termining relative stabilities and the rotational barrier in silaethylene.

GVB Wave Functions. The energies of the ground state of silaethylene and methylsilylene were calculated by using various levels of the generalized valence bond (GVB) plus configuration interaction (CI) method.[43,47]

For the $^1A_1$ state of silaethylene, the GVB(2/4) wave function corresponds to correlating the Si–C σ and Si–C π bonds, each with the natural orbitals, leading to four natural orbitals for the two correlation pairs.

For the $^1A'$ state of methylsilylene, the GVB(2/4) wave function correlates the Si–C σ bond with a second natural orbital and the Si nonbonding orbital with an empty Si $3p_x$ orbital.

For both cases, all other orbitals are doubly occupied and calculated self-consistently. To relax the simple valence bond (perfect pairing) spin coupling restriction, we allow all configurations arising from distributing the two electrons of each GVB pair between its two natural orbitals. This leads to the GVB-RCI(4) wave function which allows all spin couplings. To include various higher order correlation effects (beyond GVB), we use correlation-consistent CI (CC-CI), in which we start with GVB pairs of each RCI and allow all single and double excitations to all GVB, valence, and virtual orbitals [denoted as $RCI(4)*D_{GVB}$]. Since the correlated wave function may want orbitals with slightly different shapes, we also allow all single excitations from the valence orbitals of the GVB-RCI(4) configurations to all GVB, valence, and virtual orbitals. Thus the full CC-CI wave function is $RCI(4)*[D_{GVB}+S_{val}]$.

Calculations carried out for the rotational barrier in silaethylene are such that the wave function at the equilibrium geometry of the Si=C double-bonded CH_2SiH_2 ($^1A_1$) dissociates correctly to the 90° twisted Si—C single-bonded $\dot{C}H_2\dot{S}iH_2$ ($^1A_2$), retaining the same level of electron correlation. In addition, we allow the 90° twisted singlet biradical state to relax to its equilibrium geometry, thus obtaining the adiabatic rotational barrier.

The GVB(2/4), GVB-RCI(4), and $RCI(4)*S_{val}$ wave functions for CH_2SiH_2 ($^1A_1$) dissociate correctly to the GVB(1/2) (which corresponds to correlating the Si–C σ bond with its natural orbital), GVB-RCI(2), and $RCI(2)*S_{val}$ wave functions for $\dot{C}H_2\dot{S}iH_2$ ($^1A_2$), respectively. The $RCI(4)*[D_\sigma+D_\pi]$ wave function dissociates to $RCI(2)*[D_\sigma+S_{open}]$ (single excitation from singlet open-shell orbitals in the RCI wave function to all virtual orbitals in addition to all single and double excitations from σ GVB pair of each RCI to all GVB, valence, and virtual orbitals) wave functions. The full DC-CI [designated as $RCI(4)*[D_\sigma+D_\pi+S_{val}]$] wave function dissociates to $RCI(2)*[D_\sigma+S_{val}]$ wave function.

GVB Basis Sets. All atoms were described with valence double-ζ (VDZ) basis sets[54] which may be described as Si(11s7p/4s3p), C(9s5p/3s2p), and H(4s/2s). In addition, one set of p-polarization functions (exponent $\alpha = 1.0$) was added to the H basis set. Sets of d-polarization functions centered on Si ($\alpha = 0.42$) and C ($\alpha = 0.62$) (exponents optimized for CH_2SiH_2 at the HF level) were added to the valence double-ζ basis sets for Si and C.

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Registry No. 1, 51067-84-6; **2**, 55544-30-4; CH_3SiD_3, 1066-43-9; $(CH_3)_2S$, 75-18-3; NH_3, 7664-41-7; CH_3CONH_2, 60-35-5; $C_6H_5NH_2$, 62-53-3; CH_3NH_2, 74-89-5; $C_6H_5CH_2NH_2$, 100-46-9; $C_2H_5NH_2$, 75-04-7; $(CH_3)_2NH$, 124-40-3; SiH_2, 13825-90-6; $SiMe_2$, 6376-86-9.

