

conversion) was 60%.

41:  $^1\text{H}$  NMR (60 °C) 7.01 (d, 1 H,  $J = 8.4$  Hz), 6.7–6.5 (m, 1 H), overlapped by 6.67 (dd, 1 H,  $J = 8.4, 1.8$  Hz), 4.11 (q, 2 H,  $J = 7.2$  Hz), 3.7–3.55 (m, 2 H), 3.41 (t, 2 H,  $J = 7.8$  Hz), 3.3–3.15 (m, 2 H), 2.79 (t, 2 H,  $J = 7.8$  Hz) overlapped by 2.72 (s, 2 H), 2.1–1.7 (m, 4 H), 1.27 (t, 3 H,  $J = 7.2$  Hz), 0.07 (s, 9 H); IR (film) 3200, 1670, 1600, 1570; CIMS  $m/z$  (relative intensity) 393 ( $\text{M}^+ + 1$ , 100), 294 (10);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 170 (e), 157 (e), 156 (e), 147 (o), 137 (e), 129 (e), 127 (o), 117 (o), 113 (o), 61 (e), 51 (e), 50 (e), 45 (e), 26 (e, 2 carbons), 24 (e), 14 (o), -2 (o, 3 carbons). Anal. Calcd for  $\text{C}_{20}\text{H}_{32}\text{N}_2\text{O}_4\text{Si}$ : C, 61.19; H, 8.22. Found: C, 61.18; H, 8.25.

42:  $^1\text{H}$  NMR 1.23 (rotamer A) and 1.26 (rotamer B) (t,  $J = 6.9$  Hz, 3 H,  $\text{OCH}_2\text{CH}_3$ ), 1.72–1.94 (m, 5 H,  $\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2$  and H-4), 2.07–2.11 (m, 1 H, H-4), 2.37–2.44 (m, 1 H, H-8), 2.64 (dd,  $J = 17.7, 4.8$  Hz, 1 H, H-8), 2.86–2.90 (m, 1 H, H-8a), 3.33–3.45 (m, 1 H, H-1), 3.46–33.52 (m, 6 H,  $\text{CH}_2\text{NCH}_2$  and H-3), 3.77–3.81 (m, 1 H, H-1), 4.06–4.14 (m, 2 H,  $\text{OCH}_2\text{CH}_3$ ), 6.09 (d,  $J = 10.1$  Hz, 1 H, H-6), 6.78 (d,  $J = 10.1$  Hz, 1 H, H-5);  $^{13}\text{C}$  NMR 14.6 ( $\text{OCH}_2\text{CH}_3$ ), 23.1, 27.0, 31.6, 38.7, 44.1, 44.7, 47.7, and 48.2 ( $\text{CH}_2$  peaks), 36.0 (C-8a), 47.3 (C-4a), 61.5 ( $\text{OCH}_2\text{CH}_3$ ), 129.5 (C-6), 150.1 (C-5), 155.7 (carbamate C=O), 170.0 (amide C=O), 198.0 (enone C=O); IR 2974, 2874, 1694, 1627, 1453, 1344, 1243, 1141  $\text{cm}^{-1}$ ; EIMS  $m/e$  (rel intensity) 320 ( $\text{M}^+$ , 28), 222 (34), 205 (22), 192 (100), 129 (33), 121 (14); HRMS (EI)  $m/e$  320.1757 ( $\text{M}^+$ ,  $\text{C}_{17}\text{H}_{24}\text{O}_4\text{N}_2$  requires 320.1736).

**Preparation of Maleate and Fumarate Derivatives 33 and 35.** A solution of maleic anhydride (0.91 g, 9.2 mmol) in MeOH (20 mL) was stirred at reflux for 1 h, cooled, and concentrated in vacuo to give an oil. To a solution of the oil in benzene (20 mL) was added thionyl chloride (1.0 mL, 13.6 mmol). The mixture was stirred at reflux for 2 h, cooled, and concentrated in vacuo to give the acid chloride 34.<sup>19</sup> To a solution of the acid chloride 34 in  $\text{CH}_2\text{Cl}_2$  (20 mL) was added  $\text{Et}_3\text{N}$  (2.3 mL, 17 mmol) and

*N*-benzyl-*N*-(trimethylsilyl)methylamine (20) (3.0 g, 15 mmol). The reaction mixture was stirred at 25 °C for 1 h, washed with aqueous  $\text{NaHCO}_3$  and brine, dried, and concentrated in vacuo. The residue was subjected to preparative TLC (silica gel, EtOAc:hexane = 1:6) to give a 1:1 mixture of the maleate 33 and fumarate 34 isomers (33% overall).

