The Mechanism of Friedel-Crafts Chlorination Historically Reconsidered

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Abstract

This short review proposes a revision to the currently accepted textbook mechanism for the direct Friedel-Crafts chlorination of benzene. After briefly reviewing the history of Friedel-Crafts chemistry and the origins of the current textbook mechanism for the direct chlorination of benzene, it is pointed out how this mechanism is at variance with the predictions of both generalized Lewis acid-base chemistry and simple frontier orbital theory, which require that dichlorine should function as a sigma antibonding electron-pair acceptor (σ^*-EPA) or electrophile (Lewis acid) rather than as a pi antibonding electron-pair donor (π^*-EPD) or nucleophile (Lewis base). A modification of the currently accepted mechanism consistent with these concepts is then proposed. After reviewing the debates over the structure of the active catalyst, previous proposals for the modification of the current mechanism, and other examples in which the dihalogens function as σ^*-EPA electrophiles, the revised mechanism is evaluated using DFT calculations.

Keywords: Friedel-Crafts, chlorination, electrophilic aromatic substitution, historical perspective, mechanism

1. Introduction

One of the original goals of most journals dealing with chemical education was, and hopefully still is, to alert teachers to potential textbook errors and to provide evidence for their correction. This paper deals with such a potential error in the currently accepted mechanism for Friedel-Crafts chlorination of benzene--a topic that appears in all undergraduate organic chemistry textbooks. We will first summarize the history of the current textbook mechanism, and then present the theoretical, experimental, and computational reasons for why this mechanism should be revised. We will also update teachers on the most current Lewis acid-base terminology that can be used when discussing organic mechanisms. This paper also gives teachers the opportunity to explain to students that mechanisms "are not written in stone", but rather change as more data are collected and more is learned about any transformation.

2. Historical Background

In 1877, the French chemist Charles Friedel (Figure 1), and his American collaborator James Mason Crafts (Figure 2), first reported the ability of aluminum trichloride to catalyze organic reactions (Friedel & Crafts, 1877a). Though their initial focus was on the application of the new catalyst to alkylation, it was soon extended to the catalysis of a wide variety of other processes, so that by 1941 it would take a 972-page monograph to summarize all of the various applications (Thomas, 1941). By 1963, a similar attempt to survey the pertinent literature would require six volumes and more than 5000 pages (Olah, 1963). Though Friedel and Crafts soon discovered that other metal halides, such as iron trichloride, would also work as catalysts, aluminum trichloride has remained one of the most effective (Friedel & Crafts, 1877b).
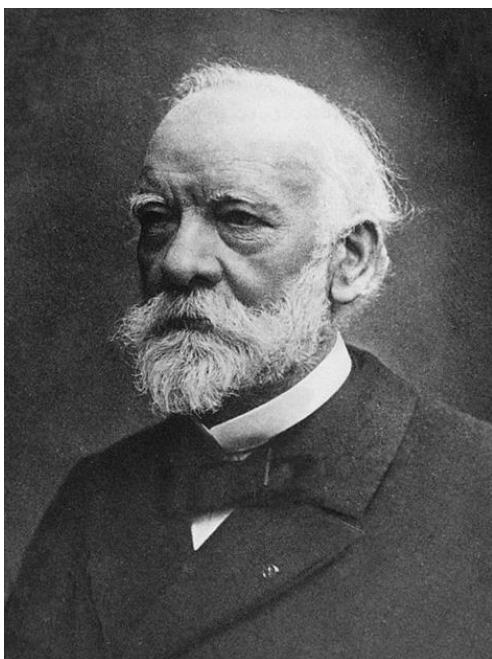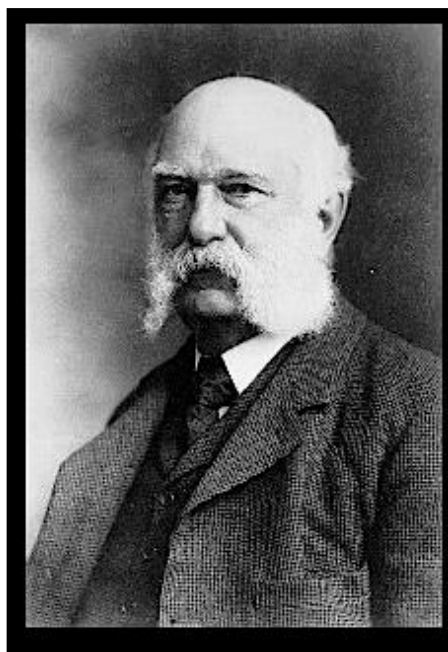
Figure 1. Charles Friedel (1832-1899)   Figure 2. James Mason Crafts (1839-1917)