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Experimental Determination of Internal Energy Barriers in the Gas-Phase Aromatic Alkylation by Dimethylchloronium Ions

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Abstract: The temperature and pressure dependence of the substrate selectivity of the alkylation of mesitylene (M) and *p*-xylene (X) by radiolytically formed $CH_3ClCH_3^+$ ions have been investigated in CH_3Cl gas at pressures between 50 and 760 Torr in the range 40–140 °C. The Arrhenius plot of the empirical k_M/k_X ratio measured at 760 Torr is linear over the entire temperature range investigated, and its slope corresponds to a difference of 2.2 ± 0.2 kcal mol^{-1} between the activation energy for the $CH_3ClCH_3^+$ methylation of *p*-xylene and mesitylene. A pressure-dependence study of the same competition reactions carried out at 100 °C points to 300 Torr as the pressure limit, below which the correspondence between the phenomenological Arrhenius-plot slope and the actual activation-barrier difference is not any longer warranted. This conclusion is further corroborated by a comparison of the present results with those derived for the same reactions from reactant ion monitoring (RIM) "high-pressure" mass spectrometry at 0.5–1.2 Torr. The large discrepancy observed is interpreted as evidence that above 300 Torr the activation mechanism of the $CH_3ClCH_3^+$ methylation of arenes, a typical ion-molecule process, is essentially thermal and that, below this limit, coexistence of both thermal and electrostatic activation mechanisms as well as incomplete equilibration of the internal energy of the reactants make Arrhenius plots hardly a measure of the activation barriers involved in the gas-phase aromatic alkylations.

Ion–molecule reactions are normally investigated in the gas phase with different mass spectrometric methods, whose common feature is the low operating pressure (≤5 Torr). Under such conditions, the relevant kinetics are dominated by long-range ion–dipole attractive forces and found to fit Brauman's double-well energy surface model, involving an internal energy barrier E^*_0 at the transition state (curve a in Figure 1a).[1] Magnera and

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(1) (a) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 3715. (b) Farneth, W. E.; Brauman, J. I. *Ibid.* **1976**, *98*, 7891. (c) Jasinski, J. M.; Brauman, J. I. *Ibid.* **1980**, *102*, 2906.

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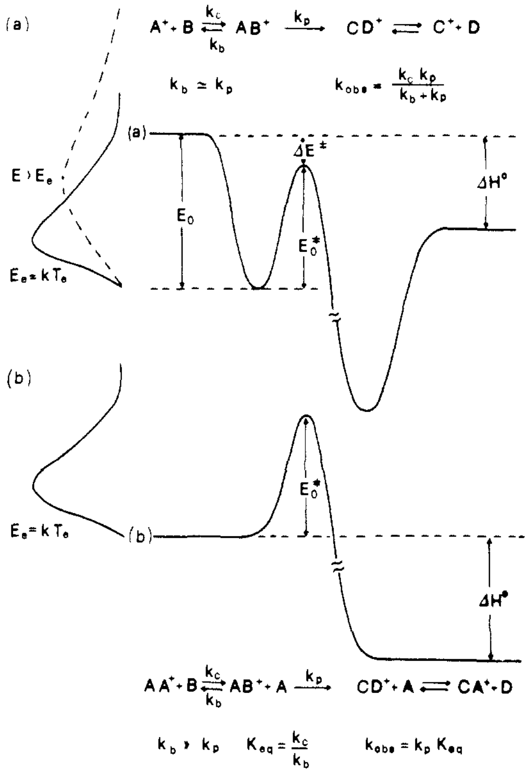

Figure 1. Change of potential energy along reaction coordinate for a typical gas-phase ion–molecule reaction of low collision efficiency governed by electrostatic activation (low pressure) (curve a) and by ordinary thermal activation (above high-pressure limit) (curve b).

Kebarle[2] have shown that, for gas-phase exothermic reactions of low collision efficiency, the energy E_0 developed in the preliminary electrostatic interaction between the ionic reactant A^+ and the substrate molecule B (Figure 1a) can overcome the intrinsic "chemical" activation barrier E^*_0 involved in the subsequent addition step by several kcalories per mol ($-\Delta E^* = 0$–10 kcal mol^{-1}). This energy gap, which can be considered as a *negative* "activation" energy for the ion–molecule reaction, is responsible for the experimentally observable *negative* temperature dependence of the relevant apparent rate constants (k_{obsd}) normally characterizing such processes, whose slope however cannot be taken as a measure of the *negative* "activation" barrier $-\Delta E^*$ and, therefore, of E^*_0.[3] It follows that an accurate analysis of the intrinsic "chemical" activation barrier E^*_0 of a gas-phase ion–molecule reaction is hardly allowed by the exclusive application of mass-spectrometric methodologies of investigation, necessarily operating under low-pressure conditions.