35: (rotamer A:B = 0.75:0.25)  $^1\text{H}$  NMR 0.04 (rotamer A) and 0.07 (rotamer B) (s, 9 H,  $\text{SiMe}_3$ ), 2.88 (rotamer B) and 2.92 (rotamer A) (s, 2 H,  $\text{NCH}_2\text{Si}$ ), 3.73 (rotamer A) and 3.77 (rotamer B) (s, 3 H,  $\text{CO}_2\text{CH}_3$ ), 4.57 (rotamer A) and 4.64 (rotamer B) (s, 2 H,  $\text{NCH}_2\text{Ph}$ ), 6.82 (rotamer A) and 6.88 (rotamer B) (d,  $J = 15.2$  Hz, 1 H,  $\text{CHCO}_2$ ), 7.11–7.35 (m, 5 H, ArH), 7.41 (rotamer B) and 7.42 (rotamer A) (d,  $J = 15.2$  Hz, 1 H,  $\text{CHC=O}$ );  $^{13}\text{C}$  NMR -1.6 (rotamer B) and -1.2 (rotamer A) ( $\text{SiMe}_3$ ), 38.7 (rotamer B) and 39.1 (rotamer A) ( $\text{NCH}_2\text{Si}$ ), 52.0 (rotamer A) and 52.1 (rotamer B) ( $\text{CO}_2\text{CH}_3$ ), 50.9 (rotamer B) and 53.6 (rotamer A) ( $\text{NCH}_2\text{Ph}$ ), 126.6, 127.6, 127.9, 128.0, 128.6, 128.9 (rotamer A and B) (aromatic para, ortho, meta), 130.7 (rotamer A) and 131.0 (rotamer B) ( $\text{CHCO}_2$ ), 133.8 (rotamer A) and 134.1 (rotamer B) ( $\text{CHC=O}$ ), 136.0 (rotamer A) and 136.6 (rotamer B) (ipso), 163.9 (rotamer A) and 164.0 (rotamer B) (amide C=O), 166.2 (ester C=O); IR 3031, 2952, 1726, 1649, 1621, 1440, 1400, 1294, 1249, 1166, 854  $\text{cm}^{-1}$ ; EIMS  $m/e$  (rel intensity) 305 ( $\text{M}^+$ , 2), 290 (3), 274 (5), 246 (7), 214 (4), 91 (100); HRMS (EI)  $m/e$  305.1446 ( $\text{M}^+$ ,  $\text{C}_{18}\text{H}_{23}\text{NO}_3\text{Si}$  requires 305.1447).

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**Supplementary Material Available:** Procedures for the preparation and spectroscopic data for intermediates in the syntheses of the 2,5-cyclohexadienones used in this study and  $^1\text{H}$  NMR spectra for all compounds listed in the Experimental Section (44 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.

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## Reactions of Positively Charged Chlorine Species in the Gas Phase

Carol A. Haney,<sup>†</sup> Suzanne T. Purrington,<sup>\*†</sup> Halbert H. Carmichael,<sup>†</sup> and Robert D. Voyksner<sup>†</sup>

Department of Chemistry, North Carolina State University, P.O. Box 8204, Raleigh, North Carolina 27695-8204, and Analytical and Chemical Sciences, Research Triangle Institute, P.O. Box 12194, Research Triangle Park, North Carolina 27709

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The mechanism of chlorine addition to aromatic compounds in the gas phase is probed using an ion trap mass spectrometer (ITMS). Chloronium ion ( $\text{Cl}^+$ ) and chlorine radical cation ( $\text{Cl}_2^{+\bullet}$ ) are formed and trapped in the mass spectrometer and then reacted with a variety of aromatic compounds. The data are consistent with a two-step mechanism involving formation of a radical cation of the aromatic compound through single-electron transfer (SET) to  $\text{Cl}^+$  followed by quenching of the resulting radical cation by neutral chlorine. Although  $\text{Cl}_2^{+\bullet}$  reacts with aromatic compounds through SET, the aromatic cation formed gives the chlorine addition product with only two of the compounds studied. Formation of the chlorine addition product with aromatic compounds can be qualitatively related to the thermodynamics of the reaction and the stability of the aromatic cation radical. There appears to be a similarity between chlorine addition in the gas phase and the intermediate formed in electrophilic aromatic substitution. The structure of the chlorine addition product is probed using MS/MS and by studying the reaction of the chlorine addition in the presence of pyridine. The results suggest that the chlorine addition product is a  $\sigma$ -complex.

### Introduction

Electrophilic aromatic halogenation reactions have been well studied in solution.<sup>1,2</sup> Mechanistically, they have been shown to proceed by a  $\pi$ -complex, a  $\sigma$ -complex (cyclohexadienyl carbocation), or single-electron transfer (SET)

depending on the experimental conditions. In this study, we prepared chlorine electrophiles in the gas phase and have investigated their reaction with aromatic compounds. The ion that is formed is compared with that which results

<sup>†</sup>North Carolina State University.

