to what would be expected for a significant nonbonded F⋯F attraction in the cis isomer.

Further, higher level theoretical investigations of the properties of the *cis*- and *trans*-1,2-difluorocyclopropane molecules are needed. To date, neither polarization functions nor configuration interaction has been applied to calculations of the difluorocyclopropanes. The accurate geometric parameters and the dipole moments of both isomers reported in the present papers as well as the observed energy difference should be a stimulus to such work.

Conclusions

The complete gas-phase structure of *cis*-1,2-difluorocyclopropane was determined from microwave spectral data. The C–C bonds have shortened relative to the ring bonds in cyclopropane. All the C–C bonds are longer in *cis*-1,2-difluorocyclopropane than the corresponding bonds in *trans*-1,2-difluorocyclopropane. The C–F bond distance in the cis isomer is within the range of C–F bond distances which have been observed for other fluorinated cyclopropanes. However, the trans C–F bond is unusually long.

An ab initio investigation by Skancke and Boggs of *cis*- and *trans*-1,2-difluorocyclopropane at the 4-21 level determined geometry optimized structures which are in qualitative agreement with the experimental structures.[4] For the trans isomer, the amount of bond shortening is underestimated by 0.02 Å for both types of ring bonds. In the case of the cis isomer, the agreement is better for these ring bonds. A second ab initio study by Deakyne et al. employing charge density difference maps predicts the observed shortening of the C_1-C_2 bond in the cis isomer. However, it does not find bond shortening for the adjacent C_2-C_3 bond in the cis isomer. This result is contrary to the observed shortening of 0.011 Å and may be due to difficulty in interpreting the charge density difference map for a situation where both $C_{1,2}$ and C_3 carbon displacements are significant.

The microwave structural results also provide support for theoretical interpretations of the observed −2800 ± 200 cal/mol cis-to-trans energy difference of 1,2-difluorocyclopropane.[12] According to Bingham's qualitative argument, greater destabilization is found in the cis form due to larger electron delocalization in the antibonding "FCCF" orbital.[40] Skancke and Boggs indicate that their ab initio calculations offer support for Bingham's proposal.[4] The microwave studies find a shorter C–F bond and a longer C_1-C_2 bond in the cis isomer. These results tend to support Skancke and Boggs' work and are consistent with the electron-delocalization explanation.

Several structural results suggest that nonbonded attractions between vicinal fluorines[36–39] are not significant for the 1,2-difluorocyclopropanes. The F⋯F distances are almost identical for *cis*-1,2-difluoroethylene and *cis*-1,2-difluorocyclopropane in spite of the reversal in energy differences of the two isomeric pairs. Also, the CCF angles and the τ_F angles are virtually the same for *cis*- and *trans*-1,2-difluorocyclopropane.

Registry No. CHFCHFCH₂, 57137-41-4; CDFCDFCH₂, 57137-43-6; ¹³CDFCDFCH₂, 99797-86-1; CDFCDF¹³CH₂, 99797-87-2; CHFCHFCD₂, 57137-45-8; ¹³CHFCHFCD₂, 99797-88-3.

Supplementary Material Available: Rotational transitions and centrifugal distortion corrections for cyclopropane compounds (12 pages). Ordering information is given on any current masthead page.

Temperature Dependence of the Substrate and Positional Selectivity of the Aromatic Substitution by Gaseous *tert*-Butyl Cation

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Abstract: The temperature dependence of the substrate and positional selectivity of the alkylation of benzene and toluene by radiolytically formed *t*-Bu⁺ ions has been investigated in isobutane gas at 720 torr in the range 0–140 °C. The Arrhenius plot of the empirical k_T/k_B ratio is linear over an extended (0–100 °C) interval, and its slope corresponds to a difference of 3.6 ± 0.4 kcal mol⁻¹ between the activation energy for the *tert*-butylation of benzene and of toluene. The positional selectivity of the alkylation is affected by the temperature as well, the p:¹/₂m ratio decreasing from ca. 27 at 0 °C to 7.5 at 140 °C. The results are interpreted as evidence that under conditions typical of radiolytic experiments the activation mechanism of the addition of *t*-Bu⁺ to arenes, a typical ion–molecule reaction, is essentially thermal, as expected at the high-pressure limit of gas-phase ionic processes.

