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Computational Study of Aluminum Chloride Activation for Toluene Chlorination

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Aluminum chloride, in the absence of solvent and moisture, was observed to exert a negligible catalytic effect upon the chlorination of toluene, but in the presence of atmospheric moisture, a very large catalytic effect was evident. DFT calculations were performed on a number of possible intermediates involved in the chlorination process. The calculations suggest that dimeric aluminum chloride predominates in the absence of solvents or moisture, and it is not active as a catalyst. It is suggested that HCl is produced by reaction of water with the aluminum chloride leading to the formation of monomeric complexes with molecular chlorine. These complexes are believed to serve as the electrophile during catalytic toluene chlorination. The results further suggest that very strong complexes can form between water and monomeric aluminum chloride. Complexes between aluminum chloride and toluene were also identified in the calculations, but their catalytic significance remains unclear.

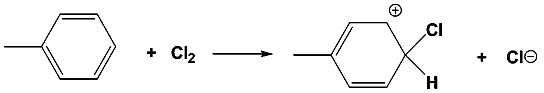
Introduction

It was recently noted that the rate of “uncatalyzed” toluene chlorination changes by over 7 orders of magnitude as the solvent is varied.[1] The rate varies systematically with the dielectric constant of the solvent. It is possible, in the systems with the highest dielectric constants (which display the highest rates), that the solvent also functions as a catalyst. However, a computational study of the solvent effect indicates that for solvent dielectric constants less than ca. 40 the variation in rate can be explained in terms of differences in the stability of reaction intermediates and without invoking any additional, specific, catalytic action by the solvent. The calculations also indicate that there is a subtle change in the reaction mechanism when the dielectric constant of the medium falls at or below that of acetic acid (dielectric = 6.19).

At higher dielectric constants, as described in most organic chemistry texts,[2−4] the rate-limiting process is the reaction between toluene and chlorine to form an intermediate arenium cation, Scheme 1. At dielectric constants characteristic of acetic acid and smaller, computational results indicate that the reaction occurs in a single bimolecular event that forms the product directly, without formation of an intermediate arenium cation.[1] When the dielectric constant is low, it is energetically unfavorable to form an arenium cation, and transition states have been identified that lie on a direct path from reactants to products. The predicted activation energy based upon these transition states compares very favorably with the experimentally observed value.

Generally, in a commercial process, it is preferable to avoid the use of a solvent. In the case of aromatic chlorination, a Lewis acid catalyst is typically employed. The dielectric constant of toluene is 2.38, which is well within the regime wherein the reaction is suggested to occur via a direct pathway that does not involve an arenium cation. According to March,[3] “when a Lewis-acid catalyst is used with chlorine or bromine, the attacking entity may be Cl^+ or Br^+, formed by $FeCl_3 + Br_2 \rightarrow FeCl_3Br^- + Br^+$, or it may be Cl_2 or Br_2, polarized by the catalyst.” The computational results just described suggest that formation of ionic species may be energetically unfavorable when the reaction is conducted in toluene without a solvent. It is then interesting to ask whether the more likely electrophile is a polarized halogen molecule or a halogen cation, and, if the former electrophile is more likely, what are the structures and properties of such catalyst−chlorine complexes.

SCHEME 1: Arenium Cation Chlorination Mechanism



A few investigations have been reported wherein aluminum chloride (a Lewis acid) was used as the catalyst for chlorination of toluene in the presence of some amount of solvent.[5−8] However, the present authors are unaware of any studies wherein aluminum chloride has been used to catalyze toluene chlorination without any solvent being added. Consequently, the qualitative results of such an experiment are reported here. The results, to be described, suggest that it may be necessary to activate aluminum chloride before it can function as a chlorination catalyst in a solvent-free system. The results of a computational study to probe the possible nature of this catalyst activation are also presented.

Experimental Section

Only two chlorination experiments will be considered here. The experimental procedure for these experiments is similar to that used in previous study of the uncatalyzed chlorination of toluene.[1] Briefly, a stirred, 100 mL, Pyrex round-bottomed flask served as the reactor. Chlorine (ultrahigh purity, Matheson) was dissolved in toluene (anhydrous, 99.8%, Aldrich) until the latter was saturated at room temperature. The lights were extinguished and an amount (ca. 0.5 g) of aluminum chloride was added to the contents of the flask which were vigorously stirred. Using a pipet, samples were withdrawn from the reactor to be titrated for chlorine concentration. To do so, the sample was mixed with

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TABLE 1: Molecular Species Considered during This Investigation and Their Energies

specie	E_{el} solution, hartree	ZPE, kcal/mol	E_0, kcal/mol,	$H_{thermal-298}$, kcal/mol	H_{298}, kcal/mol	$G_{thermal-298}$, kcal/mol	G_{298}, kcal/mol
Reactants							
Cl_2	−920.404403	1.212	-5.7756×10^5	2.1150	-5.7756×10^5	−13.7050	-5.7757×10^5
C_7H_8	−271.637971	80.147	-1.7038×10^5	4.2502	-1.7037×10^5	−18.3672	-1.7039×10^5
o-C_7H_7Cl	−731.260117	74.519	-4.5880×10^5	4.9287	-4.5879×10^5	−19.6864	-4.5882×10^5
m-C_7H_7Cl	−731.260792	73.960	-4.5880×10^5	5.2211	-4.5879×10^5	−20.6452	-4.5882×10^5
p-C_7H_7Cl	−731.260045	74.220	-4.5880×10^5	5.0881	-4.5879×10^5	−19.9944	-4.5882×10^5
HCl	−460.835837	4.160	-2.8917×10^5	2.0737	-2.8917×10^5	−11.2285	-2.8919×10^5
Al_2Cl_6	−3246.713064	6.768	-2.0373×10^6	8.1897	-2.0373×10^6	−26.1964	-2.0374×10^6
$AlCl_3$	−1623.341574	2.895	-1.0187×10^6	3.9857	-1.0187×10^6	−19.5504	-1.0187×10^6
H_2O	−76.454544	13.333	-4.7963×10^4	2.3717	-4.7960×10^4	−11.4866	-4.7974×10^4
Intermediates							
Cl^+	−459.761813	0.000	-2.8850×10^5	1.4812	-2.8850×10^5	−9.4270	-2.8851×10^5
o-C_7H_8Cl+	−731.600545	80.701	-4.5901×10^5	5.3858	-4.5900×10^5	−20.4597	-4.5903×10^5
m-C_7H_8Cl+	−731.593869	80.758	-4.5900×10^5	5.3698	-4.5900×10^5	−20.4119	-4.5902×10^5
p-$C_7H_8Cl^+$	−731.602675	80.709	-4.5901×10^5	5.4414	-4.5900×10^5	−20.6513	-4.5903×10^5
Cl^-	−460.374193	0.000	-2.8889×10^5	1.4812	-2.8889×10^5	−9.4270	-2.8890×10^5
$AlCl_4{}^-$	−2083.801426	3.604	-1.3076×10^6	5.0930	-1.3076×10^6	−21.1733	-1.3076×10^6
$AlCl_4{}^+$	−2083.195509	3.545	-1.3072×10^6	5.2848	-1.3072×10^6	−22.0892	-1.3072×10^6
Cl_2-AlCl_3	−2543.751027	4.126	-1.5962×10^6	6.5557	-1.5962×10^6	−24.3528	-1.5962×10^6
$HCl-AlCl_3$	−2084.186391	8.442	-1.3078×10^6	5.7598	-1.3078×10^6	−21.9894	-1.3079×10^6
o-$AlCl_3-C_7H_8$	−1894.994391	83.933	-1.1890×10^6	8.7428	-1.1890×10^6	−25.8242	-1.1891×10^6
m−$AlCl_3-C_7H_8$	−1894.995116	83.992	-1.1890×10^6	8.7537	-1.1890×10^6	−26.0055	-1.1891×10^6
p-$AlCl_3-C_7H_8$	−1894.996630	83.828	-1.1890×10^6	8.8364	-1.1890×10^6	−26.6861	-1.1891×10^6
1-$AlCl_3-C_7H_8$	−1894.989394	84.041	-1.1890×10^6	8.7786	-1.1890×10^6	−25.7524	-1.1891×10^6
$AlCl_2OH$	−1238.956849	10.443	−7.7745 × 105	4.1286	-7.7744×10^5	−19.0390	-7.7747×10^5
$HAlCl_4-AlCl_3$	−3707.543238	11.634	-2.3265×10^6	9.7831	-2.3265×10^6	−27.4682	-2.3265×10^6
Al_2Cl_5OH	−2862.327377	14.091	-1.7961×10^6	8.4645	-1.7961×10^6	−26.1064	-1.7961×10^6
$H_2O-AlCl_3$	−1699.851483	18.382	-1.0667×10^6	5.9176	-1.0666×10^6	−21.9751	-1.0667×10^6
$Cl_2-AlCl_3-H_2O$	−2620.258846	19.077	-1.6442×10^6	9.0069	-1.6442×10^6	−27.2460	-1.6442×10^6
$Cl_2-H_2O-AlCl_3$	−2620.258923	19.293	-1.6442×10^6	8.8406	-1.6442×10^6	−26.7978	-1.6442×10^6
(s)*p*-$AlCl_4-C_7H_8Cl$	−2815.429291	81.608	-1.7666×10^6	11.6324	-1.7666×10^6	−28.6925	-1.7667×10^6
p-$AlCl_4-C_7H_8Cl$	−2815.435334	81.681	-1.7666×10^6	11.5469	-1.7666×10^6	−27.9880	-1.7667×10^6
$AlCl_4-C_7H_8Cl$	−2815.445002	81.103	-1.7666×10^6	11.6083	-1.7666×10^6	−28.1465	-1.7667×10^6