The situation is totally different if the ion–molecule reaction can be studied in unreactive bath gases at relatively high pressures (e.g. 760 Torr). In this case, the ionic reactant A^+ is thermalyzed by multiple collisions with the inert bath molecules A and eventually establishes electrostatic interactions with A to yield more or less organized electrostatic adducts (AA^+ in Figure 1b) *well before* the encounter with the substrate B. In this way, the encounter between A^+ and B takes place via a B-to-A molecule displacement in the AA^+ adduct, involving an energy balance drastically reduced with respect to E_0 and reflecting the stability difference between the AA^+ and AB^+ electrostatic adducts.[4] Moreover, the ion–substrate interaction is accompanied by fast thermal equilibration of the ensuing adduct AB^+ by extremely frequent collisions with the bath gas molecules A (collision frequency at room temperature $>10^{10}$ s^{-1}), so that its internal energy conforms rapidly to the thermal distribution ($E_e = kT_e$ of Figure 1a,b). It follows that, in a properly selected bath gas at sufficiently high pressure, gas-phase ion–molecule reactions are not any longer governed by electrostatic activation (curve a of Figure 1a) but conform to ordinary thermal kinetics (curve b of Figure 1b), much like classical processes in solution, wherein a temperature-dependence analysis of k_{obsd} allows direct measurement of E^*_0.

The above concepts recently have been embodied in a first experimental kinetic determination of the relative activation parameters of the gas-phase alkylation of benzene and toluene by $t\text{-}C_4H_9^+$ ions in isobutane at 720 Torr and in the temperature range 0–140 °C.[5] The relevant parameters ($\Delta E^*_0 = E^*_0$(benzene) $-$ E^*_0(toluene) $= 3.6 \pm 0.4$ kcal mol^{-1}; pre-exponential factor ratio: A(benzene)/A(toluene) ≈ 6) were obtained from regression analysis of the competition kinetic data falling on the *linear portion* of the corresponding Arrhenius plot (0–100 °C), which displays a marked deviation from linearity above 100 °C, owing to extensive back-dissociation of the $[t\text{-}C_4H_9\text{-benzene}]^+$ intermediates.

A similar high-pressure study, carried out in the range from 50 to 760 Torr, is reported in this paper aimed at determining the substrate selectivity of the classical aromatic methylation reaction 1 over an extended temperature range (40–140 °C). The choice of the $CH_3ClCH_3^+$ ion as the gaseous methylating electrophile has been suggested by the fact that it can be conveniently formed as the predominant stable species in the γ-radiolysis of CH_3Cl gas.[6] Its addition to a variety of substrates, including arenes, is an unusually well characterized reaction, as a result of extensive radiolytic and mass spectrometric studies, which have provided inter alia crucial mechanistic[6] and equilibrium data.[3] In addition, reaction 1 has been kinetically examined in the range 75–250 °C at pressures below 4 Torr by mass-spectrometric approaches[3,7] and a comparative analysis of the relevant activation parameters measured under these conditions with those from the present study would be of particular interest in view of the above considerations. In this perspective, the investigation has been restricted to a single pair of competing arenes, i.e., mesitylene (M) and *p*-xylene (X), on account of (i) their adequate reactivity toward $CH_3ClCH_3^+$ above room temperature,[6e,f,7a] (ii) the formation of a single methylation product, i.e., isodurene from M and 1,2,4-trimethylbenzene from X, and (iii) their very similar capture cross section by $CH_3ClCH_3^+$ in the gas phase (k_c in eq 1), due to the absence of a permanent dipole moment in both substrates and to their similar polarizability. The same factors account for the comparable stability of the ensuing electrostatic adduct (K_{eq} in Figure 1b).[4]

$$CH_3ClCH_3^+ + \text{arene} \underset{k_b}{\overset{k_c}{\rightleftharpoons}} [\text{arene-}CH_3ClCH_3]^+ \xrightarrow{k_p} \text{arene-}CH_3^+ + CH_3Cl \quad (1)$$

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[2] Magnera, T. F.; Kebarle, P. In *Ionic Processes in the Gas Phase*; Almoster Ferreira, M., Ed.; D. Reidel Publishers: Doderecht, Holland, 1984; NATO ASI Series. It should be pointed out that reaction inefficiency and negative temperature dependence can occur in the absence of a large internal energy barrier E^*_0 as well, if loss of external rotations of the collision partners in the first electrostatic adduct (locked rotors) occurs at a position where $-\Delta E^*$ is small. This case normally occurs when the electrostatic adduct is very weakly bonded. It should also be pointed out that, at low pressures, the E_0 term may include some contribution from the excitation energy of A^+, due to the exothermicity of its formation process.

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[4] As an example, $E_0 \approx 12$ kcal mol^{-1} in the formation of the "loose" electrostatic adduct between $CH_3ClCH_3^+$ and toluene, and ≈ 6 kcal mol^{-1} in the $[CH_3ClCH_3 - ClCH_3]^+$ association, cf. ref 3a and 6d, respectively. The association energies between $CH_3ClCH_3^+$ and the apolar mesitylene and *p*-xylene molecules are estimated to be comparable to that measured for the $CH_3ClCH_3^+/CH_3Cl$ pair, cf: Ausloos, P.; Lias, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 3641.

[5] Cacace, F.; Ciranni, G. *J. Am. Chem. Soc.* **1986**, *108*, 887.