It was not until 1898 that Mouneyrat and Pouret first reported that aluminum trichloride could catalyze the direct chlorination of benzene at room temperature (Mouneyrat & Pouret, 1898):

$$Cl_2 + C_6H_6 \rightarrow C_6H_5Cl + HCl \qquad [1]$$

Though most textbooks restrict the use of the adjective "Friedel-Crafts" to the alkylation and acylation reactions originally studied by them, a generalized definition proposed by Olah would apply the term to reaction 1 as well (Olah, 1973):

... today we consider Friedel-Crafts type reactions to be any substitution, isomerization, elimination, cracking, polymerization, or addition reactions taking place under the catalytic effect of Lewis acid type acidic halides (with or without co-catalyst) or proton acids.

Mouneyrat and Pouret also proposed a two-step reaction mechanism to account for reaction 1 that, by today's standards, would be considered highly improbable:

$$C_6H_6 + AlCl_3 \rightarrow C_6H_5\text{-}AlCl_2 + HCl \qquad [2]$$

$$C_6H_5\text{-}AlCl_2 + Cl_2 \rightarrow C_6H_5Cl + AlCl_3 \qquad [3]$$

The currently accepted mechanism, which appears in many introductory organic textbooks, involves the generation of a Cl_2-$AlCl_3$ complex and this is followed in some textbooks by the formation of a Cl^+ electrophile (Klein, 2021; Mullins, 2021; Loudon & Parise, 2021; Karty, 2018; Brown, Iverson, Anslyn, & Foote, 2018; Wade & Simek, 2017; Ege, 2004; Streitwieser, Heathcock, & Kosower, 1992):

$$Cl_2 + AlCl_3 \rightarrow Cl\text{-}Cl\text{-}AlCl_3 \rightarrow AlCl_4^- + Cl^+ \qquad [4]$$
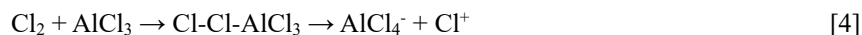
This electrophile is then attacked by the nucleophilic benzene ring to form a cationic chloronium $C_6H_6Cl^+$ intermediate:

$$Cl^+ + C_6H_6 \rightarrow C_6H_6Cl^+ \qquad [5]$$

followed by removal of one of its hydrogens as a proton, via the assistance of the tetrachloroaluminate anion formed in reaction 4, to give monochlorinated benzene, hydrogen chloride, and the regenerated catalyst:

$$C_6H_6Cl^+ + AlCl_4^- \rightarrow C_6H_5Cl + HCl + AlCl_3 \qquad [6]$$
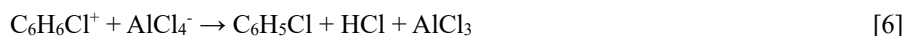
As required of all reaction mechanisms, these three steps sum to give the net reaction in equation 1.

Though we have been unable to unambiguously pin down who first proposed this mechanism, it begins to appear in introductory organic textbooks in the late 1930's when they first began employing the newer electronic theory of organic chemistry and the use of Lewis dot diagrams. Thus, in the 1937 textbook by Frank Whitmore, we find reaction 4 represented as shown in Figure 3 (Whitmore, 1937).
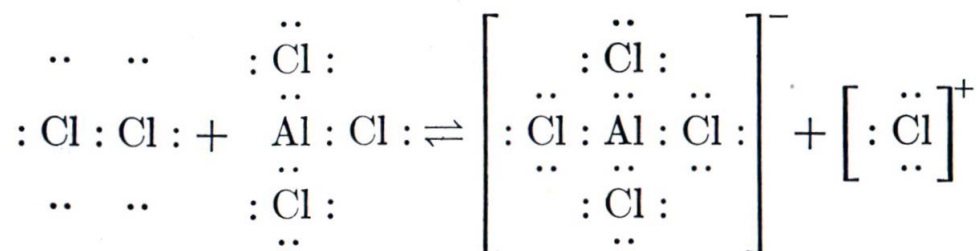
Figure 3. Whitmore's 1937 Lewis dot representation of equation 4

