Thermodynamic Stability of Trichlorocyclopropenyl Cation. An Experimental (FTICR) and Computational [G2(MP2)] Study[†]

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The standard Gibbs energy change for the halide transfer between *tert*-butyl chloride and trichlorocyclopropenyl cation has been determined by means of Fourier transform ion cyclotron resonance mass spectrometry. Trichlorocyclopropenyl cation is found to be substantially more stable than *tert*-butyl and 1-adamantyl cations. This reaction and cognate processes were also studied at the ab initio G2(MP2) level. The agreement between experimental and calculated changes of thermodynamic state functions is remarkably good. On the basis of these results, isodesmic and homodesmotic reactions were constructed. They led to the delocalization energy in **1** and to the quantitative assessment of substituent effects on the stability of the aromatic 2π-electron system.
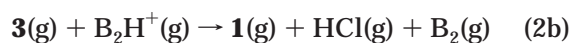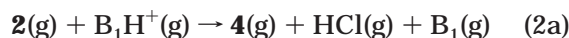
Introduction

Cyclopropenium ion, $(CH)_3^+$, is the simplest Hückel $4n + 2$ π-electron monocyclic system. This ion and cognate species have recently received considerable attention.[1] Its standard enthalpy of formation has been determined experimentally (1075 kJ mol^{-1})[2] and calculated at the G2 level (1074 kJ mol^{-1}).[1b] Here we report the results of a quantitative experimental study of the thermodynamic stability of trichlorocyclopropenyl ion, $(CCl)_3^+$,[1] in the gas phase. To our knowledge, this is the first study of this kind on substituted cyclopropenium ions.[1] Data thus obtained are compared to quantum-mechanical calculations at the G2(MP2) level.[3]

$\Delta G^{\circ}{}_{(1)}$, the standard Gibbs energy change for the chloride exchange between *tert*-butyl chloride (**2**) and **1** in the gas phase [reaction 1], was determined by means of Fourier transform ion cyclotron resonance spectrometry (FT ICR).[4]

Use was made of a bracketting technique known as the "dissociative proton attachment method" (DPA).[5] In this method, $\Delta G^{\circ}{}_{(1)}$ is given by the difference of the gas-phase basicities,[6] GB, of the two bases, B_1 and B_2,

$$2(g) + B_1H^+(g) \rightarrow 4(g) + HCl(g) + B_1(g) \quad (2a)$$

$$3(g) + B_2H^+(g) \rightarrow 1(g) + HCl(g) + B_2(g) \quad (2b)$$
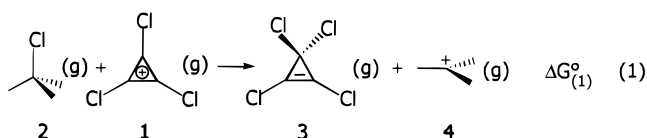
defining the onset of reactions 2a and 2b under the same experimental conditions:

Experimental Section

A. The FT ICR Spectrometer. The study was carried out on a modified Bruker CMS 47 FT ICR mass spectrometer[4c] used in previous studies.[5,7] A detailed description is given in refs 5a and 7. Some modifications have been introduced with respect to the standard instrument. They are described in these references. The substancial field strength of the supraconducting magnet, 4.7 T, allows the monitoring of ion–molecule reactions for relatively long periods of time, and also, the use of relatively high pressures (of the order of 5×10^{-4} mbar) during a few seconds.

B. DPA Experiments. The basic concepts of the method have been developed in ref 5. The experimental technique is quite similar to that used in these studies. Some minor changes are introduced in order to avoid the unwanted deprotonation of $R^+(g)$ by $B(g)$ (this possibility exists in the case of *t*-Bu$^+$(g)). In general, the reference base B is introduced into the high-vacuum section of the instrument and subject to electron ionization (using nominal energies in the range of 10−13 eV). Nominal pressures of B are ca. 2×10^{-7} mbar. Charged fragments from B act as primary proton sources. In general, after 1−2 s, the main ion present is $BH^+(g)$. After

[†] Dedicated to Professor Erwin Buncel.