25 mL of 5% w/v potassium iodide solution (Fisher Scientific) and titrated using 0.001 N sodium thiosulfate (prepared by dilution of 0.1 N volumetric standard solution (Aldrich)) in 5 mL micro-burets with starch solution (Fisher) as indicator. The chlorination experiment was performed two times. Each time a new, previously unopened, bottle of aluminum chloride was used. One experiment was conducted in a lab hood open to the atmosphere; the other was conducted in a glovebox under a dry nitrogen atmosphere.

The structure and energetics of different chemical species were calculated using Jaguar, version 4.1.[9] Density functional theory (DFT) was employed using B3LYP hybrid exchange and correlation functionals, and a 6-311G** basis set. Fine DFT grids were employed, and ultrafine geometry convergence was specified. Symmetry constraints were not imposed upon any of the species investigated. Neither frequencies nor zero-point energies were scaled, and any basis set superposition errors were not corrected. The polarized continuum model for solvation[10] that is included in the Jaguar program was used to optimize structures and calculate energetics in solution in toluene. One estimate for the partial atomic charges was calculated by fitting the electrostatic potential (ESP) to the atom centers while constraining the total charge to equal that of the species. A natural bond orbital (NBO) analysis was performed on each optimized molecular structure.[11] This provided a second estimate for the partial atomic charges within each species. The NBO analysis also provided an indication of the orbitals involved in bonding and their occupancy. When it was desirable to visualize orbitals, a Boys localization was performed on the valence orbitals of the final wave function and Molden[12] then was used to generate pictures of the molecular orbitals.

Results

Without a catalyst or a solvent present, the rate of toluene chlorination is extremely small at room temperature.[1] Two important observations were made when aluminum chloride was added to the toluene−chlorine mixture in the laboratory hood. First, when the new, unopened jar of aluminum chloride was opened, the material visibly fumed as some was removed and transferred to the reaction flask. Second, as soon as the aluminum chloride was added, the rate increased tremendously. Indeed, by the time a sample was withdrawn from the flask, virtually all of the chlorine had been consumed. In contrast, the toluene−chlorine mixture without catalyst could stand for hours after which only a small fraction of the chlorine was gone, and a significant portion of that due to volatilization, not reaction.[1]

The results of a replicate experiment conducted in a glovebox filled with dried nitrogen were entirely different. Before the catalyst was added to the flask, the rate of reaction was imperceptibly small, as before. When the new, unopened jar of aluminum chloride was opened in the glovebox, fuming was not observed. Unexpectedly, when the aluminum chloride was added to the toluene−chlorine mixture there was no apparent change in the rate of reaction. That is, the rate remained imperceptibly small even after the aluminum chloride had been added. A few small particles of aluminum chloride were noticed to have adhered to the neck of the flask instead of falling into the toluene−chlorine mixture. These particles slowly darkened in color over time. After this, the liquid within the flask was swirled so as to sweep the darkened particles into the liquid. Reaction was immediately and visibly apparent when these darkened particles entered the liquid.

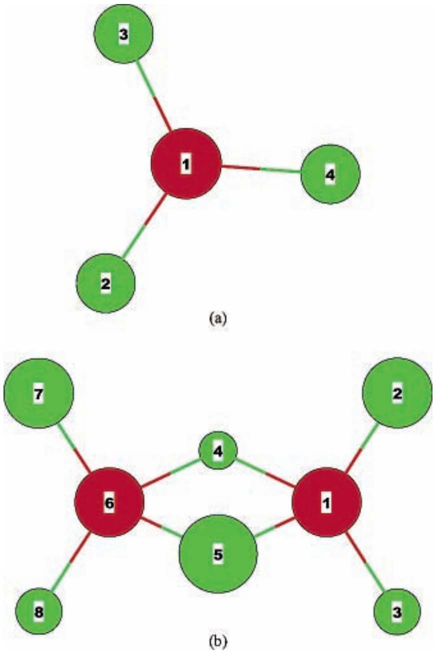

Figure 1. Optimized solution geometries for aluminum chloride monomer (a, Al = 1; Cl = 2−4) and dimer (b, Al = 1,6; Cl = 2−5,7,8) in toluene solvent.

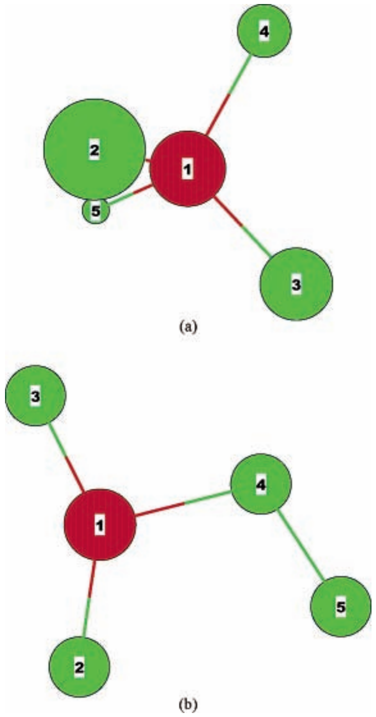

Figure 2. Optimized solution geometries for $AlCl_4^-$ (a, Al = 1; Cl = 2−5) and $AlCl_4^+$ (b, Al = 1; Cl = 2−5) in toluene solvent.

TABLE 2: Geometric Parameters for the Optimized Structures of Aluminum Chloride Species in Toluene Solution

species	distances (Å)			angles (degrees)			
$AlCl_3$	Al1	Cl2	2.085	Cl3	Al1	Cl2	120.4
	Al1	Cl3	2.085	Cl4	Al1	Cl2	119.7
	Al1	Cl4	2.086	Cl4	Al1	Cl3	119.9
Al_2Cl_6	Al1	Cl2	2.091	Cl3	Al1	Cl2	120.9
	Al1	Cl3	2.091	Cl4	Al1	Cl2	110.3
	Al1	Cl4	2.283	Cl4	Al1	Cl3	110.4
	Al1	Cl5	2.282	Cl5	Al1	Cl2	110.4
	Cl4	Al6	2.283	Cl5	Al1	Cl3	110.3
	Cl5	Al6	2.282	Cl5	Al1	Cl4	90.4
	Al6	Cl7	2.091	Al6	Cl4	Al1	89.6
	Al6	Cl8	2.091	Al6	Cl5	Al1	89.6
				Cl5	Al6	Cl4	90.4
				Cl7	Al6	Cl4	110.4
				Cl7	Al6	Cl5	110.3
				Cl8	Al6	Cl4	110.3
				Cl8	Al6	Cl5	110.4
				Cl8	Al6	Cl7	120.8
$AlCl_4^-$	Al1	Cl2	2.165	Cl3	Al1	Cl2	109.5
	Al1	Cl3	2.165	Cl4	Al1	Cl2	109.5
	Al1	Cl4	2.166	Cl4	Al1	Cl3	109.4
	Al1	Cl5	2.166	Cl5	Al1	Cl2	109.4
				Cl5	Al1	Cl3	109.5
				Cl5	Al1	Cl4	109.4
$AlCl_4^+$	Al1	Cl2	2.034	Cl3	Al1	Cl2	145.1
	Al1	Cl3	2.038	Cl4	Al1	Cl2	112.5
	Al1	Cl4	2.334	Cl4	Al1	Cl3	102.4
	Cl4	Cl5	2.066	Cl5	Cl4	Al1	108.8