<sup>\*</sup>Research Triangle Institute.

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during classic electrophilic aromatic chlorinations.

Recent advances in ion trap mass spectrometry make it possible to select ions of a specific mass to charge ratio ( $m/z$ ), react these ions with neutral molecules, and follow the abundance of charged species with time.<sup>3,4</sup> Chlorine has two abundant isotopes in nature, of which only ions containing  $^{35}\text{Cl}$  were trapped in our experiment. Specifically, it is possible to generate both chloronium,  $^{35}\text{Cl}^+$ , and chlorine radical cation,  $^{35}\text{Cl}_2^{+\bullet}$ , and selectively trap ions at  $m/z$  35 or  $m/z$  70, respectively. Using this technique we have probed the mechanism of chlorine addition to aromatic compounds in the gas phase and investigated the potential for  $^{35}\text{Cl}^+$  and  $^{35}\text{Cl}_2^{+\bullet}$  to undergo electrophilic aromatic substitution in the gas phase.

### Experimental Section

The data were acquired on a Finnigan-MAT ion trap mass spectrometer, ITMS (San Jose, CA). Instrument design and operation of ion selection are thoroughly discussed elsewhere.<sup>5-11</sup> A mixture of 3% chlorine in helium (Matheson, Sunnyvale, CA) was introduced via a pulsed gas introduction valve (IOTA ONE, General Valve Co., Fairfield, NJ). When chlorine was continuously introduced into the ITMS, charge exchange to residual chlorine from chloronium competes with the reaction of the aromatic compounds. The pulsed gas introduction of chlorine was optimized for the formation of  $^{35}\text{Cl}^+$  ( $m/z$  35), and a 160- $\mu\text{s}$  valve opening was used for all experiments. By using the pulsed valve the concentration of residual chlorine after ionization is greatly diminished, reducing its interference in the reaction between chloronium ion and aromatic compound. The aromatic compounds, obtained from Aldrich, were introduced continuously into the ITMS through a controlled leak valve at an optimized uncalibrated gauge pressure reading of  $1.8 \times 10^{-6}$  Torr. Helium was introduced through a second leak valve such that the total pressure reading was  $1.2 \times 10^{-5}$  Torr. The pressures reported are directly from ion gauge readings. The helium pressure reading can be adjusted to give an estimated time between collisions on the other 0.1 ms.<sup>4</sup> This assures multiple collisions and the opportunity to follow the course of the ion-molecule reactions. The helium buffer gas has been shown to increase instrument performance (sensitivity) by collapsing the ion beam toward the center of the trap, reducing the spread of ions. In the ion trap, additional energy may be lost through collision with the helium buffer gas. The total ion current was found to decrease with time on the order of 10–25% during the 100-ms reaction.

The scan function for reaction of chloronium ion with the aromatic compound involved ionization, ion isolation, reaction time, and product mass spectrum generation. The start triggered the sequence beginning with the 160- $\mu\text{s}$  pulse of chlorine gas into the trap followed by a 29-ms ionization pulse. Standard 70-eV electron ionization was used. After a 1.1-ms settling time, the chloronium ion ( $m/z$  35) was isolated by ramping the rf voltage and then applying a dc voltage, followed by ramping the rf and dc voltages back to their initial settings so that all ions formed by reaction of the isolated ions and neutral molecules are stored. Isolation of the single mass to charge ion took 3.2 ms. The same procedure was used for the generation of chlorine radical cations,  $^{35}\text{Cl}_2^{+\bullet}$ , and aromatic cation radical reactants. Mass spectra were

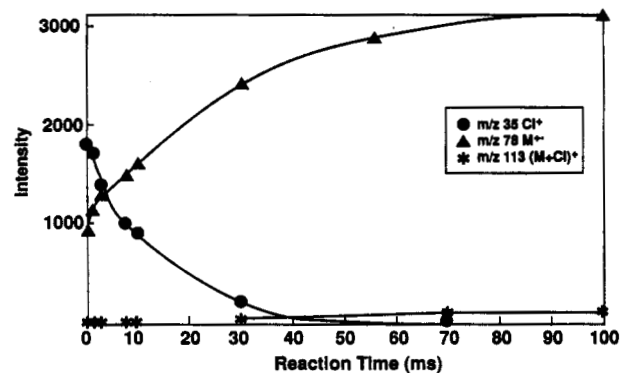


Figure 1. Reaction of  $\text{Cl}^+$  with benzene.