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(1) See, e.g., the following and references therein: (a) Glukhotsev, M. N. *J. Chem. Educ.* **1997**, *74*, 132−136. (b) Glukhotsev, M. N.; Laiter, S.; Pross, A. *J. Phys. Chem.* **1996**, *100*, 17801−17806. (c) Burk, P.; Abboud, J.-L. M.; Koppel, I. A. *J. Phys. Chem.* **1996**, *100*, 6992−6997. (d) Jemmis, E. D.; Srinivas, G. N.; Leszczynski, J.; Kapp, J.; Korkin, A. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1995**, *117*, 11361−11362. (e) Budzelaar, P. H. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 3967−3970. (f) An important experimental study of $C_3Cl_3^+/AlCl_4^-$ (X-ray structure) and HF/6-311G(d,p) calculations on $C_3Cl_3^+$ have recently been published: Clark, G. R.; Taylor, M. J.; Steele, D. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3597−3601.

(2) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(3) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293−1298.

(4) (a) Bowers, M. T.; Aue, D. H.; Webb, H. M.; McIver, R. T. *J. Am. Chem. Soc.* **1971**, *93*, 4314−4315. (b) Freiser, B. In *Techniques for the Study of Ion−Molecule Reactions*; Farrar, J. M., Saunders, W., Jr., Eds.; Wiley: NewYork, 1988; Chapter 2. (c) Laukien, F. H.; Allemann, M.; Bischofberger, P.; Grossmann, P.; Kellerhals, H. P. Kopfel, P. In *Fourier Transform Mass Spectrometry. Evolution, Innovations and Applications*; Buchanan, M. V., Ed.; ACS Symposium Series 359; American Chemical Society: Washington, DC, 1987; Chapter 5.

(5) (a) Abboud, J.-L. M.; Castaño, O.; Herreros, M.; Elguero, J.; Jagerovic, N.; Notario, R.; Sak, K. *Int. J. Mass Spectrom., Ion Proc.* **1998**, *175*, 35−40. (b) Abboud, J.-L. M.; Castaño, O.; Della, E. W.; Herreros, M.; Müller, P.; Notario, R.; Rossier, J.-C. *J. Am. Chem. Soc.* **1997**, *119*, 2262−2266. (c) Abboud, J.-L. M.; Notario, R.; Ballesteros, E.; Herreros, M.; Mó, O.; Yáñez, M.; Elguero, J.; Boyer, G.; Claramunt, R. *J. Am. Chem. Soc.* **1994**, *116*, 2486−2492.

(6) The gas-phase basicity GB(B) of base B is the standard Gibbs energy change pertaining to the reaction: $BH^+(g) \rightarrow B(g) + H^+(g)$. See, e.g., ref 2.

(7) Abboud, J.-L. M.; Herreros, M.; Notario, R.; Esseffar, M.; Mó, O.; Yáñez, M. *J. Am. Chem. Soc.* **1996**, *118*, 1126−1130.

Table 1. Experimental Determination of DPA Onsets[a] for Species 2 and 3

compd	ref,[b] (GB)[c] transfer?	ref,[d] (GB)[c] transfer?	DPA onset[e]
2	t-C$_4$H$_9$CN (186.2), yes	n-C$_4$H$_9$OCH$_3$ (189.2), no	188.4
	t-C$_4$H$_9$SH (187.6), yes	CH$_3$COOCH$_3$ (189.3), no	
3	(n-C$_3$H$_7$)$_2$S (199.1), yes	2-cyanopyridine (201.0), no	200.5
	(CH$_3$CO)$_2$CH$_2$ (199.9), yes	(n-C$_4$H$_9$)$_2$S (201.4), no	

[a] All values in kcal mol^{-1}. [b] Strongest base able to lead to DPA. [c] Gas-phase basicities of the reference bases, taken from ref 9. See text. [d] Weakest base not leading to DPA. [e] Average of the two closest GB values from columns 2 and 3.