Computational geometry optimizations and vibrational analyses were performed for a number of aluminum chloride species in solution in toluene. Table 1 summarizes all of the species that were considered, including some that will not be discussed here. This table reports the electronic energies, the zero point energies, the zero-point corrected energies, thermal contributions to the enthalpy and free energy, and corresponding enthalpies and free energies at 298 K. Hereafter, energy changes reported in tables and figures refer to changes in the zero-point corrected energies, unless otherwise noted. To begin, aluminum chloride, $AlCl_3$, and its dimer, Al_2Cl_6, were studied, along with the following ionic species that might form from them (perhaps in combination with molecular chlorine): Cl^+, Cl^-, $AlCl_4^-$, and $AlCl_4^+$. The optimized structures of aluminum chloride monomer and dimer are shown in Figure 1, and those of the $AlCl_4$ ions are shown in Figure 2. Corresponding geometric parameters are presented in Table 2. It can be seen that $AlCl_3$ has a planar structure. In Al_2Cl_6, the two aluminum atoms and the two bridging chlorine atoms comprise opposite corners of a square with the terminal chlorine atoms lying in a perpendicular plane. The $AlCl_4^-$ anion has a tetrahedral geometry, whereas the cation is again planar. Table 3 lists the ESP and NBO estimates for the atomic charges in the two ionic species. In the anion, all four chlorine atoms are equally negative. In contrast, in the cation, the two chlorines that are bonded only to aluminum have a partial negative charge, whereas the chlorines that are bonded to each other exhibit partial positive charges.

Complexes that might form via the interaction of aluminum chloride with HCl were considered next. Both the monomeric and dimeric forms of aluminum chloride were examined, and the resulting optimized geometries for HCl−$AlCl_3$ and HCl−$AlCl_3$−$AlCl_3$ are shown in Figure 3. The corresponding geometric parameters are given in Table 4. The $AlCl_3$ unit of the HCl−$AlCl_3$ complex is no longer planar; the three Cl−Al−Cl angles sum to 352.5°. HCl apparently can insert into one of the bridging Al−Cl bonds of the dimer leading to a structure wherein one aluminum is nearly tetrahedral with two terminal chlorine atoms, a terminal HCl unit, and a single bridging chlorine atom. The bond from the other aluminum atom to this bridging chlorine is longer than its three bonds to terminal chlorines, giving this aluminum more of a trigonal pyramid structure.

Figure 4 presents optimized structures that would result from reaction or complexation of water with aluminum chloride. In the case of the monomer, two species were identified: one where a hydroxyl group has substituted for one of the chlorines and a complex. For the dimer, a corresponding complex was not identified, but a minimum energy structure with a substitutional hydroxyl was located. The geometric parameters for these

TABLE 3: Estimated Atomic Charges of Aluminum Chloride Ions in Toluene Solution

species	atom	ESP Charge	NBO Charge
$AlCl_4^-$	Al1	0.72435	1.26614
	Cl2	−0.43101	−0.56641
	Cl3	−0.43052	−0.56632
	Cl4	−0.4313	−0.56673
	Cl5	−0.43152	−0.56668
$AlCl_4^+$	Al1	0.77202	1.50376
	Cl2	−0.09788	−0.39139
	Cl3	−0.06036	−0.38199
	Cl4	0.19773	0.11122
	Cl5	0.1885	0.1584

TABLE 4: Geometric Parameters for the Optimized Structures of HCl−Aluminum Chloride Species in Toluene Solution

species	distances (Å)			angles (degrees)			
$HCl-AlCl_3$	Al1	Cl2	2.110	Cl3	Al1	Cl2	117.9
	Al1	Cl3	2.107	Cl4	Al1	Cl2	116.5
	Al1	Cl4	2.110	Cl4	Al1	Cl3	118.1
	Al1	Cl5	2.527	Cl5	Al1	Cl2	101.0
	Cl5	H6	1.300	Cl5	Al1	Cl3	95.9
				Cl5	Al1	Cl4	100.7
				H6	Cl5	Al1	103.0
$HCl-AlCl_3-AlCl_3$	Al1	Cl2	2.090	Cl3	Al1	Cl2	122.6
	Al1	Cl3	2.091	Cl5	Al1	Cl2	109.1
	Al1	Cl5	2.252	Cl5	Al1	Cl3	110.7
	Al1	Cl9	2.335	Cl9	Al1	Cl2	105.9
	Cl4	Al6	2.197	Cl9	Al1	Cl3	106.7
	Cl5	Al6	2.356	Cl9	Al1	Cl5	99.1
	Al6	Cl7	2.102	Al6	Cl5	Al1	117.2
	Al6	Cl8	2.100	Cl5	Al6	Cl4	101.2
	Cl9	H10	1.391	Cl7	Al6	Cl4	112.2
				Cl7	Al6	Cl5	102.9
				Cl8	Al6	Cl4	112.0
				Cl8	Al6	Cl5	106.4
				Cl8	Al6	Cl7	119.8
				H10	Cl9	Al1	97.3

species are presented in Table 5. Similar to the $HCl-AlCl_3$ complex, the formation of the $H_2O-AlCl_3$ complex causes the $AlCl_3$ unit to become nonplanar. The structures of the two substituted molecules, $AlCl_2OH$ and Al_2Cl_5OH, are very similar to their parent aluminum chlorides.

Because the role of a Lewis acid catalyst can involve the polarization of a chlorine atom, attempts were made to find complexes between Cl_2 and a number of different aluminum chloride species, particularly the monomer, dimer, and water complex. Searches for a complex between Cl_2 and the aluminum chloride dimer were not successful. Figure 5a shows the structure of a complex with the monomer, Cl_2-AlCl_3. The corresponding geometric parameters are presented in Table 6 and atomic charges in Table 7 (which also includes results for the $HCl-AlCl_3$ complex). This species is similar to both the $HCl-AlCl_3$ and $H_2O-AlCl_3$ complexes. The $AlCl_3$ unit is nonplanar with the aluminum sticking slightly up out of the plane of the three terminal chlorines and with the complexing Cl_2 unit above the aluminum. The atomic charge estimates suggest very little charge on the complexed Cl_2 or HCl (boldface entries in Table 7).

In light of energetic considerations yet to be presented, an attempt was made to identify a complex that involved both H_2O and Cl_2. Specifically, two initial geometries were used, both based upon the $H_2O-AlCl_3$ complex shown in Figure 4(a). In both cases a Cl_2 molecule was placed on the axis passing through the O and the Al. In one case, the Cl_2 was on the opposite side of the $AlCl_3$ unit from the water ($Cl_2-AlCl_3-H_2O$), and in the other case, the water was between the aluminum chloride and the chlorine ($Cl_2-H_2O-AlCl_3$). Starting from either of these initial geometries, an energy minimization led to a structure like that shown in Figure 5b. The geometric parameters for this structure are presented in Table 6 and the atomic charge estimates in Table 7. Effectively, the final structure represents

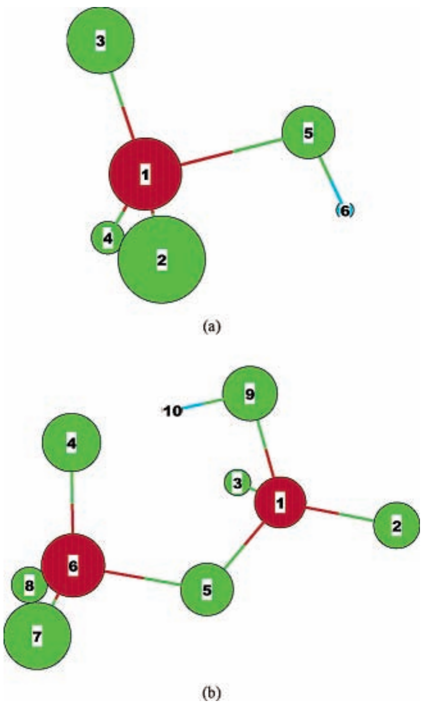

Figure 3. Optimized solution geometries for complexes between HCl and aluminum chloride in toluene solvent: $HCl-AlCl_3$ (a, Al = 1; Cl = 2−5; H = 6) and $HCl-AlCl_3-AlCl_3$ (b, Al = 1,6; Cl = 2−5,7−9; H = 10).