3. Some Theoretical Difficulties

In 1980, the first author of this paper published (Jensen, 1980) an advanced monograph on the Lewis acid-base definitions based on the generalized MO versions of these concepts first proposed by Mulliken in the 1950's (Mulliken, 1969). This update expanded the traditional definition of a Lewis base as a species interacting via a filled nonbonding orbital, and thus functioning as a <u>n</u>onbonding <u>e</u>lectron-<u>p</u>air <u>d</u>onor or n-EPD agent, to use Gutmann's proposed acronyms,[*] so as to also include π-EPD and σ-EPD bases or agents as well (Gutmann, 1971). Likewise, they expanded the traditional definition of a Lewis acid as a species interacting via an empty nonbonding orbital, and thus functioning as a <u>n</u>onbonding <u>e</u>lectron-<u>p</u>air <u>a</u>cceptor or n-EPA agent, so as to also include π*-EPA and σ*-EPA agents. As shown in Table 1, this leads to the formation of nine possible kinds of acid-base or electron-pair donor-electron pair acceptor (EPD-EPA) complexes. In the frontier orbital extension of the MO definitions, the donor orbital on the EPD usually corresponds to the highest-occupied MO or HOMO and the acceptor orbital on the EPA usually corresponds to the lowest-unoccupied MO or LUMO (Fleming, 1976).

Table 1. The nine possible kinds of EPD-EPA complexes predicted by the extended MO definitions of Lewis acids and bases

		EPA		
		n	π^*	σ^*
EPD	n	$n \cdot n$	$n \cdot \pi^*$	$n \cdot \sigma^*$
	π	$\pi \cdot n$	$\pi \cdot \pi^*$	$\pi \cdot \sigma^*$
	σ	$\sigma \cdot n$	$\sigma \cdot \pi^*$	$\sigma \cdot \sigma^*$

Applying these concepts to the Cl_2 molecule quickly reveals that its HOMO or donor orbital is a π*-antibonding orbital (Figure 4) and not a nonbonding lone pair as assumed in the simple Lewis dot picture (Jorgensen & Salem, 1973). This means that in equation 4, dichlorine is acting as an improbable π*-EPD and the aluminum trichloride monomer as an n-EPA. Consequently, removal of electron density from the donor orbital of Cl_2 should lead not to cleavage of the Cl–Cl bond, as postulated in reaction 4, but rather to its strengthening.

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[*] We prefer Gutmann's acronyms to either the terms Lewis acid-base or the terms electrophile-nucleophile. The terms acid and base have been overworked and refer to multiple definitions. Likewise, the terms electrophile and nucleophile, as originally defined by Ingold, also included oxidizing and reducing agents, and there is also ambiguity as to whether they refer to the kinetics rather than the thermodynamics of the reactions in question, not to mention their regrettable anthropomorphic overtones. For teachers who still prefer to use the terms Lewis acid-base or electrophile-nucleophile, the following substitutions can be made when discussing with your students: an electron pair donor (EPD) = a nucleophile = a Lewis base; and an electron pair acceptor (EPA) = an electrophile = a Lewis acid.
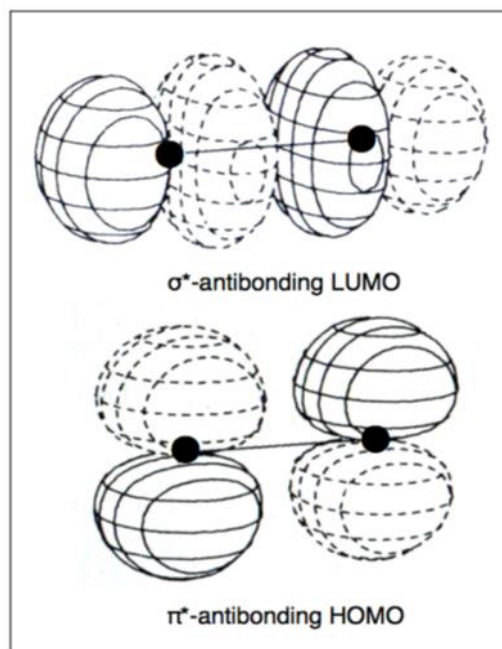
Figure 4. The acceptor and donor orbitals for the dichlorine molecule