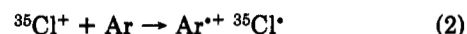
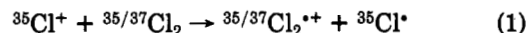
generated at several points within 0–500 ms after isolation. For a “zero time” reaction, the multiplier was activated and the rf scan was initiated as soon as the isolation sequence was complete and represents approximately 3–5-ms elapsed time. The source temperature was maintained at 60 °C for all experiments. Data were collected using various combinations of aromatic reactant pressures and helium buffer gas pressures.

MS/MS experiments were performed by trapping an ion of selected mass to charge ratio as described above and then applying a short (30-ms) low-voltage rf (0.5–2.0-V) pulse (tickle voltage, Vp-p) at the resonance frequency of the ion. This increases the kinetic energy of the mass selected ion causing the ion to undergo larger oscillations resulting in collisional activation by the buffer gas (helium) followed by dissociation of the parent ion. An rf scan yields the daughter ion spectrum.

For the reactions in the presence of base (pyridine), the chloronium ion is generated and isolated as described above. Benzene- $d_6$  was added through a controlled leak valve for an ion gauge reading of  $1.0 \times 10^{-6}$  Torr above background. Helium buffer gas pressure was  $2.0 \times 10^{-6}$  Torr based on the ion gauge reading. Chlorine gas was added through the pulsed gas valve. The reaction of  $^{35}\text{Cl}^+$  with neutral benzene- $d_6$  and pyridine was studied by collecting spectra after reaction times of 0, 30, 70, and 100 ms. The experiment was carried out at three different pressures of pyridine ( $1 \times 10^{-7}$  Torr,  $3 \times 10^{-7}$  Torr, and  $8 \times 10^{-7}$  Torr). In other experiments, ions corresponding to the chlorine addition product with benzene- $d_6$  were isolated as a range of ions ( $m/z$  117–123) to include both isomers of chlorine ( $m/z$  119–121). These ions were allowed to react with residual neutral benzene- $d_6$ ,  $\text{Cl}_2$ , and pyridine ( $8 \times 10^{-7}$  Torr). Spectra were recorded at times from 0 to 100 ms after isolation of the aromatic chlorine addition product. The experiment was repeated except that the ion corresponding to the benzene- $d_6$  cation radical formed via charge exchange ( $m/z$  84) was isolated instead of the chlorine addition products.

### Results and Discussion

The first objective was the generation, trapping, and storage of chloronium ions ( $^{35}\text{Cl}^+$ ) followed by the optimization of reaction conditions to form the chlorine addition product to the aromatic ring. Generation is easily achieved by electron ionization of the  $^{35}/^{37}\text{Cl}_2$  gas, followed by the selective trapping of the chloronium ion at  $m/z$  35. There is residual  $^{35}/^{37}\text{Cl}_2$  and aromatic substrate present since neutral molecules cannot be ejected by the ITMS. The trapped chloronium ions rapidly react with both neutral species by charge exchange. The two competing reactions for  $^{35}\text{Cl}^+$  are given in eqs 1 and 2.



The concentration of aromatic substrate remains essentially constant and in large excess relative to the concentration of  $^{35}\text{Cl}^+$ . The concentration of  $^{35}/^{37}\text{Cl}_2$  is decreasing with time due to the pulsed introduction of chlorine. The pulsed introduction of chlorine reduces

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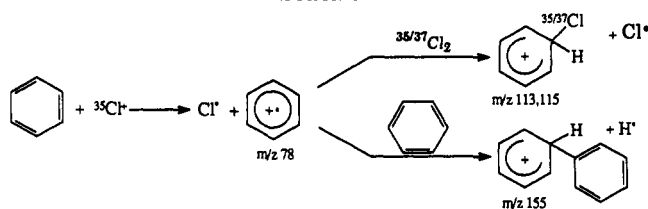
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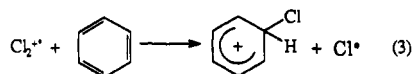
Scheme I



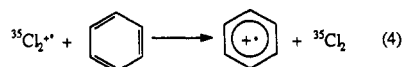
interference from the reaction shown in eq 1.

For the reaction of  $^{35}\text{Cl}^+$  with benzene, a plot of ion intensity as a function of reaction time (Figure 1) reveals several interesting points. First,  $^{35}\text{Cl}^+$  undergoes a charge-exchange process with benzene to form the benzene cation radical ( $m/z$  78). The appearance of ions at  $m/z$  113 and 115 (intensity ratio 3:1) indicates that the benzene radical cation ( $m/z$  78) reacted with residual neutral  $^{35/37}\text{Cl}_2$  to form the chlorine addition product. Signals for the addition product with benzene exhibit a standard chlorine isotope pattern, indicating that the chloronium ion ( $^{35}\text{Cl}^+$ ) does not add directly to the aromatic ring. Had any of the trapped chloronium ion added to benzene, the ratio of  $m/z$  113 to  $m/z$  115 would have been larger than expected for a standard chlorine isotope pattern. In addition, an ion  $m/z$  155 corresponding to a diaryl cation ( $\text{C}_{12}\text{H}_{11}^+$ ) is noted after 70 ms. The diaryl cation, formed from the reaction of the benzene cation radical ( $m/z$  78) with residual benzene, is further evidence of the intermediacy of an aromatic cation radical.<sup>12</sup> These results are summarized in Scheme I.