Aromatic substitution by gaseous cations has been the focus of considerable interest, and the subject of extensive investigations, carried out by mass spectrometric,[1] radiolytic,[2] and nuclear decay[3]

techniques over a pressure range of several orders of magnitude. However, very little is known on the temperature dependence of the reaction rate, since most of the studies have been carried out

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at a fixed temperature, and even the few ones covering a limited temperature range are primarily focused on thermodynamic, rather than kinetic, aspects.[4]

The present study deals with the temperature dependence of the substrate and positional selectivity of the alkylation of benzene and toluene by t-Bu[+] ions in isobutane gas at nearly atmospheric pressure, measured over an extended (0–140 °C) temperature range. The choice of the t-Bu[+] ion as the gaseous electrophile has been suggested by the fact that its addition to arenes is an unusually well characterized ion–molecule reaction, as a result of extensive radiolytic[5] and mass spectrometric studies, which have provided, inter alia, crucial thermochemical and equilibrium data.[4a] The ionic reactant has been obtained, according to a well established technique,[5] from the γ radiolysis of isobutane gas at nearly atmospheric pressure.[5] In such a system, t-Bu[+] represents the only significant cation, being formed in high yields either directly or via hydride ion transfer from i-C_4H_{10} to primary fragment ions.[6,7] The cation is thoroughly thermalized by many unreactive collisions with isobutane molecules, before interacting with the aromatic substrates present at low concentrations in the gas.

The objectives of the study described herein are twofold. In the first place, it represents an attempt to a quantitative evaluation of the activation parameters of a typical gas-phase ionic reaction. The results could be of unusually general interest to the theory of aromatic substitution, owing to the free, unsolvated state of the reactants and to the inherent simplicity of the gaseous reaction environment. Furthermore, the results could prove helpful in enlightening certain kinetic aspects of gas-phase ionic chemistry, especially since the work has been carried out in a virtually unexplored, if kinetically significant, pressure domain, far above the range accessible to current mass spectrometric approaches.

Experimental Section

Materials. The gases, having a stated purity in excess of 99.99 mol %, were obtained from Matheson Gas Products Inc., as well as from local sources. The substrates, i.e., benzene and toluene, were gas chromatographic standards from C. Erba Co., while the chemicals used for reference purposes in GLC were obtained from commercial sources or prepared according to unexceptional procedures.

Procedure. The samples were prepared by introducing fragile ampoles, containing weighed amounts of benzene/toluene mixtures of known composition, into 100-mL Pyrex bulbs, equipped with a break-seal arm, and connected to a greaseless vacuum line. Following the introduction of the gaseous components (isobutane, oxygen, and ammonia) at the desired partial pressures into the carefully evacuated and outgassed vessels, the latter were then allowed to come to room temperature, the fragile ampoles broken, and the gaseous components allowed to mix before being subjected to the irradiation. The latter was carried out in a 220 Gammacell from Nuclear Canada Ltd., fitted with a thermostatic device designed to maintain the irradiated samples at any desired tem-
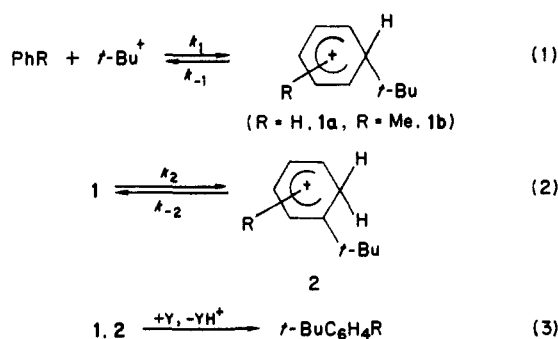
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(4) Cf., for instance, the detailed mass spectrometric study on the gas-phase *tert*-butylation of benzene: (a) Sen Sharma, D. K.; Ikuta, S.; Kebarle, P. *Can. J. Chem.* **1982**, *60*, 2325. A negative temperature dependence of the rate has been established by high-pressure mass spectrometry for the methylation of benzene by Me_2Cl^+ [(b) Sen Sharma, D. K.; Kebarle, P. *J. Am. Chem. Soc.* **1982**, *104*, 19] and for the benzylation of benzene by $PhCH_2^+$ [(c) Sen Sharma, D. K.; Kebarle, P. *Can. J. Chem.* **1981**, *55*, 1592].