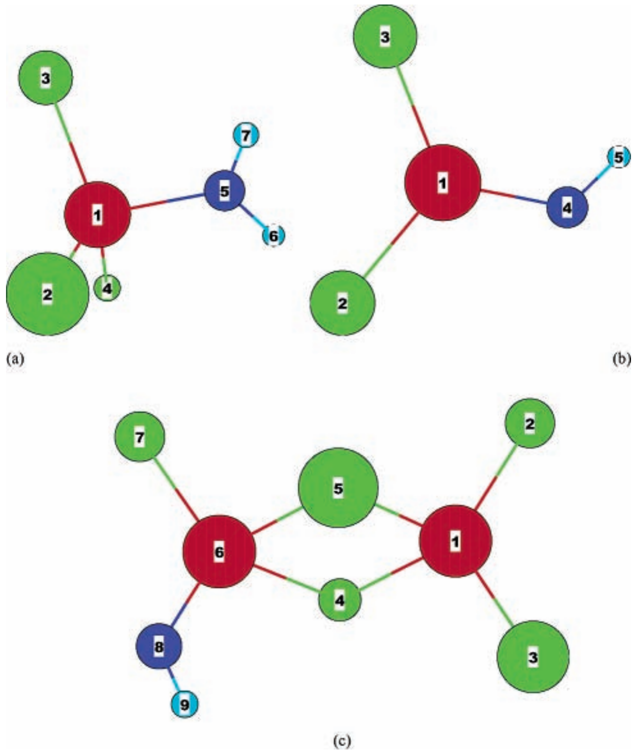

Figure 4. Optimized solution geometries for complexes and compounds involving H_2O and aluminum chloride in toluene solvent: $H_2O-AlCl_3$ (a, Al = 1; Cl = 2−4; O = 5; H = 6,7), $AlCl_2OH$ (b, Al = 1; Cl = 2,3; O = 4; H = 5), and Al_2Cl_5OH (c, Al = 1,6; Cl = 2−5,7; O = 8; H = 9).

TABLE 5: Geometric Parameters for Optimized Structures of Species Resulting from the Interaction of Aluminum Chloride with Water in Toluene Solution

species	distances (Å)			angles (degrees)			
$AlCl_2OH$	Al1	Cl2	2.091	Cl3	Al1	Cl2	118.8
	Al1	Cl3	2.100	O4	Al1	Cl2	118.6
	Al1	O4	1.690	O4	Al1	Cl3	122.7
	O4	H5	0.961	H5	O4	Al1	124.4
Al_2Cl_5OH	Al1	Cl2	2.094	Cl3	Al1	Cl2	120.5
	Al1	Cl3	2.098	Cl4	Al1	Cl2	110.9
	Al1	Cl4	2.274	Cl4	Al1	Cl3	109.8
	Al1	Cl5	2.272	Cl5	Al1	Cl2	110.9
	Cl4	Al6	2.306	Cl5	Al1	Cl3	109.9
	Cl5	Al6	2.307	Cl5	Al1	Cl4	90.8
	Al6	Cl7	2.094	Al6	Cl4	Al1	90.0
	Al6	O8	1.689	Al6	Cl5	Al1	90.0
	O8	H9	0.959	Cl5	Al6	Cl4	89.1
				Cl7	Al6	Cl4	109.3
				Cl7	Al6	Cl5	109.0
				O8	Al6	Cl4	112.9
				O8	Al6	Cl5	112.9
				O8	Al6	Cl7	119.5
				H9	O8	Al6	129.3
$H_2O-AlCl_3$	Al1	Cl2	2.128	Cl3	Al1	Cl2	115.0
	Al1	Cl3	2.127	Cl4	Al1	Cl2	114.3
	Al1	Cl4	2.126	Cl4	Al1	Cl3	116.8
	Al1	O5	1.916	O5	Al1	Cl2	105.2
	O5	H6	0.968	O5	Al1	Cl3	100.4
	O5	H7	0.968	O5	Al1	Cl4	102.4
				H6	O5	Al1	125.2
				H7	O5	Al1	124.1
				H7	O5	H6	109.7

TABLE 6: Geometric Parameters for Optimized Structures of Complexes between Chlorine and Aluminum Chloride in Toluene Solution

species	distances (Å)			angles (degrees)			
Cl_2-AlCl_3	Al1	Cl2	2.100	Cl3	Al1	Cl2	118.9
	Al1	Cl3	2.109	Cl4	Al1	Cl2	117.9
	Al1	Cl4	2.100	Cl4	Al1	Cl3	118.9
	Al1	Cl5	2.590	Cl5	Al1	Cl2	100.9
	Cl5	Cl6	2.061	Cl5	Al1	Cl3	88.8
				Cl5	Al1	Cl4	100.9
				Cl6	Cl5	Al1	109.5
$Cl_2-AlCl_3-H_2O$	Al1	Cl2	2.125	Cl3	Al1	Cl2	114.5
	Al1	Cl3	2.135	Cl4	Al1	Cl2	117.2
	Al1	Cl4	2.126	Cl4	Al1	Cl3	114.6
	Al1	O7	1.915	O7	Al1	Cl2	101.5
	Cl5	Cl6	2.064	O7	Al1	Cl3	104.9
	O7	H8	0.968	O7	Al1	Cl4	101.3
	O7	H9	0.968	H8	O7	Al1	125.1
				H9	O7	Al1	125.2
				H9	O7	H8	109.8

TABLE 7: Estimated Atomic Charges of Complexes between Chlorine, HCl, and/or Water and Aluminum Chloride in Toluene Solution

species	atom	ESP charge	NBO charge
Cl_2-AlCl_3	Al1	0.66	1.30
	Cl2	−0.29	−0.49
	Cl3	−0.24	−0.47
	Cl4	−0.29	−0.49
	Cl5	**0.06**	**0.08**
	Cl6	**0.09**	**0.06**
$HCl-AlCl_3$	Al1	0.64	1.29
	Cl2	−0.30	−0.50
	Cl3	−0.27	−0.49
	Cl4	−0.30	−0.50
	Cl5	**−0.09**	**−0.13**
	H6	0.32	0.33
$Cl_2-AlCl_3-H_2O$	Al1	0.73	1.43
	Cl2	−0.35	−0.52
	Cl3	−0.31	−0.52
	Cl4	−0.32	−0.52
	Cl5	**−0.04**	**0.00**
	Cl6	**0.00**	**−0.02**
	O7	−0.77	−0.95
	H8	0.53	0.55
	H9	0.53	0.55

two distinct molecules. Visualization of the molecular orbitals gives no indication of any bond between the $H_2O-AlCl_3$ complex and the chlorine molecule. Similarly, the NBO analysis does not find a bond between these two units. It can also been seen that there is essentially no charge on the chlorine atoms in the Cl_2 molecule (boldface entries in Table 7).

Finally, four complexes between toluene and $AlCl_3$ were analyzed, namely, 1-$AlCl_3-C_7H_8$, *o*-$AlCl_3-C_7H_8$, *m*-$AlCl_3-C_7H_8$, and *p*-$AlCl_3-C_7H_8$. The four structures are similar and are shown in Figure 6. In all instances, the $AlCl_3$ unit is situated above the plane of the aromatic ring. Looking down from above the ring, the $AlCl_3$ unit is outside the aromatic ring and close to one of the carbons (1, *o*, *m*, or *p*). The $AlCl_3$ unit is nonplanar, with the aluminum projecting out of the plane of the terminal chlorine atoms toward the relevant carbon atom of the aromatic ring. The hydrogen atom (or methyl group in the case of the 1-isomer) bonded to the ring carbon closest to the complexing $AlCl_3$ unit is bent down out of the plane of the remaining ring carbons and hydrogens. A similar structure has been described for a complex between $AlCl_3$ and benzene.[13,14] Table 8 presents the geometric parameters for *p*-$AlCl_3-C_7H_8$, with selected atomic charges for all of the isomers listed in Table 9. The ESP charge estimates are not particularly instructive. The NBO charge estimates suggest that the ring carbon closest to the complexing $AlCl_3$ unit becomes significantly more negatively charged than the other ring carbons, whereas the hydrogen bonded to this carbon becomes slightly more positively charged than the other hydrogens bonded to ring carbons. The relevant charges are boldface in Table 9.