The possibility of isotope scrambling between  $^{35}\text{Cl}^+$  and residual  $^{35/37}\text{Cl}_2$  was investigated. When  $^{35}\text{Cl}^+$  was trapped and reacted with residual  $^{35/37}\text{Cl}_2$ , only charge-transfer products were detected. No ions at  $m/z$  37 were detected. The possibility that direct addition of chloronium followed by fragmentation gives rise to the benzene radical cation was also considered, but that pathway would preclude a standard isotope pattern in the addition product and cannot readily explain the ion at  $m/z$  155 (diaryl cation). The possibility of the  $\text{Cl}_2^{++}$  from eq 1 reacting with the neutral aromatic species (eq 3) was also considered. This



mechanism would give rise to a chlorine addition product with a standard chlorine isotope pattern and is energetically favorable (for reaction 3,  $\Delta H_r = -60$  kcal/mol) and is certainly a possibility. However, when  $^{35}\text{Cl}_2^{++}$  is the isolated reactant ion, no chlorine addition product with benzene is observed. The only reaction observed is shown below (eq 4). The mode of formation of the benzene



cation radical and thus the energy of the ion affects the subsequent reactions. Field et al.<sup>13</sup> found in a high-pressure, chemical ionization study, that benzene cation radical formed by electron impact was unreactive toward residual neutral benzene. However, when benzene cation radical was formed by charge transfer from a rare gas ion, dimeric products such as  $(\text{C}_{12}\text{H}_{11})^+$  and  $(\text{C}_{12}\text{H}_{12})^+$  were formed. Lastly, it should be noted that the chlorine addition product appears only after 30 ms or longer reaction times

Table I. Reactions of Aromatic Compounds with  $\text{Cl}^+$ 

compound	$\sigma^+$ <sup>a</sup>	cation radical $m/z$ (%) <sup>b</sup>	chlorine addition product <sup>c</sup> $m/z$ (%)	eq 5 $\Delta H_r^e$ (kcal/mol)
aniline	-1.3	93 (100)	none	+2
anisole	-0.78	108 (100)	143 (2)	-7
naphthalene	-0.45 <sup>d</sup>	128 (100)	163 (1)	-2
toluene	-0.31	92 (36)	127 (4)	-1
fluorobenzene	-0.07	96 (100)	131 (5)	-5
benzene	0.0	78 (100)	113 (8)	-8
chlorobenzene	+0.11	112 (100)	147 (8)	-5
phenylacetylene	+0.18	102 (100)	137 (2)	-10
methyl benzoate	+0.48	136 (3)	none	-18
benzaldehyde	+1.0	106 (9)	none	-13
nitrobenzene	+1.23	123 (20)	none	-11

<sup>a</sup> Reference 20. <sup>b</sup> Amount of molecular radical cation found in the normalized mass spectrum after 100-ms reaction time. <sup>c</sup> Percent of chlorine addition product relative to radical cation after 100-ms reaction time. <sup>d</sup> Aryl value,  $\sigma$  for 1 position; ref 20. <sup>e</sup> Using known values when available (ref 21) or estimated based on calculations from model compounds.

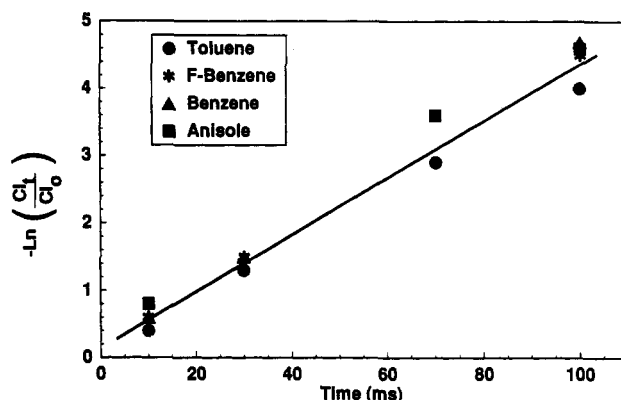
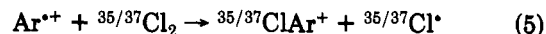


Figure 2. Disappearance of  $\text{Cl}^+$  in the presence of various aromatic compounds.

(Figure 1). This behavior supports the two-step mechanism proposed in Scheme I.