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[7] (a) Stone, J. A.; Lin, M. S.; Varah, J. *Can. J. Chem.* **1981**, *59*, 2412. (b) Stone, J. A.; Splinter, W. M.; Splinter, D. E. *Ibid.* **1984**, *62*, 1373.

The present investigation has many purposes. In the first place, it represents the first attempt to demonstrate a bona-fide linear k_{obsd} vs T Arrhenius correlation for a gas-phase irreversible ionic reaction operative in an extended T range and in a high-pressure (50–760 Torr) domain, which is hardly accessible to conventional mass-spectrometric approaches. Secondly, from a kinetic analysis of reaction 1 as a function of the pressure of the gaseous system at a given temperature, we hoped to gain insight into the pressure domains where either electrostatic or thermal activation of reaction 1 prevail and the pressure limit whereat the two activation mechanisms coexist. Thirdly, recognition of this pressure limit enables us to evaluate critically the activation parameters of process 1 measured at largely different pressures.[7] The final impetus for the present work arises from the expectation that reliable gas-phase kinetic data can shed light onto the potential energy profile of the aromatic alkylation reaction 1 and can represent the only means for discriminating the intrinsic structural factors governing a typical electrophilic aromatic substitution, such as eq 1, from complicating factors, i.e., solvation, ion-pairing, catalysis, etc., normally affecting related processes in the condensed phase.

Experimental Section

Materials. Methyl chloride, oxygen, and trimethylamine were high-purity gases from Matheson Gas Products Inc. and were used without further purification. The substrates, i.e., mesitylene and *p*-xylene, were gas chromatographic standards from C. Erba Co. The same source provided the chemicals used for reference purposes in the gas chromatographic analyses. The purity of the starting substrates, with special regard to the absence of their methylated derivatives, was checked by analytical gas chromatography on the same columns employed for the analysis of the irradiated mixtures.

Procedure. The samples were prepared by introducing fragile ampules, containing weighed amounts of mesitylene/*p*-xylene mixtures of known composition, into 85-mL Pyrex bulbs, equipped with a break-seal arm, and connected to a greaseless vacuum line. Following the introduction of the gaseous components (methyl chloride, oxygen, and trimethylamine) at the desired partial pressures into the carefully evacuated and outgassed vessels, the latter were then allowed to come to room temperature, the fragile ampules broken, and the gaseous components allowed to mix before being subjected to the irradiations. Typical composition of the irradiated systems follows: CH_3Cl, 760 Torr; O_2, 4 Torr; aromatic substrates, 0.2–0.5 Torr; [M]:[X] = 0.3–0.4; NMe_3, 1 Torr. The gaseous mixture was then preheated at the desired temperature before irradiation for ca. 1 h. Control GLC analysis of the preheated mixture excluded formation of undesired products from thermal reactions within the entire 40–140 °C range even after 24 h. Irradiations of the preheated mixtures were carried out in a ^{60}Co 220 Gammacell from Nuclear Canada Ltd., fitted with a thermostatic device designed to maintain the irradiated samples at any desired temperature (from 40 to 140 °C) with an accuracy of ca. ±3 °C. The total dose received by the samples was 3×10^4 Gy, at a dose rate of 1×10^4 Gy h^{-1}, as measured with a Fricke dosimeter. Control irradiations carried out at much higher doses (up to 1×10^5 Gy) showed no significant changes in the *relative* yields of products from the competition experiments.

Product Analysis. The analysis of the products was performed by injecting measured portions of the homogeneous reaction mixture into a Perkin-Elmer Model Sigma 1 gas chromatograph, equipped with a flame ionization detection unit. In order to prevent selective losses of the reaction products by adsorption on the glass of the reaction bulb (and to obtain reproducible and meaningful reaction yields), the analysis was repeated after careful washing of the bulb walls with freshly purified cyclohexane. Satisfactory agreement between the results of the gaseous mixture and the cyclohexane solution analysis was found in all runs. The products were identified by comparison of their retention volumes with those of authentic standard compounds on a 15-m long, 0.53-mm i.d. capillary Superox column, operating at temperatures ranging from 50 to 75 °C (1 deg min^{-1}). The identity of the products was further confirmed by GLC/MS, using a Model 5982 A Hewlett-Packard quadrupole spectrometer. The yields of the products were measured, using the internal standard method and individual calibration factors to correct for the detector response.