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(8) Even in the absence of added bases, e.g., NH_3, whose proton affinity (PA) reaches 205 kcal mol^{-1}, exothermic deprotonation of 1 and 2 is likely performed by basic products from the radiolysis of i-C_4H_{10}, e.g., the abundant isobutene, PA = 197 kcal mol^{-1}. As a comparison, the PAs of p-xylene and *tert*-butylbenzene are respectively 194 and 195 kcal mol^{-1}. All values taken from the following: Bowers, M. T., Ed. "Gas-Phase Ionic Chemistry"; Academic Press: New York, 1979; Vol. 2, p 1.

Table I. Temperature Dependence of the Substrate and Positional Selectivity[a]

temp, °C	toluene/benzene rel reactivity[b]		isomeric composition of *tert*-butyltoluenes (%)	
			para	meta
0		114 ± 5	93 ± 3	7 ± 2
40	55.5 ± 3	56.3 ± 3[c]	50.0 ± 10[d]	87 ± 5	13 ± 3
60		35.4 ± 2		
80		23.8 ± 2	81 ± 5	19 ± 5
100		21.2 ± 2		
120		20.0 ± 2	22 ± 5[d]	
140		20.8 ± 2	79 ± 5	21 ± 5

[a]System composition, isobutane 720 torr, O_2 4 torr, aromatic substrates 0.1–0.2 torr, [PhH]:[PhMe] ratio ca. 5:1, unless otherwise stated. [b]Defined by the ratio [*tert*-butyltoluenes][PhH]/[*tert*-butylbenzene][PhMe]. [c]Measured at [PhH]:[PhMe] ratios ranging from 2:1 to 11.2:1. [d]Measured in a system containing NH_3, 2 torr.

perature within the 0–150 °C range with an accuracy of ca. ±3 °C. The total dose received by the samples was 2.0 MRad, at a dose rate of ca. 1 MRad h[-1], as measured with a Fricke dosimeter.

Analysis of the Products. The irradiated vessels were cooled to –196 °C, their break seal opened, and a measured amount of MeOH added. After allowing the vessels to warm to room temperature, their inner walls were carefully rinsed with the methanol added, and the solution obtained was analyzed by GLC and GLC/MS. The analyses were performed with a Sigma 3 instrument (Perkin-Elmer Co.), equipped with flame ionization and photoionization detectors, using two 3.5-m long, 2-mm i.d. glass columns, packed respectively with Bentone 34 (5% w/w) + SP-2100 silicone fluid (1.75%) on 100-120 mesh Supelcoport, or with Carbowax 1500 (1%) + SP-2100 (1%) on the same support.

The identity of the products, established by comparison of their elution times with those of authentic samples, was confirmed by GLC/MS, using a Model 5982 A Hewlett-Packard quadrupole spectrometer, or a ZAB-2F magnetic instrument from VG-Micromass Ltd. The yields of the products were deduced from the areas of the corresponding elution peaks, using the internal standard method and individual calibration factors to correct for the response of the detector. The quadrupole mass spectrometer, operated in the chemical ionization (CI) mode, was used to record isobutane CI spectra at various source temperatures.

Results

Nature and Yields of the Products. Consistent with earlier results,[5a] the alkylation of benzene and toluene by radiolytically formed t-Bu[+] in isobutane at nearly atmospheric pressure is found to yield *tert*-butylbenzene and respectively a mixture of m- and p-*tert*-butyltoluenes, without detectable traces of the ortho isomer. The *absolute* yields of the products, measured by their G_{+M} value, depend on the composition of the system and on the total dose, both effects being easily rationalized in terms of a competition for the t-Bu[+] ions between the arenes and other nucleophiles, either initially present in the system as impurities or formed during its radiolysis, e.g., butenes, octenes, t-BuOH, etc. Under the conditions prevailing in this work, where the mole fraction of arenes was kept below 3×10^{-4}, *tert*-butylated aromatics are formed with typical G_{+M} values around 0.3, corresponding to an *absolute* yield of 10%, based on the total number of t-Bu[+] ions formed in the irradiation.[5a]

A convincing argument can be made that the processes responsible for the formation of *tert*-butylated arenes are of ionic nature. First, occurrence of thermal ("dark") reactions has been ruled out by the results of blank runs, involving no γ irradiation. Furthermore, in order to suppress radicalic pathways, the irradiations were performed in the presence of an effective scavanger (O_2), at concentrations considerably *higher* than those of the arenes. Additional evidence is provided by the dramatic depression of the yields caused by the addition of recognized[7b] interceptors of the t-Bu[+] ions, e.g., NH_3. Finally, charged species whose m/e ratios correspond to those of *tert*-butylated adducts are abundant in the isobutane chemical ionization (CI) mass spectra of benzene and toluene.[4a] On the basis of these considerations, and of earlier results,[5] the reaction pathway can be outlined as follows