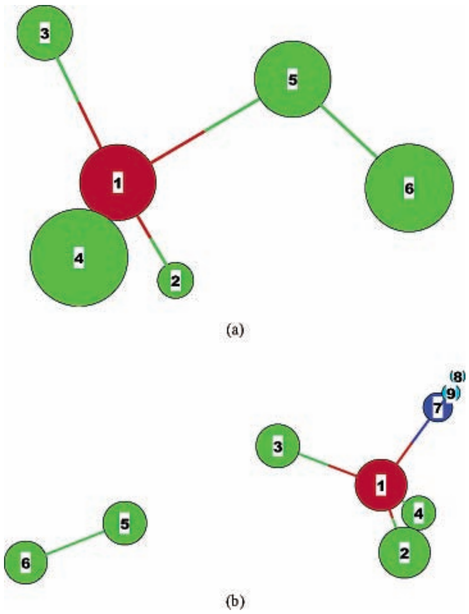

Figure 5. Optimized solution geometries for complexes between Cl_2 and aluminum chloride in toluene solvent: Cl_2-AlCl_3 (a, Al = 1; Cl = 2−6) and $Cl_2-AlCl_3-H_2O$ (b, Al = 1; Cl = 2−6; O = 7; H = 8,9).

The energy of each species, including the unscaled correction for the zero-point energy, was computed. The aluminum chloride dimer was chosen as a reference point. Figure 7 plots the relative energies of ionic species that might form from Al_2Cl_6 in toluene solution. It can be seen that formation of Cl^+, Cl^-, $AlCl_4^+$, and $AlCl_4^-$, in any combination, is highly unfavorable. Any dis-

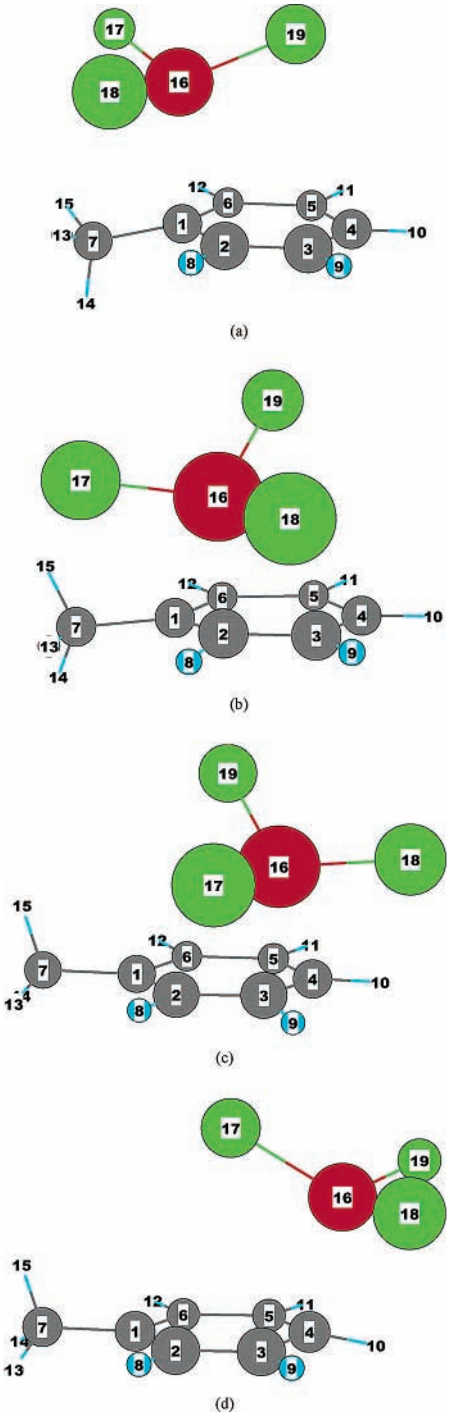

Figure 6. Optimized solution geometries for complexes between toluene and aluminum chloride in toluene solvent: 1-$AlCl_3-C_7H_8$ (a), *o*-$AlCl_3-C_7H_8$ (b), *m*-$AlCl_3-C_7H_8$ (c), and *p*-$AlCl_3-C_7H_8$ (d). (In all four figures, C = 1−7; H = 8−15; Al = 16; Cl = 17−19.)

sociation that produces either Cl^+ or Cl^- requires over 200 kcal mol^{-1}, and even the formation of the $AlCl_4^+$ and $AlCl_4^-$ ion pair requires 75 kcal mol^{-1}. Species that might form in the absence of water are compared in Figure 8. Here the energies are smaller, but still in most cases unfavorable. Only the formation of a *p*-$AlCl_3-C_7H_8$ complex is exothermic, by ca. 2 kcal mol^{-1}. It is noteworthy that formation of monomers from a dimer requires 17.8 kcal mol^{-1} and that formation of Cl_2-AlCl_3 complexes (which are believed to be the attacking electrophile in toluene chlorination) requires 11.5 kcal mol^{-1}. Complexes or reactions that involve water are compared in Figure 9. For the dimer, the substitution of a hydroxyl group in place of a chlorine involves negligible energy change (less than a kcal mol^{-1}), whereas formation of similarly substituted monomers requires almost 20 kcal mol^{-1}. Figure 9 shows that of all of the species considered, the $H_2O-AlCl_3$ complexes are energetically most favorable; formation of $H_2O-AlCl_3$ from the Al_2Cl_6 dimer is exothermic by 47 kcal mol^{-1}. Despite the observations that the $Cl_2-AlCl_3-H_2O$ shows no indication of a bond between the Cl_2 and the $H_2O-AlCl_3$, the calculations indicate that $Cl_2-AlCl_3-H_2O$ is almost 5 kcal mol^{-1} lower in energy than the separate energies of Cl_2 and the $H_2O-AlCl_3$ complex.

TABLE 8: Geometric Parameters for *p*-$AlCl_3-C_7H_8$ in Toluene Solution

distances (Å)			angles (degrees)			
C1	C2	1.404	C6	C1	C2	118.9
C1	C6	1.404	C7	C1	C2	120.5
C1	C7	1.503	C7	C1	C6	120.6
C2	C3	1.386	C3	C2	C1	121.0
C2	H8	1.085	H8	C2	C1	119.5
C3	C4	1.415	H8	C2	C3	119.5
C3	H9	1.084	C4	C3	C2	120.1
C4	C5	1.415	H9	C3	C2	120.3
C4	H10	1.089	H9	C3	C4	119.7
C4	Al16	2.315	C5	C4	C3	119.0
C5	C6	1.387	H10	C4	C3	119.5
C5	H11	1.084	H10	C4	C5	119.5
C6	H12	1.085	Al16	C4	C3	98.5
C7	H13	1.092	Al16	C4	C5	97.8
C7	H14	1.092	Al16	C4	H10	87.8
C7	H15	1.096	C6	C5	C4	120.1
Al16	Cl17	2.127	H11	C5	C4	119.7
Al16	Cl18	2.136	H11	C5	C6	120.2
Al16	Cl19	2.134	C5	C6	C1	120.9
			H12	C6	C1	119.6
			H12	C6	C5	119.5
			H13	C7	C1	111.5
			H14	C7	C1	111.5
			H14	C7	H13	108.9
			H15	C7	C1	109.8
			H15	C7	H13	107.5
			H15	C7	H14	107.5
			Cl17	Al16	C4	108.9
			Cl18	Al16	C4	101.8
			Cl18	Al16	Cl17	114.5
			Cl19	Al16	C4	102.3
			Cl19	Al16	Cl17	114.8
			Cl19	Al16	Cl18	112.7

Discussion

All of the calculations in the present study were performed at the same level of theory (DFT-B3LYP/6-311G**). In a

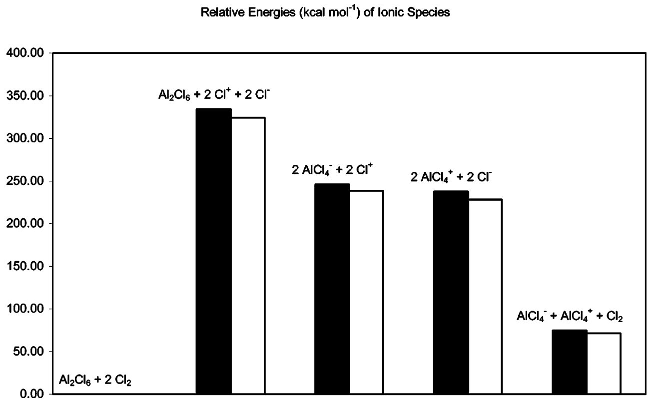

Figure 7. Relative zero-point corrected energies (black) and free energies (white) of ionic species that might form during catalyzed chlorination of toluene.