Table 2. Computational Results at the G2(MP2) Level[a,b]

species	enthalpy	Gibbs energy
(CCl)$_3^+$, **1**	−1492.916633	−1492.955329
t-C$_4$H$_9$Cl, **2**	−617.226718	−617.264073
C$_3$Cl$_4$, **3**	−1952.950661	−1952.993256
t-C$_4$H$_9^+$, **4**	−157.169332	−157.206640
C$_3$Cl$_5^+$	−2412.335136	−2412.381853
C$_3$Cl$_6$	−2872.452549	−2872.499932
(CH)$_3^+$	−115.492839	−115.518867
C$_3$H$_3$Cl	−575.525577	−575.557431

[a] All values in hartrees. [b] See text.

reaction times of ca. 5 s, all ions, with the exception of BH$^+$(g), are ejected off of the ICR cell[8] by means of radio frequency ejection "chirps" (broad band). Great care is taken in order to prevent the excitation of this ion, and so, use is made of an "ejection safety belt" (a feature of the Bruker software that strictly prevents the irradiation of a preselected frequency range around the resonance frequency of BH$^+$ in order to avoid its accidental excitation). At this point, a "burst" of R−X(g) is allowed to enter the high-vacuum section of the spectrometer by means of a pulsed piezoelectric valve.

These pulses last some 0.1 s, and the total pressure reaches values of ca. 5×10^{-4} mbar. The pressure goes down to ca. 1×10^{-6} mbar in about 3 s. During this period of time, the main reaction observed is the formation of R$^+$(g). The system is routinely monitored over a period of about 20 s after the injection of R−X(g). The same experimental protocol was applied to both **2** and **3**. Given the very low pressures prevailing in these experiments, reactions 2a and 2b are essentially irreversible (the partial pressure of XH is extremely small), and so, while a true equilibrium is not reached, the onset of the DPA process can be clearly observed.

C. Samples. Compounds **2** and **3** were Aldrich products. Their purity was assessed by standard methods.

The experimental results are summarized in Table 1.
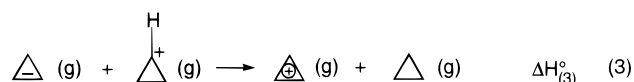
Computational Details

Calculations were performed on a Silicon Graphics "Challenge" computer using the Gaussian 94 package of programs.[10] Calculations at the G2(MP2) level[3] were performed on the species **1**−**4**. The results are reported in Table 2.

Discussion

The computed $\Delta G°_{(1)}$ value amounts to 51.2 kJ mol^{-1}, in remarkably good agreement with the experimental

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(9) *NIST Chemistry WebBook. NIST Reference Database*; No. 69. August 1997 release. http://webbook.nist.gov/chemistry/. Proton Affinity Data: compiled by E. P. Hunter, S. G. Lias. Neutral Thermochemical Data: compiled by H. Y. Afeefy, J. F. Liebman, and S. E. Stein.

(10) Gaussian 94, Revision B.3. Frisch, M. J.; Trucks, C. W.; Schlegel, H. B.; Gill, D. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andrés, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J., Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; González, C., Pople, J. A. Gaussian lnc.: Pittsburgh, PA, 1995.

value, 50.6 ± 11.8 kJ mol^{-1} (from data in Table 1). Combining this datum with the entropy change computed at the MP2/6-31G(d) level for reaction 1, $\Delta S°_{(1)} = 33.0$ J mol^{-1} K^{-1}, we obtain a value of $\Delta H°_{(1)}$ of 60.5 ± 11.8 kJ mol^{-1}. The G2(MP2) value is 61.3 kJ mol^{-1}. Thus, from the standpoint of the chloride-ion affinity, **1**(g) appears as substantially more stable than *tert*-butyl and, even, 1-adamantyl cation.[12]

The experimental value of the standard enthalpy of formation of **3**(g), $\Delta_f H°_m$(**3**,g), is not yet available. It was thus computed at the G2(MP2) level using the data from Table 2, including the spin−orbit correction.[11] A value of 128.9 kJ mol^{-1} was obtained. Combining this datum with the experimental values of $\Delta H°_{(1)}$ (this work), $\Delta_f H°_m$(**2**,g)[9] and $\Delta_f H°_m$(**4**,g),[9] we get $\Delta_f H°_m$(**3**,g) = 964.6 kJ mol^{-1}.