The two kinds of striping indicate the positive and negative lobes. The diagrams were originally for F_2 but the same MO sequence and shapes also apply to Cl_2.

On the other hand, the LUMO or acceptor orbital on Cl_2 is a σ*-antibonding orbital (Figure 4) and transferring electron density to this orbital will lead to the required bond cleavage (Mulliken & Person, 1969). The most likely donor source for this would not be the $AlCl_3$ catalyst but rather the π-bonding system of the benzene molecule itself. Thus reaction 7 becomes the initial step:

$$C_6H_6 + Cl_2 \rightarrow C_6H_6^{\cdots}Cl^{\delta+\cdots\cdots}Cl^{\delta-} \qquad [7]$$

in which benzene functions as a π-EPD and dichlorine as a σ*-EPA. Indeed π-EPD--σ*-EPA charge-transfer complexes of this sort formed between benzene and the various dihalogens, in the absence of the requisite catalyst for halogen substitution, have been known at least since the 1940's (Benesi & Hildebrand, 1948; Ferguson, 1956), and are supported by the value (-7.50 kcal/mol) for the heat of solution of dichlorine in benzene (Lohse & Deckwar, 1981). In addition, the dichlorine-benzene complex has been observed spectroscopically in solution, in the solid state, and in a matrix (Fredin & Nelander, 1974; Anthosen & Moller, 1977). In each case, as shown in Figure 5c, the dichlorine interacts with the benzene ring over one of the edges and not over the center of the ring. This interaction polarizes and weakens the Cl–Cl bond.

Whether the degree of donation is sufficient to cleave the Cl–Cl bond, or merely to weaken and polarize it, is unknown. In either case, the incipient chloride anion is then removed by the aluminum trichloride catalyst to form the cation and a tetrachloroaluminate anion. These have been represented as an ion pair in reaction 8 because it is unlikely that free dissociated ions would form in a non-polar solvent like benzene.

$$C_6H_6^{\cdots}Cl^{\delta+\cdots\cdots}Cl^{\delta-} \;+\; AlCl_3 \;\rightarrow\; [C_6H_6Cl]^+ \; [AlCl_4]^- \qquad [8]$$

Finally, the ion pair undergoes a proton transfer to give neutral monochlorobenzene, hydrogen chloride, and the regenerated catalyst:

$$[C_6H_6Cl]^+ \; [AlCl_4]^- \;\rightarrow\; C_6H_5Cl + HCl + AlCl_3 \qquad [9]$$