TABLE 9: Estimated Atomic Charges in Complexes between Aluminum Chloride and Toluene in Toluene Solution

species	atom	ESP charge	NBO charge
1-$AlCl_3-C_7H_8$	**C1**	0.34	−0.18
	C2	−0.16	−0.19
	C3	−0.15	−0.18
	C4	−0.04	−0.15
	C5	−0.15	−0.18
	C6	−0.16	−0.19
	H8	0.15	0.24
	H9	0.16	0.23
	H10	0.14	0.23
	H11	0.16	0.23
	H12	0.15	0.24
o-$AlCl_3-C_7H_8$	C1	0.33	0.06
	C2	−0.18	**−0.46**
	C3	−0.03	−0.16
	C4	−0.21	−0.21
	C5	0.04	−0.12
	C6	−0.28	−0.20
	H8	0.14	**0.27**
	H9	0.14	0.24
	H10	0.16	0.23
	H11	0.13	0.22
	H12	0.17	0.22
m-$AlCl_3-C_7H_8$	C1	0.27	0.00
	C2	−0.19	−0.16
	C3	−0.03	**−0.44**
	C4	−0.07	−0.16
	C5	−0.16	−0.19
	C6	−0.11	−0.13
	H8	0.16	0.24
	H9	0.13	**0.27**
	H10	0.14	0.24
	H11	0.16	0.23
	H12	0.16	0.22
p-$AlCl_3-C_7H_8$	C1	0.47	0.07
	C2	−0.33	−0.20
	C3	0.01	−0.13
	C4	−0.14	**−0.47**
	C5	0.01	−0.14
	C6	−0.33	−0.21
	H8	0.18	0.23
	H9	0.13	0.24
	H10	0.14	**0.27**
	H11	0.13	0.24
	H12	0.18	0.23

previous study of uncatalyzed toluene chlorination, different levels of theory were compared,[1] and on the basis of those results, it was felt that the present calculations would be sufficiently accurate. Furthermore, no corrections were made for basis set superposition error (BSSE) because it is not expected that it will change the relative energies of the species significantly. Ball[15] reported that in the case of water complexation with $AlCl_3$ at the MP2/6-31G(d,p) level of theory the correction for BSSE lowered the energy of formation by ca. 2.4 kcal mol^{-1} (10 kJ mol^{-1}). The primary purpose of the present calculations is to determine what species might be present during catalytic chlorination and to obtain a preliminary assessment of their relative stabilities. If subsequent analyses are performed seeking to determine reaction pathways and accurately assess associated energetics, it will likely be necessary to compare to results obtained using higher levels of theory.

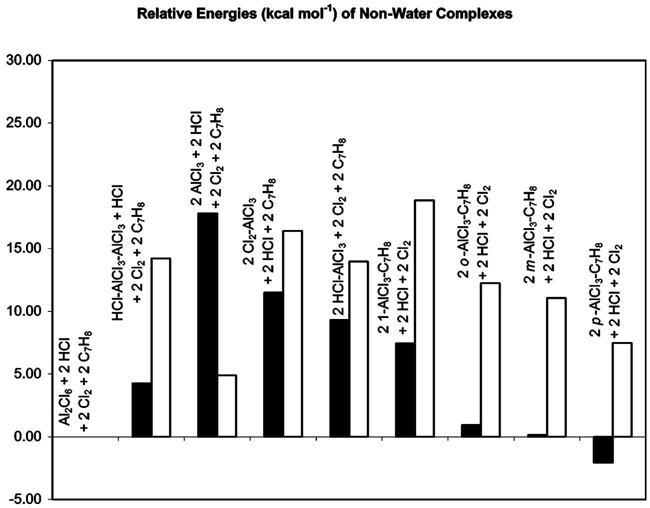

Figure 8. Relative zero-point corrected energies (black) and free energies (white) of species that might form during toluene chlorination in the absence of moisture.

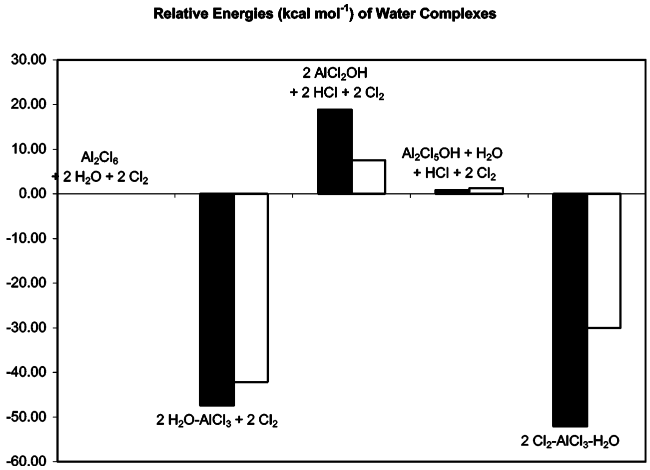

Figure 9. Relative zero-point corrected energies (black) and free energies (white) of species that might form during toluene chlorination in the presence of moisture.

TABLE 10: Dissociation Energy of Aluminum Chloride Dimer at Varying Solvent Dielectric Constants as Calculated Using the Polarized Continuum Model without Correction for ZPE

dielectric	ΔE ($Al_2Cl_6 \rightarrow 2AlCl_3$)
2.379	18.77
5	17.55
10	16.85
15	16.60
20	16.46
25	16.38
30	16.32
35	16.28
40	16.25

In the aforementioned study of uncatalyzed toluene chlorination, it was seen that the simple polarized continuum model of solvation was sufficient to account for observed solvent effects, at least at low dielectric constants.[1] Here it has proven necessary to consider specific interactions between molecules, while still applying the polarized continuum model, as well. For example, the experimental data indicate that in the absence of solvent the aluminum chloride dimer does not dissociate into monomers but that addition of a small amount of water favors such dissociation. Simply increasing the dielectric constant used in the polarized continuum model is not sufficient to mimic this behavior. This is shown in Table 10 which lists the calculated dissociation energy at several different dielectric constants. The dielectric constant used in the polarized continuum model can be increased from its value in toluene (2.379) to a value of 40, and the dissociation energy is not significantly affected. In contrast, Figure 9 shows that when interaction with water is explicitly included, dissociation (to an $H_2O-AlCl_3$ complex) is strongly favored.

All calculations here were for molecules dissolved in toluene. Many of the same molecules have been studied in the vapor phase either computationally or experimentally. The results from such studies provide a useful basis of comparison for the present results. As expected, calculated geometric parameters vary depending upon the basis sets used and the level of theory applied, and there is also some smaller variation in experimentally determined geometric parameters. Several authors have considered $AlCl_3$.[15−21] It appears to be generally accepted that the molecule is planar with D_{3h} symmetry. Computational Al−Cl distances vary from 2.05 to 2.164 Å. Experimentally, distances between 2.06 and 2.068 Å have been reported. The Al−Cl distance found here for $AlCl_3$ dissolved in toluene (2.085 Å) is in good agreement with these other studies as is the planar, trigonal geometry that resulted from the current geometry optimization. Wilson et al.[17] report unscaled vibrational frequencies at the HF/6-31G* level of 156.6, 213.5, 399.5, and 642.3 cm^{-1}, whereas Ystenes et al.[18] give scaled frequencies of 148−153, 204−214, 381−383, and 614−628 cm^{-1}, depending upon the level of theory. Here, for $AlCl_3$ in toluene solution, frequencies (unscaled) of 138.4, 187.9, 372.6, and 596.4 cm^{-1} were calculated. The (unscaled) ZPE calculated here for $AlCl_3$ in toluene, 2.90 kcal mol^{-1}, falls between values reported for vapor phase $AlCl_3$,[19,22] 2.82 and 3.11 kcal mol^{-1}.

The Al−Cl(bridging) distance, Al−Cl(terminal) distance, and Al−Cl(bridging)−Al angle are key geometric parameters of Al_2Cl_6. Computational findings (at various levels of theory)[21,23] give values for the Al−Cl(bridging) distance that range from 2.188 to 2.402 Å compared to experimental values[20,23] between 2.25 and 2.252 Å. The value found here for Al_2Cl_6 in toluene is 2.283 Å. For the Al−Cl(terminal) distance, calculated distances range from 1.998 to 2.163 Å, compared to experimental values between 2.061 and 2.065 Å. The value found here, in toluene, is 2.091 Å. Experimental Al−Cl(bridging)-Al angles are 89 and 90°, compared to calculated values from 87.6 to 95.7° and a value, here, in toluene of 90.4°. Again, the geometric parameters of Al_2Cl_6 from the present study fall within the range calculated in previous studies of its gas-phase structure.