Results

Methylation of mesitylene (M) and *p*-xylene (X) by radiolytically formed $CH_3ClCH_3^+$ ions in CH_3Cl at 40–140 °C within the 50–760 Torr pressure range is found to yield isodurene and 1,2,4-trimethylbenzene, respectively, without detectable traces of any other conceivable product. In fact, blank runs, carried out under the same conditions of the competition experiments with either M or X as single substrate, excluded formation of 1,2,4-trimethylbenzene and *p*-xylene from M and of mesitylene and isodurene from X. The absolute yields of the products, measured by their G values, i.e., by the number of molecules of product formed per 100 eV of energy absorbed by the gaseous mixture, depend upon the composition of the mixture and on the total dose, both effects being easily rationalized in terms of a competition of the $CH_3ClCH_3^+$ ions between the arenes and other nucleophiles, either initially present in the system, i.e., NMe_3, or formed during its radiolysis, e.g., CH_2Cl_2, MeOH, etc. Under the conditions prevailing in this work, where the mole fraction of arenes was kept below 6×10^{-4}, methylated aromatics are formed with typical G values around 0.5–1.0. These values correspond to an absolute yield of ca. 12–25%, based on the total number of $CH_3ClCH_3^+$ ions formed in the irradiation, taken equal to the dimethyl ether molecules produced when the ions are trapped by methanol.[6e]

Concerning the ionic character of the processes responsible for the formation of the methylated products, the occurrence of thermal processes in the heated gaseous mixtures has already been excluded by the results of control experiments involving no γ-irradiation. Furthermore, in order to eliminate radical pathways, the irradiations were invariably carried out in the presence of an effective thermal radical scavenger (O_2, 5×10^{-3} mol %) at concentrations considerably higher than those of the arenes (<6 × 10^{-4} mol %). Additional evidence is provided by the dramatic decrease (over 90%) of the yields caused by a tenfold addition of NMe_3 (ca. 1×10^{-2} mol %), acting as a powerful interceptor of $CH_3ClCH_3^+$.[6g]

On the basis of these considerations, and of earlier results,[6e,f] the reaction pathways operative in the competition experiments can be outlined as follows:

$$\underset{(M)}{1,3,5\text{-}C_6H_3(CH_3)_3} + CH_3ClCH_3^+ \xrightarrow{k_M} \underset{(MMe^+)}{\left[C_6H_3(CH_3)_4^+\right]} \xrightarrow[\substack{+N \\ -NH^+}]{k_N} \underset{(MMe)}{1,2,3,5\text{-}C_6H_2(CH_3)_4} \qquad (2)$$

$$\underset{(X)}{1,4\text{-}C_6H_4(CH_3)_2} + CH_3ClCH_3^+ \xrightarrow{k_X} \underset{(XMe^+)}{\left[C_6H_4(CH_3)_3^+\right]} \xrightarrow[\substack{+N \\ -NH^+}]{k_N} \underset{(XMe)}{1,2,4\text{-}C_6H_3(CH_3)_3} \qquad (3)$$

where, at high pressures, phenomenological k_M and k_X are conveniently expressed by the corresponding k_pK_{eq} factors of Figure 1b, and N represents a gaseous base (e.g., NMe_3).[8] Reactions 2 and 3 are totally independent methylation channels. In fact, control experiments carried out by varying the [M]:[X] ratio by two orders of magnitude (from ca. 10 to ca. 0.1), or by adding an appreciable amount of a gaseous base (NMe_3, 5×10^{-3} mol %) to the irradiated mixture, have shown no significant change in the relative yields of methylated products (i.e., MMe and XMe), thus excluding occurrence of undesired intermolecular methyl group transfers between the methylated intermediate MMe^+ (or XMe^+) and the competing neutral X (or M).

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(8) In the presence of added bases, such as NMe_3, whose proton affinity (PA = 225.1 kcal mol^{-1}) exceeds those of isodurene (PA = 203.2 kcal mol^{-1}) and 1,2,4-trimethylbenzene (PA ≈ 197 kcal mol^{-1}), rapid neutralization of the corresponding methylated intermediates MMe^+ and XMe^+ is ensured. The PA value of NMe_3 was taken from Lias et al. [Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695], that of isodurene from Stone et al. [Stone, J. A.; Li, X.; Turner, P. A. *Can. J. Chem.* **1986**, *64*, 2021], while the PA of 1,2,4-trimethylbenzene was estimated from the PAs of mesitylene and *p*-xylene, by using the group additivity rules (Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976).

(9) The reaction between CH_3ClH^+ and CH_3Cl to give $CH_3ClCH_3^+$ and HCl shows a slight negative dependence of the temperature by decreasing from ca. 6×10^{-10} cm^3 $molecule^{-1}$ s^{-1} at 25 °C to ca. 2×10^{-10} cm^3 $molecule^{-1}$ s^{-1} at 150 °C; cf: Sen Sharma, D. K.; Kebarle, P. *J. Am. Chem. Soc.* **1978**, *100*, 5826. A similar behavior has been observed for the formation of $CH_3ClCH_3^+$ (and CH_2Cl_2) from $CH_3ClCH_2Cl^+$ (and CH_3Cl), whose rate however never exceeds 10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 170 °C and 0.9 Torr; cf. ref 7b.