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$$PhR + t\text{-}Bu^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad (1)$$

(R = H, **1a**, R = Me. **1b**)

$$\mathbf{1} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \quad (2)$$

2

$$\mathbf{1, 2} \xrightarrow{+Y, -YH^+} t\text{-}BuC_6H_4R \quad (3)$$

where Y represents a gaseous base.[8]

Dependence of the Selectivity on the Temperature. The results summarized in Table I demonstrate the high substrate selectivity of the alkylation, whose apparent k_T/k_B ratio exceeds 100 at 0 °C. Experiments carried out by modifying the benzene/toluene ratio at 40 °C, or adding a gaseous base (NH₃) at 40 and 120 °C, have shown no significant changes of the substrate selectivity. The isomeric composition of the *tert*-butyltoluenes formed depends as well on the temperature, the proportions of the meta isomer increasing from ca. 7% at 0 °C to over 20% at 140 °C. The Arrhenius plot of the apparent k_T/k_B ratios (Figure 1) is linear over an extended (0–100 °C) temperature range, while a marked inflection occurs above 100 °C, which denotes a *decrease* of the relative reactivity of benzene at higher temperatures.

Discussion

Before proceeding to discuss the results summarized in the previous paragraph, the preliminary problem arises of establishing whether the observed trend reflects indeed the temperature dependence of the electrophilic attack (processes 1 and 2) rather than of other steps of the reaction sequence which eventually yields the neutral alkylated arenes.

In fact, temperature changes could conceivably affect the processes responsible for the formation of the ionic reactant and/or the deprotonation step 3.

The first possibility can safely be ruled out on the following grounds. $t\text{-}Bu^+$ is formed from the radiolysis of $i\text{-}C_4H_{10}$ either by direct, temperature-independent primary ionization or via hydride ion abstraction by fragment ions, e.g., Et^+, Pr^+, $i\text{-}Pr^+$, from isobutane. The available data show that the negative temperature dependence of several such processes is by far too low to cause detectable kinetic effects in the temperature range of interest.[9] Such conclusion is confirmed by the experimental observation that $t\text{-}Bu^+$ remains by far the predominant ion in the CI mass spectra of isobutane, even at temperatures well above the range investigated in this work.

The second possibility, i.e., that the observed temperature dependence can be traced to process 3, has been ruled out by carrying out the alkylation at two widely different temperatures (40 and 120 °C) in the presence of NH₃, a strong base which undoubtedly ensures fast deprotonation of **1** and **2**.[10] No significant changes of the apparent k_T/k_B ratios could be detected, showing that, even in the absence of added bases, step 3 and therefore its temperature dependence are not kinetically significant.

In conclusion, the available evidence suggests that the observed temperature dependence can indeed be traced to the alkylation step.

Another preliminary problem concerns the inflection of the Arrhenius plot which occurs above 100 °C. A reasonable explanation can be based on the data of Kebarle and co-workers,[4a] showing that the equilibrium constant of addition 1 to benzene
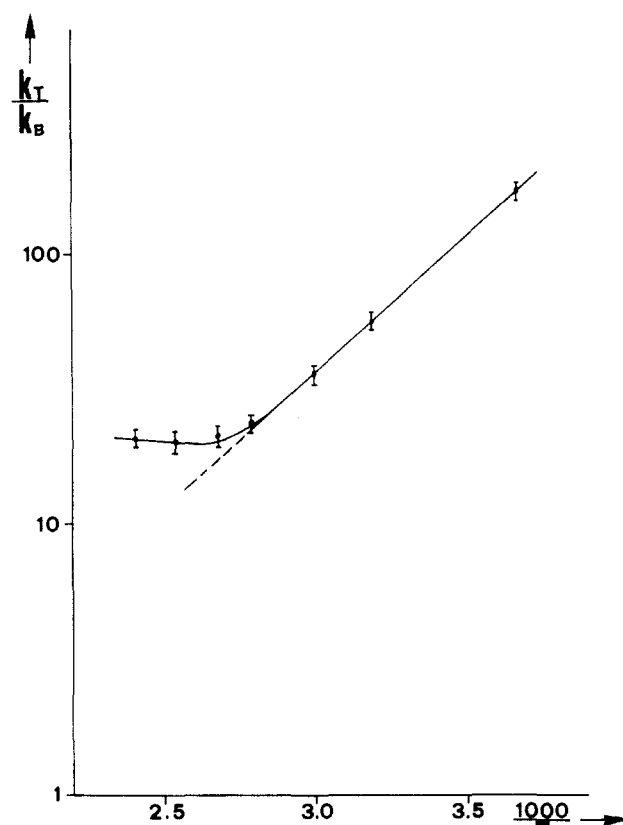