$AlCl_4^-$ has a tetrahedral geometry. The Al−Cl distance found here for this species in toluene, 2.166 Å, compares favorably with values calculated in other studies,[18,21] 2.15−2.245 Å, and is a little greater than the experimental value of 2.12 Å. An $HCl-AlCl_3$ complex has been examined in at least three computational studies[17,21,22]. The Al−Cl(terminal) distances are not all equal for such a complex due to interactions with the HCl. Previous studies have indicated 2.08 or 2.09 Å for the one shorter Al−Cl(terminal) distance and 2.09 or 2.095 Å for the two longer Al−Cl(terminal) distances. The Al−Cl(H) distance has been calculated between 2.52 and 2.718 Å and the H−Cl distance as between 1.26 and 1.284 Å. The present results, Table 4, are in reasonable agreement. Finally, there has been at least one study of an $H_2O-AlCl_3$ complex which found Al−Cl distances between 2.095 and 2.119 Å and Al−O distances between 1.957 and 1.985 Å. The present result, calculated for this complex in toluene solution indicates comparable Al−Cl distances with a slightly smaller Al−O distance.

The energetics of Al_2Cl_6, $HCl-AlCl_3$, and $H_2O-AlCl_3$ dissociation have also been reported for gas-phase calculations. In addition, for Al_2Cl_6, the heat of dissociation has been estimated from thermodynamic equilibrium data. Table 11 compares these results to those found in the present study for the same species in solution in toluene. For each complex, the gas phase and solution phase energies are comparable. However, there is a very wide range of values for the dissociation of the dimer into monomers. The present results fall within the range reported in other studies, but the disparity in the values and the large difference between the calculated value and the experimental value suggests that this energy should be regarded with caution and that the true value may be significantly greater. In Figures 7−9, energies are reported with respect to the aluminum chloride dimer, Al_2Cl_6. The data in Table 11 suggest that perhaps these relative energies should be taken as lower bounds on the associated transformations.

TABLE 11: Calculated Dissociation Energies of Aluminum Chloride Species

reaction	state	dissociation energy (kcal mol^{-1})	ref
$Al_2Cl_6 \rightarrow 2\ AlCl_3$	gas	29.4[a]	24
	gas	17.6−70.7	18
	gas	31.8	21
	gas	19.7	this study
	toluene solution	17.8	this study
$HCl-AlCl_3 \rightarrow HCl + AlCl_3$	gas	5.5	17
	gas	7.8	21
	toluene solution	4.2	this study
$H_2O-AlCl_3 \rightarrow H_2O + AlCl_3$	gas	30.2	15
	toluene solution	32.6	this study
$Cl_2-AlCl_3 \rightarrow Cl_2 + AlCl_3$	gas	3.1	this study

[a] This is an experimental enthalpy change derived from equilibrium measurements.

Stable complexes of $AlCl_3$ with toluene were identified and are shown in Figure 6. Very similar complexes between benzene and $AlCl_3$ have been described by Tarakeshwar et al.[13,14] Here, the complexing $AlCl_3$ can be situated over any of the ring carbons. In all cases, the interaction is sufficiently strong to distort the $AlCl_3$ unit from its planar structure so that the central aluminum atom projects toward the carbon in question while the three chlorine atoms are pushed back away from the ring. The complex with the $AlCl_3$ at the 1-position is significantly less stable than the others, probably due to steric interactions with the nearby methyl group.

As already noted, these calculations were undertaken to examine what species might be present during the solvent-free chlorination of toluene using aluminum chloride as a catalyst. Lebedev and Baltadzhi[5] studied chlorination of toluene using aluminum chloride as catalyst. These studies were conducted in carbon tetrachloride solvent and also included nitrobenzene which was added to homogenize the reaction mass. The authors noted that the reactivity increased more than 20-fold when the nitrobenzene was added compared to previous studies where it was not added. The activation energy was reported to equal 5.4 kcal mol^{-1} over the temperature range from 278 to 293 K. Olah et al.[8] noted that the presence of any small particulate solids (incompletely dissolved aluminum chloride) affected the results of their kinetic experiments. They studied the reaction using an equimolar mixture of $AlCl_3$ and CH_3NO_2 as the catalyst but did not report an activation energy or rate coefficient. Caille and Corriu[6,7] studied toluene chlorination using aluminum chloride, but again in nitrobenzene solution. They noted that the catalyzed reaction was rapid (85% complete within 5 min at 288 K). From the data they present at 273 and 288 K, it is possible to estimate the apparent activation energy to be 8.3 kcal mol^{-1}.

It was observed in the present study that when aluminum chloride was added to a toluene−chlorine mixture in a dry atmosphere and without any other solvents, the resultant catalytic activity at room temperature is minimal. When conducted in an open atmosphere, but otherwise the same experiment, the catalytic activity is visibly apparent. The latter result agrees with Caille and Corriu's finding that the reaction is rapid at 288 K. In each of the reported studies, a solvent has been used, and there is evidence suggesting that the solvent significantly affects the reaction rate. In the experiments done here, it was necessary to allow the presence of moisture in order to observe catalytic activity.

In short, the experimental evidence is consistent with the assertion, that when dry aluminum chloride is added to neat toluene, it exists in the dimeric form and that the dimeric form is not catalytically active. The experimental results are also consistent with the hypothesis that some agent is needed to facilitate the dissociation of the dimer into a more catalytically active, monomeric form. Atmospheric moisture is believed to be the agent that effected this activation of the catalyst. Hence, the fuming that was observed when the experiment was performed in an open atmosphere may be related to reaction of the dimeric aluminum chloride with water. One may speculate that other solvents, like nitromethane or nitrobenzene, may similarly activate aluminum chloride.

The results shown in Figure 7 suggest that an ionic pathway is quite unlikely when chlorination takes place in the absence of a solvent. This is not particularly surprising in light of the similar results for the uncatalyzed chlorination reaction.[1] The energies required to form ionic species in toluene are simply too great; they are much greater than the activation energy for the catalyzed reaction (5.4−8.3 kcal mol^{-1}). It does not seem likely that the small amount of moisture that leads to activation of the catalyst is sufficient to stabilize ionic species such as $AlCl_4^+$ or $AlCl_4^-$.

Figure 8 shows relative energies of species which might form in the absence of water. First, it can be noted that dissociation of Al_2Cl_6 to $AlCl_3$ is unfavorable. Even if the resulting monomers form complexes with Cl_2, the stabilization afforded by such complexation is not sufficient to render the overall process energetically favorable. Attempts to identify complexes between Cl_2 and nondissociated Al_2Cl_6 were unsuccessful. The other possibility for complexation is between the aluminum chloride and toluene. The figure suggests that this is energetically more feasible, at least for complexation at the ortho, meta, and para positions. Noting that no reaction is observed in the absence of moisture, one may surmise that either these complexes are not catalytically significant (i.e., they form but do not lead to reaction) or that a significant activation barrier exists to preclude their formation. Given the existence of two bridging chlorine atoms in the dimer structure, it seems probable that such a barrier might exist.

Routes to dissociation of the dimer might involve insertion of a species into one of the bridging chlorine bonds. As noted, no interaction was found for Cl_2, and it seems improbable that toluene would insert in such a manner. Another possiblility would involve the insertion of HCl into the bridging bonds of the dimer. In principle, HCl can be expected to be present eventually via its generation in the uncatalyzed chlorination reaction. (The experiments conducted here were likely too short in duration for the generation of an appreciable amount of HCl given that the time scale for the uncatalyzed reaction is days compared to minutes for the catalyzed reaction.[1]) Indeed, the formation of an insertion compound, denoted as $HCl-AlCl_3-AlCl_3$ here, is seen in Figure 8 to be endothermic by less than 5 kcal mol^{-1}. Subsequent reaction of this species with HCl to yield two $HCl-AlCl_3$ complexes is endothermic by an additional 5 kcal mol^{-1}. This appears to be a viable pathway for the dissociation of the Al_2Cl_6 dimer. If it is, then it most likely was not observed in the drybox experiments because an insufficient amount of HCl was present. It would be informative to probe this possibility experimentally either by waiting to see if the catalyst was slowly activated through the generation of HCl from uncatalyzed chlorination or by adding anhydrous hydrochloric acid to a dry mixture of toluene, chlorine, and aluminum chloride and observing whether it renders the catalyst active.