(10) In principle, the slightly different mass and polarizability of M and X lead to the corresponding electrostatic adducts with $CH_3ClCH_3^+$ with different electrostatic energy E_0^M and E_0^X. Under the same low-pressure conditions, partial collisional deactivation may leave the electrostatic adducts with a different residual excitation energy E_r^M and E_r^X, since starting from different levels of initial electrostatic interaction energies, and involving excited adducts with different molecular complexity.

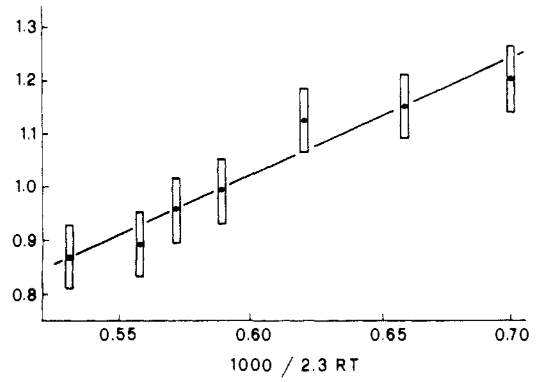

Figure 2. Temperature dependence of the k_M/k_X ratio in the gas-phase alkylation of mesitylene and *p*-xylene by Me_2Cl^+ ions in MeCl at 760 Torr.

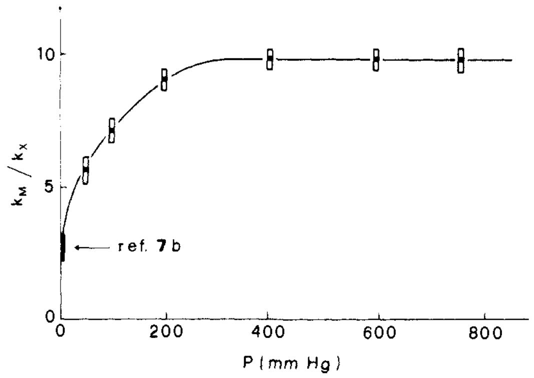

Figure 3. Pressure dependence of the k_M/k_X ratio in the gas-phase alkylation of mesitylene and *p*-xylene by Me_2Cl^+ ions in MeCl at 100 °C.

Accordingly, application of the steady-state approximation to the independent methylation channels 2 and 3 provided the $k_M/k_X = [NMe][X]/[XMe][M]$ equation, used for estimating the k_M/k_X ratio from the relative yield of the methylated products.

The results of the competition kinetics carried out at 760 Torr are reported in Figure 2. They demonstrate the appreciable substrate selectivity of $CH_3ClCH_3^+$ toward the competing aromatics, whose apparent k_M/k_X ratios range from 16.0 (40 °C) to 7.4 (140 °C). The relevant Arrhenius plot is characterized by an acceptable linear trend (correlation coefficient $r = 0.967$) over the entire temperature interval investigated (40–140 °C). Figure 3 reports the phenomenological k_M/k_X ratios, measured at 100 °C, as a function of the partial pressure of the CH_3Cl bath gas, the relative proportions of the other gaseous additives being kept constant. The k_M/k_X values, measured from the radiolytic experiments, invariably exceed that estimated, at the same temperature, at low pressure (0.5–1.2 Torr) from mass spectrometric kinetic measurements ($k_M/k_X \approx 2.8$)[7b] and increase with the CH_3Cl pressure (5.7 at 50 Torr; 7.1 at 100 Torr; 9.0 at 200 Torr) to reach the constant value of 9.8 above 300 Torr.

Discussion

In discussing the results summarized in the previous section, the question arises as to whether the observed relative reactivity trends reflect indeed the temperature and pressure dependence of the electrophilic methylation reactions 2 and 3 rather than of other steps of the reaction sequences which eventually lead to the neutral methylated products. In fact, temperature and pressure changes may in principle affect the processes responsible for the formation of the ionic methylating reactant as well as the final deprotonation step (k_N). The latter possibility has been ruled out by carrying out the methylation at a given temperature (60 and 100 °C) and pressure (50 and 760 Torr) with variable concentrations of NMe_3 (2 to 6 × 10^{-3} mol %). The large gas-phase basicity of the added NMe_3 (P.A. = 225.1 kcal mol^{-1}) with respect to that of the methylated products[8] ensures fast deprotonation of MMe^+ and XMe^+ with a corresponding k_N close to the collision limit. No significant changes of the apparent k_M/k_X ratios with the NMe_3 concentration could be detected, showing the substantial insensitivity of the deprotonation rate constants k_N with pressure and temperature.