In addition to benzene, a number of substituted aromatic compounds were reacted with  $^{35}\text{Cl}^+$  (Table I). In each case the initial process observed is charge transfer from  $^{35}\text{Cl}^+$ . A plot of the disappearance of chloronium ion ( $-\ln \text{Cl}_t^+ / \text{Cl}_0^+$ ) with time gave a straight line with a half-life of  $16 \pm 1$  ms with all neutral aromatic reactants (Figure 2). Therefore, the rate of the charge exchange reaction is unaffected by the substituents on the aromatic substrate. However, the formation of the chlorine addition product is affected by the aromatic substituents. The substituent effects can be explained by examining the thermodynamics of the second step of the reaction (eq 5).



The heat of reaction,  $\Delta H_r$ , for each step of the process leading to the chlorine addition product (eq 2 and 5) for various aromatic substrates was calculated using Hess's Law. The first step (charge transfer) is highly exothermic for all aromatic species studied. Thus, the aromatic cation radical ( $\text{Ar}^{++}$ ) is a highly energetic species. In experiments where the aromatic cation radical is generated by standard electron ionization, chlorine addition is observed only with anisole and toluene. This result suggests that the initial charge-transfer step provides the necessary excitation energy for the subsequent chlorine addition step to occur.

The heat of reaction for the second step (eq 5) of the reaction proved more difficult to calculate since the heats of formation,  $\Delta H_f$ , for the chlorine addition product ions

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of only benzene, aniline, and toluene are known. The  $\Delta H_f$  values for the other chlorine addition product ions were estimated using model reactions for comparison.<sup>14</sup> The calculated  $\Delta H_f$  values for the chlorine addition (eq 5) are shown in Table I.

Of the compounds studied, aniline, methyl benzoate, benzaldehyde, and nitrobenzene failed to give chlorine addition products in the time frame of these experiments. Based on our calculations, aniline cation radical reacting with residual  $^{35/37}\text{Cl}_2$  to give the chlorine addition product of  $\text{Cl}^+$  is endothermic by 2 kcal/mol (Table I). For this reason, addition to the aniline cation radical is not expected.

The reactions of the other aromatic species studied are slightly exothermic in the second step and are thus thermodynamically feasible using  $\Delta H_f$  as a criterion. Anisole, toluene, phenylacetylene, naphthalene, chlorobenzene, and fluorobenzene all show addition of chlorine as evidenced by detection of ions of appropriate mass to charge ratio with the standard chlorine isotope pattern observed, supporting the proposed two-step mechanism. For methyl benzoate, benzaldehyde, and nitrobenzene, the molecular cation radical formed by charge transfer is too short lived (loss of fragmentation) to react with residual chlorine.

This apparent substrate selectivity invites a comparison between the identity of the chlorine addition product and the intermediate formed in electrophilic aromatic substitution. To address the question of the structure of the addition product, several MS/MS experiments were performed. The ion corresponding to the chlorine addition product to benzene ( $m/z$  113) was isolated and collisionally activated, and the fragments were observed. The daughter ions detected were  $m/z$  77 (loss of HCl) and  $m/z$  51 (ring-opening fragment). Isobutane chemical ionization was used to generate a protonated chlorobenzene molecular ion ( $m/z$  113). This ion was isolated and collisionally activated. The daughter ion spectrum was identical to that generated in the previous experiment. That the same spectra are observed indicates that the carbon-chlorine bond in both species is a  $\sigma$ -bond.

Next, a series of MS/MS experiments was performed on the protonated chlorotoluenes ( $m/z$  127). Isolation of the chlorine addition product with toluene  $\text{C}_7\text{H}_8\text{Cl}^+$  ( $m/z$  127) followed by collisional activation gives a daughter ion spectrum with two ions:  $m/z$  91 (loss of HCl) and  $m/z$  65 (ring-opening fragment) (Figure 3A). Isobutane chemical ionization of 2-chlorotoluene gives a protonated molecular ion at  $m/z$  127. Again, isolation of this ion followed by collisional activation yields a daughter ion spectrum identical to the chlorine addition product (Figure 3B). These results, again, suggest that the chlorine addition product is  $\sigma$ -bonded. MS/MS experiments on the protonated molecular ions ( $\text{C}_7\text{H}_8\text{Cl}^+$   $m/z$  127) of 3-chlorotoluene and 4-chlorotoluene show daughter ion spectra identical to 2-chlorotoluene. Therefore, conclusions concerning positional selectivity in the chlorine addition product are not possible. Substitution at the ipso position must also be considered. However, no conclusions may be reached concerning substitution at this site since protonation of a carbene would be required to generate the appropriate  $\text{C}_7\text{H}_8\text{Cl}^+$ . Thus, there is no evidence for or against chlorine addition at this site. Chlorine addition