In the presence of moisture, the catalyst becomes very active catalytically, and Figure 9 indicates that the formation of $H_2O-AlCl_3$ complexes is also very favorable energetically. Thus, in the presence of water, there is clearly a strong driving force for the dissociation of the dimer. One possibility is that water might insert directly into the bridging bonds of the dimer. This would be expected to lead directly to the formation of the stable $H_2O-AlCl_3$ complexes. The problem then becomes one of explaining the observed catalytic activity. It seems highly unlikely that the $H_2O-AlCl_3-Cl_2$ species shown in Figure 5b can serve as an electrophile to attack toluene. In particular, there is little energetic stabilization against dissociation (<2.4 kcal mol^{-1}), the NBO analysis does not find a bond to the Cl_2 molecule, and an examination of the molecular orbitals fails to find any orbital that places electron density between the chlorine molecule and the aluminum. Furthermore, the chlorine molecule does not appear to be polarized (Table 7). In short, although an $H_2O-AlCl_3$ complex is apparently very stable, it does not appear capable of activating Cl_2 directly.

In contrast, the Cl_2-AlCl_3 complex does appear to be a potential electrophile for toluene chlorination. There is evidence of a weak bond between the aluminum atom and the chlorine molecule from the NBO analysis, in the distortion of the $AlCl_3$ unit and by visual inspection of the orbitals. Although the energetic stabilization against dissociation is nearly zero (Table 11), there does appear to be a slight positive charge on the chlorine molecule (Table 7) as expected in an electrophile.[3] One immediately notices, however, that it is quite unfavorable to generate a Cl_2-AlCl_3 complex from an $H_2O-AlCl_3$ complex (+29.4 kcal mol^{-1}). If $H_2O-AlCl_3$ complexes are produced by insertion of water directly into a dimer, it would not seem likely that Cl_2-AlCl_3 complexes would ever form, and so it would be difficult to explain the observed catalytic activity.

It is alternatively possible that some of the water reacts with the dimer to give Al_2Cl_5OH and HCl. The calculations indicate that the energy change associated with this process is negligible (Figure 9). This would generate HCl which could then insert into the bridging bonds of the dimer as already described, leading to $HCl-AlCl_3$ complexes. The generation of an electrophilic Cl_2-AlCl_3 complex from an $HCl-AlCl_3$ complex is much less demanding (+1.1 kcal mol^{-1}) than its generation from an $H_2O-AlCl_3$ complex (+29.4 kcal mol^{-1}). Of course, in the presence of additional moisture, a large driving force would remain for the conversion of this electrophile into an $H_2O-AlCl_3$ complex. Indeed, given sufficient water, the computational results would suggest that all of the catalyst would be "tied up" in the form of these complexes, and again, no catalytic activity would be observed. The reason for the observed catalytic activity, then, according to this model, must be that there was not a sufficient amount of water present. This suggests that an experimental study of the quantitative effect of water concentration upon activity might also be quite revealing. That is, there may exist an optimum amount of water for promoting catalytic chlorination: too little, and the activity is low because of insufficient concentration of the monomeric Cl_2-AlCl_3 electrophile; too much, and the activity is low because most of the $AlCl_3$ is tied up in $H_2O-AlCl_3$ complexes.

To reiterate, a possible reaction pathway for the situation where toluene is in excess and the amount of moisture is very small initially involves a reaction of the Al_2Cl_6 dimer with water, reaction 1. This generates HCl (which could also be generated much more slowly by the uncatalyzed chlorination reaction) that can insert into an Al_2Cl_6 dimer, reaction 2 generating a species such as that shown in Figure 3b. Reaction, as in reaction 3, of this $HCl-AlCl_3-AlCl_3$ complex with another HCl molecule completes the catalyst activation/initiation part of the pathway. Steps 4 and 5 then comprise the propagation portion of the mechanism. Finally, the calculated energetics indicate that if too much moisture is present, the majority of the catalyst will exist in the form of very stable $H_2O-AlCl_3$ complexes, and consequently the catalytic activity will be low.

$$Al_2Cl_6 + H_2O \leftrightarrows Al_2Cl_5OH + HCl \tag{1}$$

$$Al_2Cl_6 + HCl \leftrightarrows HCl-AlCl_3-AlCl_3 \tag{2}$$

$$HCl-AlCl_3-AlCl_3 + HCl \leftrightarrows 2\ HCl-AlCl_3 \tag{3}$$

$$HCl-AlCl_3 + Cl_2 \leftrightarrows Cl_2-AlCl_3 + HCl \tag{4}$$

$$Cl_2-AlCl_3 + C_7H_8 \leftrightarrows C_7H_7Cl + HCl-AlCl_3 \tag{5}$$

$$HCl-AlCl_3\ (\text{or } Cl_2-AlCl_3) + H_2O \leftrightarrows H_2O-AlCl_3 + HCl\ (\text{or } Cl_2) \tag{6}$$

The $AlCl_3$-toluene complexes are interesting, and it remains unclear whether they are catalytically significant. The atomic charges derived from the ESP are not particularly revealing, but those from the NBO analysis do show a few systematic trends which have already been noted. In contrast to the $1\text{-}AlCl_3-C_7H_8$ complex, the ortho-, meta-, and para complexes each show a significantly more negative charge on the associated ring carbon. One could speculate that this would allow attack on the affected carbon (from the opposite side of the aromatic ring) by a weaker electrophile. At the same time, however, the hydrogen that is bonded to the affected ring carbon is more positively charged and it projects out of the ring on the side that such an attack would occur. In any case, the relative stability of such complexes may suggest that their concentration may be comparable to the water and chlorine complexes, especially under circumstances where the amount of toluene is greatly in excess of the latter molecules.

As already described, when chlorination was conducted under a dry nitrogen atmosphere within a glovebox, no catalytic activity was apparent. This has been attributed to the high stability of Al_2Cl_6 dimers. In that same experiment, some of the catalyst adhered to the neck of the flask and discolored over time. Subsequent introduction of this discolored material into the reaction medium resulted in visibly apparent reaction. There are at least two possible explanations for this observation. The first explanation would suggest that there might have been moisture adsorbed on the surface of the glass flask; it was not baked out in a dry environment prior to its introduction to the glovebox. The discoloration then can be attributed to chemical reaction of the Al_2Cl_6 dimers with this moisture, leading to catalyst activation as already described. Alternatively, the observed activity may be the result of heterogeneous catalysis, as described by Olah et al.[8] There is insufficient information, at present, to favor either of these explanations over the other. The most important point for present purposes is that the vast majority of the aluminum chloride did go into the toluene solution at the outset, and this material was not catalytically active.

In summary, it has been observed that in the absence of moisture aluminum chloride is not initially active as a catalyst for toluene chlorination. This is probably because it exists as an Al_2Cl_6 dimer that is very stable. If moisture is present, the aluminum chloride is apparently quite active as a chlorination catalyst. It has been suggested here that moisture leads to the generation of HCl which then facilitates the dissociation of the dimer into complexed monomers. Of the species considered here, it would seem that a Cl_2-AlCl_3 complex is the most likely catalytically active electrophile. At the same time, an $H_2O-AlCl_3$ complex is much more favorable energetically, but it does not appear that it could form an effective catalytic electrophile. The calculations indicate that, in the absence of moisture, HCl might also be able to activate aluminum chloride catalytically. They also suggest that if too much water is present the catalyst would again be rendered inactive. The results highlight a need for additional, more quantitative, experiments to study the effect of H_2O and HCl concentrations upon the activation and subsequent catalytic activity of aluminum chloride for toluene chlorination in the absence of other solvents and additives. Additional calculations seeking to establish activation barriers for critical steps in the scheme postulated here would also be beneficial.

Conclusions

It was observed experimentally that aluminum chloride is not an effective catalyst for toluene chlorination if it is used in the absence of solvents or atmospheric moisture. DFT calculations were used to identify a number of stable species which might be present under chlorination conditions in the absence of solvent and to estimate their relative stability. Ionic intermediates were found to be highly unlikely due to the high energies required for their formation. It is suggested that in the absence of moisture and product HCl, the predominant form of the catalyst is Al_2Cl_6, which is not catalytically active. Water is proposed to react with this dimeric aluminum chloride, generating HCl, and subsequently a Cl_2-AlCl_3 complex which is believed to serve as the catalytic electrophile during toluene chlorination in the absence of a solvent. Stable complexes between $AlCl_3$ and toluene were also identified, but it is not clear whether they are catalytically significant. Finally, the calculations indicate that $H_2O-AlCl_3$ complexes are very stable, suggesting that too much water would kill the catalyst's activity.

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