Any conceivable effects of temperature and pressure upon the formation process of the methylating reactant $CH_3ClCH_3^+$ could be safely ruled out on the following grounds. Energetic electrons, released from interaction of γ-rays with the glass walls of the reaction vessel, collide with the CH_3Cl bath gas, inducing formation of the CH_3Cl^+, CH_2Cl^+, and CH_3^+ primary ions. Further collisions of these primary species with CH_3Cl initiate a well-documented ionic reaction pattern,[6] yielding rapidly CH_3ClH^+ and $CH_3ClCH_2Cl^+$ as intermediate precursors of $CH_3ClCH_3^+$, i.e., the final stable methylating reactant.[7] The available kinetic data show that the negative temperature dependence of several such processes, in particular the comparatively less efficient final steps of the ion pattern leading to $CH_3ClCH_3^+$,[9] is by far too low to cause detectable kinetic effects in the temperature range of interest. Their efficiency is nevertheless high enough to yield $CH_3ClCH_3^+$ as the unique stable ion after only a few collisions with CH_3Cl.[6,7] On these grounds, it can be concluded that the same steady-state concentration of $CH_3ClCH_3^+$ is formed before collision with the aromatic substrates in the present high-pressure radiolytic experiments, irrespective of the pressure and the temperature of the gaseous mixture.

In conclusion, the available evidence suggests that the observed temperature and pressure dependence of the apparent k_M/k_X ratio (Figures 2 and 3, respectively) can indeed be traced to the methylation step of the competing independent sequences 2 and 3.

In view of the pronounced exothermicities involved in the methylation steps of sequences 2 and 3 ($-\Delta H°(2) = 49$ kcal mol^{-1}; $-\Delta H°(3) = 33$ kcal mol^{-1}),[7b] and of the rapid thermal equilibration of the ensuing adducts, conceivable back-dissociation of MMe^+ and XMe^+ is highly unfavored within the entire temperature and pressure ranges investigated. This is reflected in the satisfactory linearity of the Arrhenius plot of Figure 2 all over the temperature interval studied (40–140 °C). To our knowledge, this result represents the first example of a fully linear "well-behaved" Arrhenius plot, allowing evaluation of relative activation parameters for a typical aromatic substitution of gaseous ions at atmospheric pressure and in an extended temperature range (40–140 °C), which is hardly approached in the temperature-dependence kinetic analysis of most conventional aromatic substitutions in solution.

Regression analysis of the data of Figure 2 leads to a difference in empirical activation energies E^*_0 for the methylation steps of sequences 2 and 3 equal to $\Delta E^*_0 = E^*_0(X) - E^*_0(M) = 2.2 \pm 0.2$ kcal mol^{-1}, and to a rough estimate of the pre-exponential factor ratio $A_X/A_M \approx 2$. It is noteworthy that these values compare well with the corresponding ones measured in the high-pressure study of $t\text{-}C_4H_9^+$ ion attack on aromatics.[5] Furthermore, the $A_X/A_M \approx 2$ ratio, measured from the Arrhenius plot, is surprisingly close to that expected exclusively on a statistical basis (=1.3). On the contrary, the relative activation parameters measured in the present experiments find no correspondence with those derived from reactant ion monitoring (RIM) "high-pressure" mass spectrometry (reactant gases: $[CH_3Cl]:[He] = 0.1\text{–}1.0$ at $P = 0.5\text{–}1.2$ Torr) at 75–230 °C.[7] The large discrepancy between the present kinetic results and those estimated from RIM competition experiments ($k_M/k_X \approx 2.5$ at 78 °C; $\Delta E^*_0 = E^*_0(X) - E^*_0(M) \approx 0.6$ kcal mol^{-1}; $A_X/A_M \approx 0.8$) raises the problem of how closely the empirically measured ΔE^*_0 value corresponds to the difference between the internal activation energies E^*_0 concerning the competing processes. In fact, long-range ion–molecule interactions are known to cause the formation of "loose" ionic adducts, activated by the electrostatic energy E_0, released in the process (Figure 1a). When collisional deactivation is inefficient, as presumably in the low-pressure RIM source ($CH_3Cl/He = 0.5\text{–}1.2$ Torr), the internal energy E distribution of the ionic adducts (Figure 1a) may be significantly different from the thermal distribution $E_e = kT_e$ (Figure 1a,b). As a consequence, the ionic adducts may possess a residual temperature-dependent excitation energy $E_r = E - E_e$, which may be slightly different for the different electrostatic adducts between $CH_3ClCH_3^+$ and M ($=E_r^M$) or X ($=E_r^X$).[10] Moreover, the empirical k_{obsd} is better expressed by the $k_ck_p/(k_b + k_p)$ term of Figure 1a, rather than by the k_pK_{eq} term of Figure 1b, valid for thermally activated reactions involving a fast pre-equilibrium step. In this connection, the apparent k_M/k_X ratios and their temperature-dependence trend have no relationship with the relative height of the internal "chemical" activation energies $E^{\ddagger}_0$, since reflecting instead the interplay between the $|E^{\ddagger}_0 - E_r|$ and $|E_0 - E_r|$ energy gaps for any given electrostatic adduct, and their sensitivity to temperature.

