide reasonable estimates for future experiments.

Conclusions

When proper care is taken to avoid the known inherent errors in the method, MINDO/3 has proven to be a simple, inexpensive, and useful theoretical tool for modeling reactions of alkyl carbocations, alkyl chloronium ions, and the limited series of oxonium ions included here. The generally good agreement between theory and experiment for cations and their reactions is unprecedented for semiempirical methods. Therefore, until ab initio calculations with large basis sets and electron correlation[39-41] can be done inexpensively or until another semiempirical method is given the extent of testing given MINDO/3, it is the apparent theoretical method of choice for general mechanistic study of organic cations.

Furthermore, the success in correlating energies of carbocations and chloronium ions suggests that the MINDO/3 method may adequately model the equilibria and rearrangements common to the Lewis acid–alkyl halide complexes in Friedel–Crafts reactions[1,42] and in superacid media.[43]

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Registry No. *n*-BuCl, 109-69-3; *i*-BuCl, 513-36-0; *sec*-BuCl, 78-86-4; $HClCH_3^+$, 65967-47-7; $MeClCH_3^+$, 24400-15-5; $EtClCH_3^+$, 24400-21-3; *n*-$PrClCH_3^+$, 81971-21-3; *i*-$PrClCH_3^+$, 24400-25-7; *n*-$BuClCH_2^+$, 81971-22-4; *i*-$BuClCH_3^+$, 81971-23-5; *sec*-$BuClCH_3^+$, 81971-24-6; *t*-$BuClCH_3^+$, 81971-25-7; $CH_3OH_2^+$, 17836-08-7; $CH_3OHCH_3^+$, 17009-82-4; $C_2H_5OHCH_3^+$, 52067-06-8; *i*-$C_3H_7OHCH_3^+$, 81971-26-8; *t*-$C_4H_9OHCH_3^+$, 81971-27-9.

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(39) The problems with good ab initio calculations are discussed by Pople[40] and Dewar[41] and their co-workers. Obviously, an ab initio approach is the desired one.

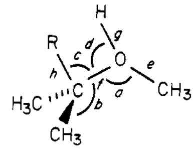
(40) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1981, *103*, 5649.

(41) Kollmar, H.; Carrion, F.; Dewar, M. J. S.; Bingham, R. C. *J. Am. Chem. Soc.* 1981, *103*, 5292.

(42) Olah, G. A., Ed. "Friedel-Crafts and Related Reactions"; Wiley-Interscience: New York, 1973.

(43) Peterson, P. E.; Bonazza, B. R.; Henrichs, P. M. *J. Am. Chem. Soc.* 1973, *95*, 2222. Henrichs, P. M.; Peterson, P. E. *Ibid.* 1973, *95*, 7449. Olah, G. A.; Westerman, P. W.; Melby, E. G.; Mo, Y. K. *Ibid.* 1974, *96*, 3565 and reference therein.

(44) Calculated structural features and properties of $(CH_3)_2CHOHCH_3^+$ and $(CH_3)_3COHCH_3^+$ are: as follows:



R = H Angles: a = 132.8°, b = 106.8°, c = 105.0°, d = 111.0°.
Lengths: e = 1.40 Å, f = 1.45 Å, g = 0.96 Å, h = 1.13 Å.
Charge on CH_3OH = 0.443; IP = 16.3 eV
R = CH_3 Angles: a = 137.6°, b = 107.1°, c = 102.5°, d = 111.8°.
Lengths: e = 1.40 Å, f = 1.48 Å, g = 0.96 Å, h = 1.52 Å.
Charge on CH_3OH = 0.393; IP = 15.9 eV