Once again, these three steps sum to give the net reaction in equation 1. See Figure 5 for a comparison of the currently accepted mechanism and our proposed mechanism.
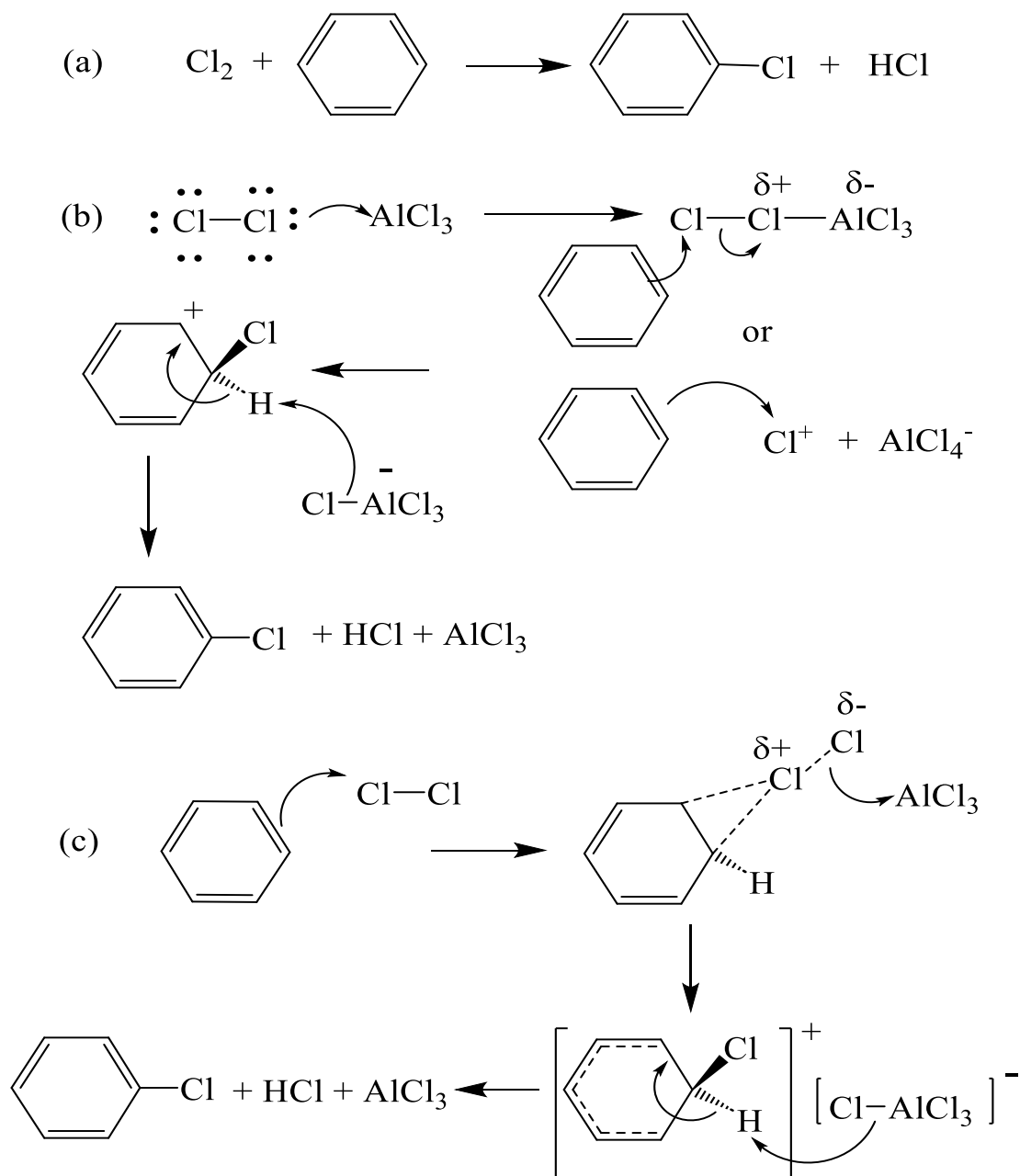
Figure 5. (a) net reaction of benzene and Cl$_2$; (b) the currently accepted mechanism for the net reaction in which Cl$_2$ is a nucleophile/Lewis base; and (c) our proposed mechanism for the net reaction in which Cl$_2$ is the electrophile/Lewis acid