This is reflected in empirical k_M/k_X ratios and the corresponding $\Delta E^{\ddagger}_0$ values, which are significantly lower than those measured under high-pressure conditions, where collision frequency is high, the reaction is thermally activated, and the temperature-dependence trend of k_{obsd} reflects the actual "chemical" activation energies $E^{\ddagger}_0$. This conclusion is corroborated by the k_M/k_X ratios, measured at 100 °C, as a function of the total pressure of the irradiated system (Figure 3). The monotonic increase of the apparent k_M/k_X values with the pressure from ca. 2.8, measured under low-pressure conditions (0.5–1.2 Torr),[7b] to a constant value of 9.8 above 300 Torr, is explained by the transition from an electrostatically activated to a thermally activated methylation reaction 1, with the latter regime prevailing above 300 Torr. Above this limit, the empirical quantity $\Delta E^{\ddagger}_0$ from the Arrhenius plot of Figure 2 represents a reasonably accurate estimate of the actual $E^{\ddagger}_0(X) - E^{\ddagger}_0(M)$ difference. Below this limit, this correspondence is not any longer warranted, raising the phenomenological $\Delta E^{\ddagger}_0$ quantity from the interplay of several kinetic factors, linked not only to the specific potential energy profile governing the reaction under those conditions (curve a vs curve b of Figure 1a,b) but also to the hardly predictable residual internal energy distribution E_r of the ionic species 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 and of its dependence upon the reaction temperature, in view of the drastic transition from electrostatic to thermal activation for ionic processes in the gas phase. Attainment of thermal activation in gas-phase ion–molecule reactions serves one of the major purposes of this field, namely to provide generalized and simplified models for related ionic processes in condensed media, which after all are themselves driven by thermal activation mechanisms.

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Registry No. $CH_3ClCH_3^+$, 24400-15-5; CH_3Cl, 74-87-3; mesitylene, 108-67-8; *p*-xylene, 106-42-3.

Gas-Phase Acid-Induced Nucleophilic Displacement Reactions. 7.[1] Structural and Stereochemical Evidence for the Existence and the Relative Stability of Alkylenebenzenium Ions in the Gas Phase

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Abstract: A comprehensive investigation on the existence and the relative stability of gaseous 2,3-butylene- and 1,2-propylenebenzenium ions was carried out by establishing the structural features and the stereochemistry of acid-induced displacement by CH_3OH on isomeric 3-phenylbutyl-2 onium and β-phenylpropyl onium intermediates. The latter were obtained in the gas phase from the reaction of radiolytically formed GA^+ ($GA^+ = D_3^+$, $C_nH_5^+$ ($n = 1, 2$), $i\text{-}C_3H_7^+$, and $CH_3FCH_3^+$) acids with isomeric 3-phenyl-2-chlorobutanes and β-phenyl-Y-propanes (Y = Cl, OH). The analysis of the isomeric distribution of the neutral substitution products allows the establishment of extensive phenyl-group participation in the displacement process, occurring in competition with methyl and hydrogen 1,2-transfers. The participating ability of a phenyl moiety adjacent to the substitution center is found to depend essentially upon the configuration of the precursor and to be related to its gas-phase nucleophilicity. The occurrence of relatively stable cyclic alkylenebenzenium ions as static intermediates in these displacement reactions is suggested by the particular isomeric and stereoisomeric distribution of the products and by its comparison with that obtained from open-chain isomeric ions. The results obtained from the present gas-phase experiments are discussed in the light of those from related gas-phase and solution studies.

The involvement of an aromatic ring leading to a bridged benzenium ion in the solvolysis of β-arylalkyl systems has been a matter of intense investigation and lively debate in the last decades.[3] The original proposal by Cram[4] that the intermediates in these reactions were π-bridged alkylenebenzenium ions **9** (eq 1) was criticized by Brown,[5] who suggested that the experimental data could alternatively be rationalized in terms of weakly π-bridged, rapidly equilibrating ions. Further solvolytic studies led to the conclusion that a continuous spectrum of species exists, from open to completely bridged ions, depending upon solvent and substitution in the ion.[6] Environmental factors intervene as well in the sensitive balance between aryl-assisted and solvent-assisted

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