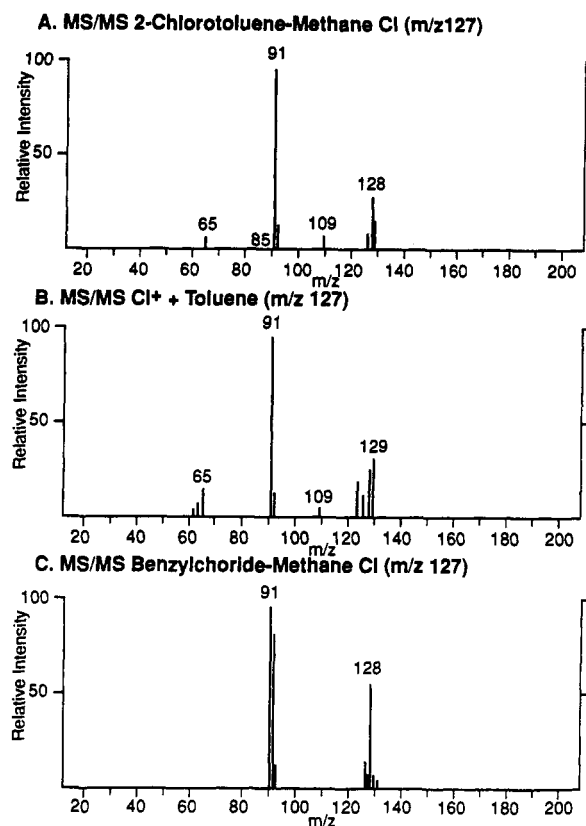


Figure 3.

to the benzylic carbon, however, can be ruled out because the daughter ion spectrum of the protonated molecular ion of benzyl chloride ( $\text{C}_7\text{H}_8\text{Cl}^+$   $m/z$  127) shows no ring fragmentation, and the base peak corresponds to the loss of chlorine ( $m/z$  92), not the loss of HCl ( $m/z$  91) (Figure 3C).

In a splendid experiment described by Schmitt et al.,<sup>15</sup> the question of structure,  $\sigma$ -complex or  $\pi$ -complex, is resolved by studying the reactivity of the addition product formed during gas-phase aromatic nitration in the presence of pyridine. The pyridine would be expected to remove the acidic proton from a  $\sigma$ -complex, but not from a  $\pi$ -complex. In this study, chloronium ion ( $^{35}\text{Cl}^+$ ) was isolated and allowed to react with the residual gases present ( $^{35/37}\text{Cl}_2$ , benzene- $d_6$ , and pyridine). Charge-transfer reactions predominated, forming benzene- $d_6$  cation radical, chlorine radical cation, and pyridine cation radical. Subsequent chlorine addition to both aromatic cation radicals was observed. As before, the chlorine addition product showed the standard chlorine isotope pattern. The interesting feature, however, was the detection of ions at  $m/z$  81 (pyridine- $d$ )<sup>+</sup>. The ions at  $m/z$  81 are the result of pyridine removing a deuterium ion, suggesting that the chlorine addition product is a  $\sigma$ -complex. The amount of (pyridine- $d$ )<sup>+</sup> increased as the pressure of pyridine in the system increased. In a second, more selective experiment, the chlorine addition product ions ( $m/z$  119–121) were isolated and allowed to react with residual benzene- $d_6$ ,  $^{35/37}\text{Cl}_2$ , and pyridine. Again, deuterium transfer to pyridine was observed. This confirms that the deuterium in the chlorine addition product is acidic and that the structure is a  $\sigma$ -complex.

In addition to examining the reactions of  $^{35}\text{Cl}^+$  with aromatic compounds, we have also examined the reaction of aromatic compounds with  $^{35}\text{Cl}_2^{++}$  ( $m/z$  70) in the ITMS.

(14) See supplementary material. These models involved calculations of the  $\Delta H_f$  for three general reactions. One is where a hydrogen atom replaced a chlorine, another, the simple addition of a hydrogen atom, or the third, simple addition of a chlorine atom. The average  $\Delta H_f$  values from the models were then used to calculate the  $\Delta H_f$  values of the chlorine addition product. Average numbers are shown for products where multiple isomers are possible.

(15) Schmitt, R. J.; Buttrill, S. F.; Ross, D. S. *J. Am. Chem. Soc.* 1984, 106, 926.

The chlorine radical cation containing only the  $^{35}\text{Cl}$  isotope was generated and trapped. This ion was allowed to react with various aromatic compounds. As with  $^{35}\text{Cl}^+$ , the main reaction is electron transfer from the aromatic compound to  $^{35}\text{Cl}_2^{*+}$ . Transfer of a substituent to an aromatic compound with simultaneous release of a neutral species is a common gas-phase reaction.<sup>16,17</sup> Reaction of  $^{35}\text{Cl}_2^{*+}$  with an aromatic compound could behave in an analogous fashion (eq 3). However, this reaction was not observed in our study.