4. Experimental Evidence and the Nature of the Catalyst

It has long been known that in benzene solutions aluminum trichloride is present as the Al$_2$Cl$_6$ dimer, rather than as the AlCl$_3$ monomer (Ely & King, 1951).   Why then have we persisted in using the monomer in equations 8 and 9? There are two reasons, one computational and the other experimental. Firstly, our density functional theory (DFT) calculations (see below) show that Cl$_2$ alone is unable to cleave the dimer due to the low EPD strength of its π^*-antibonding HOMO, as well as, the fact that the Al$_2$Cl$_6$ dimer is a very poor σ^*-EPA. Secondly, the experimental results of Spencer *et al.* on the direct Friedel-Crafts chlorination of toluene seem to suggest that water must be present in order to activate the catalyst (Spencer, Zhang, & Lund, 2005; Nesterov, Belen´kii, & Pivina, 2021; Galabov, Nalbantova, Schleyer, & Schaefer, 2016; Volkov, Timoshkin, & Suvoror, 2005). When they added the aluminum trichloride in the open air to a toluene solution saturated with Cl$_2$ gas, the rate of chlorination "increased tremendously." However, when the same experiment was performed under dry nitrogen in a glove box, no catalytic effect was observed. Since the fresh bottle of the aluminum trichloride fumed when opened in the atmosphere, but a second fresh bottle did not when opened in the glove box, the authors inferred that the humidity in the air played a role in activating the catalyst.

Though the hydrolysis reaction between water and aluminum trichloride should ideally lead to the formation of aluminum trihydroxide and hydrogen chloride:

$$AlCl_3 + 3H_2O \rightarrow \quad Al(OH)_3 + 3HCl \qquad [10]$$

in the presence of the small amounts of water found in the atmosphere one obtains instead a complex mixture of various aluminum hydroxide chlorides, oxide chlorides, oxide hydroxides, and even dialuminum trioxide. Spencer *et al.* attempted to use DFT calculations with a variety of postulated hydrolysis products in order to determine the mechanism of the catalyst activation. Among them was the formation of a stable 1:1 n-EPD--n-EPA complex between water and an $AlCl_3$ monomer that is strong enough to cleave the Al_2Cl_6 dimer and release a free unit of monomer (ΔE = -6.72 kcal/mol in benzene solution), which can then act as the catalyst – whence our continued use of the monomer in equations 8 and 9:

$$Al_2Cl_6 \quad + \quad H_2O \quad \rightarrow \quad H_2O \bullet AlCl_3 \quad + \quad AlCl_3 \qquad [11]$$
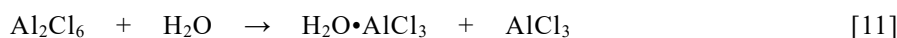
Evidence for this initial $H_2O \bullet AlCl_3$ complex has also been obtained from matrix-isolation studies (Perlovskaya, Ogden, Shilina, Smirnov, & Rostovshchikova, 2001), *ab initio* calculations (Scholz, Stösser, & Bartoll, 1996), and thermochemical, electrochemical and spectroscopic characterization in benzene solutions (Molkov, Romm, Guryanova, Nokov, & Petrov, 1992).

Though the experimental results of Spencer *et al.* were observed for the Friedel-Crafts chlorination of toluene, this compound is sufficiently similar to benzene that there is little doubt that the same mechanism, if true, applies to both.

5. Some Anticipations

The formation of an initial π-EPD--σ*-EPA charge-transfer complex between an aromatic and a dibromine molecule has long been postulated for the room-temperature bromination of aromatics with electron donating substituents. However, this was for the case of reactions in water-ethanoic acid mixtures, sans Friedel-Crafts catalysis, rather than for direct catalytic halogenation in pure benzene (Robertson, 1954; Ferguson, 1955; Breslow, 1969). We have also discovered in a famous organic textbook from the 1960's what appears to be an image of the mechanism for the Friedel-Crafts bromination of benzene identical to that proposed in equations 7-9 for chlorination, though the accompanying text seems instead to describe the traditional mechanism given in equations 4-6 (Roberts & Caserio, 1964). Neither experimental nor theoretical arguments were provided to support the pictured mechanism, and despite being nearly 60 years old, it seems, as already noted, to have had a negligible influence on current organic texts.

6. Some Parallels

Yet another consequence of our proposed mechanism, also predicted by frontier orbital theory, is that the Cl_2 molecule should interact with the benzene π-system endwise, rather than edgewise, in order to provide positive overlap with a single lobe of the Cl_2 σ*-antibonding LUMO – a geometry also in keeping with the benzene-dihalogen complexes mentioned earlier (Ferguson, 1956).