Figure 1. Temperature dependence of the k_T/k_B ratio in the gas-phase alkylation of benzene and toluene by $t\text{-}Bu^+$ ions in isobutane at 720 torr.

decreases markedly with the temperature, passing from 170 torr⁻¹ at 32 °C to ca. 0.3 torr⁻¹ at 105 °C. The relative increase of k_{-1} with the temperature can be expected to selectively depress the net rate of alkylation of benzene.[11] In fact, the facile dissociation of **1a** arises[4a] from the unfavorable entropy change, and especially from the low exothermicity (12–15 kcal mol⁻¹) of the alkylation of benzene.[12] However, the exothermicity of eq 1 and therefore the stability of the adducts **1** increase appreciably in passing from benzene to toluene. Consequently, only **1a** is likely to undergo kinetically significant back dissociation at the highest temperatures within the range investigated.

Temperature Dependence of the Substrate and Positional Selectivity. Having addressed the preliminary problems of identifying the processes responsible for the observed temperature effects and to account for the curvature of the Arrhenius plot above 100 °C, we can turn to the primary object of this study. The main conclusion is that the temperature dependence of the substrate selectivity conforms to that expected for ordinary thermal reactions. Regression analysis of the data in the linear portion of the Arrhenius plot leads to a difference of the empirical activation energies for the alkylation of benzene and of toluene

$$\Delta E = E_B - E_T = 3.6 \pm 0.4 \text{ kcal mol}^{-1}$$

and to a (rough) estimate of the preexponential factors ratio, $A_B/A_T \approx 6$.

Deducing the temperature dependence of the positional selectivity from the isomeric composition of the products is more difficult, since the latter can be affected by processes, e.g., alkyl

(9) The reaction of Et^+ with $i\text{-}C_4H_{10}$ shows no temperature dependence between 320 and 480 K, while the rate constant of the reaction of $i\text{-}Pr^+$ with $i\text{-}C_4H_{10}$ decreases from 5.8 × 10⁻¹⁰ to 1.4 × 10⁻¹⁰ cm³ s⁻¹ in passing from 300 to 600 K, see M. Meot-Ner (ref 8, Vol. 1, p 219). Considering the large excess of $i\text{-}C_4H_{10}$, changes of this order of magnitude are by far insufficient to cause any detectable decrease of $[t\text{-}Bu^+]$.

(10) Addition of NH₃ to systems irradiated at temperatures other than 40 °C has been suggested by one of the referees.

(11) In the steady-state approximation, depending on whether one considers process 2 or 3 kinetically significant, the overall rate constant of the alkylation corresponds to $k_1k_2/(k_{-1} + k_2)$, or respectively to $k_1k_3[Y]/(k_{-1} + k_3[Y])$. It seems legitimate to neglect k_{-2} with respect to k_2, in view of the unfavorable energetics of the back isomerization $\mathbf{2} \rightarrow \mathbf{1}$, cf.: Devlin, J. L., III; Wolf, J. F.; Taft, R. W.; Hehre, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 1990.

(12) According to ref 4a, $\Delta S_1 = 49 \pm 5$ cal mol⁻¹ K⁻¹, and formation of **2** (R = H) from $t\text{-}Bu^+$ and PhH entails an enthalpy change of −22 ± 2 kcal mol⁻¹ at 300 K. However, the exothermicity of (1) is considerably lower, owing to the lower stability of **1** with respect to **2**, cf. ref 9.

shifts, which alter the initial orientation. Nevertheless, assuming that the proportions of isomers reflect indeed the relative rate of attack to different ring positions, one obtains a $E_{meta} - E_{para}$ difference of 3 kcal mol^{-1}, not inconsistent with ΔE.