$$\triangle \text{ (g)} + \overset{H}{\underset{+}{\triangle}} \text{ (g)} \longrightarrow \triangle \text{ (g)} + \triangle \text{ (g)} \qquad \Delta H°_{(3)} \qquad (3)$$

The delocalization energy, ΔE_{deloc}, defined as the standard energy change (equal to the standard enthalpy change) for the homodesmotic[13] reaction 3 is of great conceptual importance[1a,14] in the case of the Hückel systems such as (CH)$_3^+$ and **1**. The best value for $\Delta H°_{(3)}$ presently available is −247.3 kJ mol^{-1} (from a G2 calculation).[1b] This is a very large value, suggestive of the "archetypal aromatic character"[1b] of (CH)$_3^+$. For **1**(g), we can similarly construct the homodesmotic reaction 4:
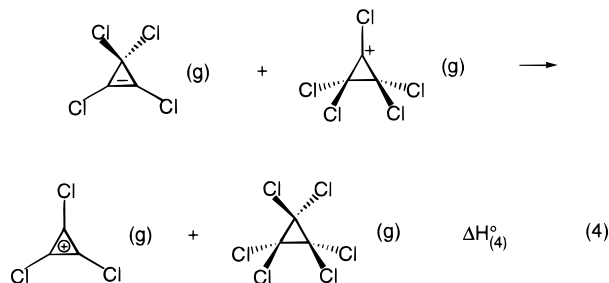
Using the data given in Table 2, we obtain the corresponding standard enthalpy change, $\Delta H°_{(4)} = -218.9$ kJ mol^{-1}. Again, this is a very substantial value, indicating that substitution has not significantly affected the delocalization energy. The existence of multiple Cl−Cl interactions prevents a more detailed comparison of $\Delta H°_{(3)}$ and $\Delta H°_{(4)}$.

(11) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063−1079.

(12) Sharma, R. B.; Sen Sharma, D. K.; Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 3747−3757.

(13) (a) Cremer, D. *Tetrahedron* **1988**, *44*, 7427−7454. (b) George, P.; Tratchman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317−323.
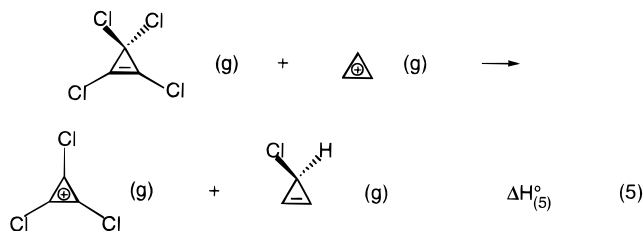
(14) Minkin, V. I.; Glukhotsev, M. N.; Simkin, B. Ya. *Aromaticity and Antiaromaticity. Electronical and Structural Aspects*; John Wiley: New York, 1994.

Furthermore, reaction 5 can be constructed. It directly links the stabilities of both ions.

Using data from Table 2, we obtain for $\Delta H^{\circ}_{(5)}$ and $\Delta G^{\circ}_{(5)}$ 3.4 and -1.7 kJ mol^{-1}, respectively. This result strongly supports the conclusion based on reaction 4.

We last compare the effect of chlorine substitution on the standard enthalpies of formation of $(CH)_3^+(g)$ and benzene. To this end, we use the isodesmic reaction 6 and compute $\Delta H^{\circ}_{(6)}$ using experimental data for all the species. We obtain $\Delta H^{\circ}_{(6)} = 19.7$ kJ mol^{-1}.

The fact that reaction 6 is slightly endothermal clearly shows that the potentially destabilizing field effect of the
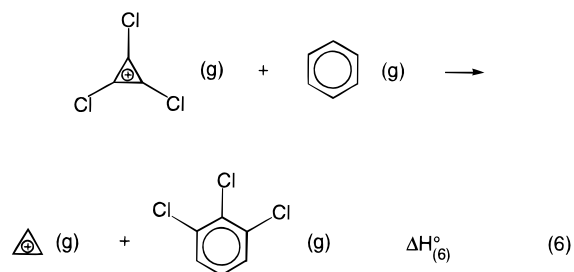
substituents in **1** is offset by their stabilizing resonance and polarizability contributions.[15]

(15) Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 1−87.