The electron-rich aromatic cation radicals of anisole and toluene subsequently react with residual  $^{35/37}\text{Cl}_2$  to form chlorine addition products which exhibit a standard chlorine isotope pattern. The other aromatic compounds studied show no chlorine addition products. The spectra of electron-deficient aromatic compounds benzaldehyde and nitrobenzene are dominated by ions resulting from fragmentation of the aromatic radical cation. These results support the mechanism of SET followed by subsequent chlorine addition; chlorine transfer to a aromatic compound does not appear to be viable competitive mechanism.

In solution, many alkenes and dienes undergo electrophilic addition with chlorine without catalysis. We have found, in general, that alkenes and dienes<sup>18</sup> do not form any chlorine addition products with either  $^{35}\text{Cl}^+$  or  $^{35}\text{Cl}_2^{*+}$  in the gas phase. 1-Acetoxy-1,3-butadiene and hexachloro-1,3-butadiene formed small amounts of chlorine addition products. Again, the two factors which affect the reactivity of alkenes and dienes with chloronium ion are

the exothermicity of the charge transfer reaction and the ability of the electron donating substituents to stabilize the radical cation product. Resonance stabilization of the radical cation intermediate is necessary to increase the lifetime of this intermediate so that secondary reactions with neutral species can occur. Thus, addition does not generally follow the charge-transfer process. The mass spectra show a high degree of fragmentation even at "zero reaction time". This observed behavior also supports the proposed two-step mechanism.

As expected,  $^{35}\text{Cl}^+$  and  $^{35}\text{Cl}_2^{*+}$  do not add directly to an aromatic compound in an electrophilic aromatic substitution process. Additionally, the aromatic chlorine addition product is not formed by transfer of  $^{35}\text{Cl}^+$  from  $^{35}\text{Cl}_2^{*+}$ . Our results indicate that the mechanism of chlorine addition in the gas phase involves two reactions resulting in a product similar to the  $\sigma$ -complex formed in solution. It is possible to explain the apparent substrate selectivity toward formation of the chlorine addition product based on thermodynamics and stability of the aromatic cation radical. It is also extremely interesting to observe the similarities in the mechanism of the usual chlorination of hexachloro-1,3-butadiene in solution phase observed by Olah<sup>19</sup> and in this gas phase study. In both cases, SET is the initial reaction followed by quenching of the radical cation by neutral species.

**Supplementary Material Available:** Procedures for calculating the heats of reaction ( $\Delta H$ ) and tables comparing known and calculated  $\Delta H_{\text{f}}^{\circ}$  for relevant compounds (18 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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## A Self-Consistent and Cross-Checked Scale of Spin-Delocalization Substituent Constants, the $\sigma_{\text{J}}^*$ Scale

Xi-Kui Jiang\* and Guo-Zhen Ji\*

Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032, China

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On the basis of the  $^{19}\text{F}$  NMR data of substituted  $\alpha,\beta,\beta$ -trifluorostyrenes and the rate constants of their thermal cycloaddition reactions, a self-consistent and cross-checked scale of spin-delocalization substituent constants  $\sigma_{\text{J}}^*$  is proposed for 21 para-substituents and for 10 meta-substituents. By means of adopting different  $\rho_{\text{mb}}$  values, three methods for the calculation of the  $\sigma_{\text{J}}^*$  values at five different temperatures and their averaged values are presented. It has been shown that at each temperature and within a range of  $\rho_{\text{mb}}$  values from -0.20 to -0.40 the same set of  $\sigma^*$  constants are obtained from these three methods. There are seven advantages to the  $\sigma_{\text{J}}^*$  approach, including the fact that the reaction is exceptionally clean, a tailor-made polar parameter  $\sigma_{\text{mb}}$  is used in the dual-parameter equation, and the validity of the approach is strongly supported by the meta substituent effect which is independent of the polar effect. Some radical reactions, EPR data of substituted benzyl radicals, and bond dissociation energies are reexamined by using the  $\sigma_{\text{J}}^*$  in conjunction with polar  $\sigma$  constants in dual-parameter equations.

Understanding structure-property relationships and reaction mechanisms is the soul of chemistry, and much

has been gained by application of the Hammett-type polar substituent parameters  $\sigma^{\text{X}}$ , i.e.,  $\sigma_{\text{P}}$ ,  $\sigma_{\text{M}}$ ,  $\sigma_{\text{R}}$ ,  $\sigma_{\text{F}}$ ,  $\sigma_{\text{a}}$ , ..., etc.<sup>1</sup>