To our knowledge, this study represents the first attempt at a quantitative evaluation of the Arrhenius parameters of a typical aromatic substitution by gaseous ions, and its extended temperature range (140 °C) has hardly been approached in the study of the temperature dependence of any aromatic substitution, irrespective of the reaction medium.

The nature of the electrophile, a free carbenium ion, and the gaseous reaction environment confer an unusual degree of generality on the results, largely unaffected by such incidental factors as the particular combinations of solvents, catalysts, counterions, etc., which variegate Friedel–Crafts reactions.

In this connection, it is noteworthy that the gas-phase selectivity considerably *exceeds* those of catalyzed alkylations, e.g., k_T/k_B = 16.6 in the homogeneous t-BuBr/SnCl$_4$/MeNO$_2$ system and 15.0 in the heterogeneous t-BuF/BCl$_3$/toluene system.[13] The positional selectivity is also generally *higher* in the gas phase than in solution.[14]

Activation Energy of Ion–Molecule Reactions in Dense Unreactive Gases.

The kinetic peculiarities of ion–molecule reactions raise the problem of how closely the empirically measured ΔE value corresponds to the difference between the intrinsic activation energies concerned. In fact, long-range interactions are known to cause the formation of "loose" ion–molecule adducts, activated by the electrostatic energy, E_o, released in the process. When collisional deactivation is inefficient, as in the low-pressure range, temperature-dependence trends reflect the $E^* - E_o$ difference, rather than E^*, the intrinsic ("chemical") activation energy.[15] The situation is different in a dense, *unreactive* bath gas, M. In fact, the ion, far from being free, is initially associated with M. This factor alone can drastically decrease E_o, reduced to the stability difference between the adducts formed by the ion with M and

respectively with the neutral reactant.[16] Furthermore, the greatly increased efficiency of collisional thermalization must be taken into account. In principle, at sufficiently high pressure and in a properly chosen bath gas, the effects of electrostatic activation vanish, and the reaction follows purely thermal kinetics, which allows E^* to be deduced from a temperature-dependence analysis. Given the above, we suggest that the conditions prevailing in this study are sufficiently close to the high-pressure limit to make the empirical quantity ΔE a reasonably accurate estimate of the E_B^* $- E_T^*$ difference. There are several arguments in favor of this contention. First, the isobutane pressure (720 torr) exceeds by orders of magnitude that (ca. 5 torr) where the onset of significant effects of collisional deactivation has clearly been observed.[17] Second, the relative reactivity of arenes toward t-Bu$^+$, measured at 37.5 °C in neopentane at 735 torr, is totally unaffected by an almost tenfold pressure decrease.[18] Finally, when dealing with activation energy *differences*, any residual effects of electrostatic activation should largely cancel out, owing to the close similarity of the two substrates involved.

In conclusion, the results of this study underline the kinetic interest attached to the exploration of the high-pressure limit of ion–molecule reactions, in view of their drastic transition from electrostatic to thermal activation. Furthermore, only at the high-pressure limit can the study of ion–molecule reactions serve one of its major purposes, namely to provide generalized and simplified models of the ionic processes in condensed media, driven by thermal, rather than electrostatic, activation mechanisms.

(13) Olah, G. A.; Flood, S. H.; Moffat, M. E. *J. Am. Chem. Soc.* **1964**, *86*, 1060.

(14) Brown, H. C.; Smoot, C. R. *J. Am. Chem. Soc.* **1956**, *78*, 6255.

(15) Depending on the sign of the $E^* - E_0$ difference, ion–molecule reactions can display a positive or negative temperature dependence, cf.: (a) Olmstead, W. N.; Brauman, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 3715. (b) Magnera, T. F.; Kebarle, P. "Ionic Processes in the Gas Phase"; Almoster Ferreira, M. A., Ed.; D. Reidel Co.: Dordrecht, 1983; p 15.

(16) As an example, $E_0 \simeq 12$ kcal mol^{-1} in the formation of the "loose" complex between Me$_2$Cl$^+$ and PhMe, and $\simeq 11$ kcal mol^{-1} in the Et$^+$/C$_2$H$_6$ association, cf. ref. 13b, p 146.

(17) Caldwell, G.; Magnera, T. F.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 963.

(18) Giacomello, P.; Cacace, F. *J. Am. Chem. Soc.* **1976**, *98*, 1823.