This requirement of an endwise attack appears to also apply to a number of other halogenation reactions. Take, for example, the well-known reaction between dichlorine gas and water to produce a mixture of hypochlorous and hydrochloric acid:

$$H_2O: + Cl_2 \rightarrow H_2O:Cl^+ + Cl^- \rightarrow HOCl + HCl \qquad [12]$$

Here there is no doubt that water acts as an n-EPD through the lone pairs on its oxygen atom and the interaction is strong enough to cleave the Cl_2 molecule rather than just polarize it.

Even more pertinent is the classic mechanism for the bromination of ethene, as first described by Dewar in 1949 (Figure 6) (Dewar, 1949). Here, as with benzene, ethene functions as a π-EPD via its double bond and the Br_2 molecule again approaches endwise rather than edgewise, leading to a two-step, rather than a one-step concerted mechanism:
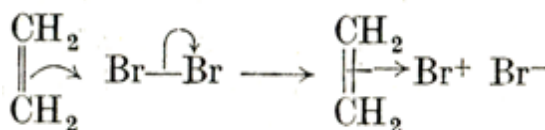
$$C_2H_4 + Br_2 \rightarrow C_2H_4Br^+ + Br^- \rightarrow C_2H_4Br_2 \qquad [13]$$

Figure 6. Dewar's 1949 mechanism for the first two steps in the bromination of ethene and his depiction of the intermediate bromonium π-complex[*]

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[*]This mechanism was first suggested in Roberts and Kimball; however, these authors postulated the formation of a three membered C_2Br^+ ring rather than a π-complex (Roberts & Kimball, 1937).

In this case, the interaction is also strong enough to cleave the Br_2 molecule rather than just polarize it, leaving a bromonium cation in which the Br^+ is attached to the ethene molecule via a three-centered, two-electron (3c-2e) C_2Br^+ bond, and generating a free Br^- ion. Dewar explicitly referred to this intermediate bromonium cation as an example of a so-called "π-complex".

This endwise attack for halogenation also provides a possible solution to the classic problem of the mechanism for the reaction between H_2 and I_2, much discussed by Pearson in his classic monograph on orbital symmetry (Pearson, 1975). Pearson gave a frontier orbital rationale for why the traditional concerted edgewise mechanism was forbidden (Figure 7). However, for some reason, he never considered the possibility of an endwise attack in which the I_2 molecule functioned as a σ*-EPA and the H_2 molecule as a σ-EPD, leading to an intermediate σ-EPD--σ*-EPA iodonium cation consisting of a 3c-2e H_2I^+ bond (Figure 8):

$$H_2 + I_2 \rightarrow H_2I^+ + I^- \rightarrow 2HI \qquad [14]$$
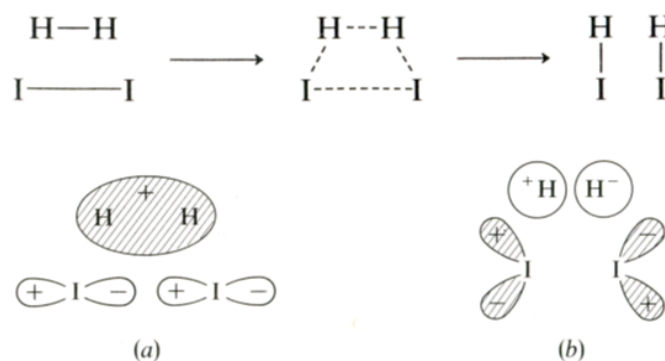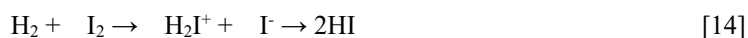

Figure 7. *Top:* The traditional depiction of the H_2-I_2 reaction involving a concerted edgewise addition of both I atoms simultaneously. *Bottom:* Pearson's frontier orbital analysis of why this type of edgewise addition is forbidden: (a) H_2 as a σ-EPD and I_2 as a σ*-EPA leading to zero net orbital overlap. (b) I_2 as an improbable π*-EPD and H_2 as a σ*-EPA leading to positive overlap but failure to cleave the I_2 bond. (Shading indicates a filled orbital, no shading indicates an empty orbital)
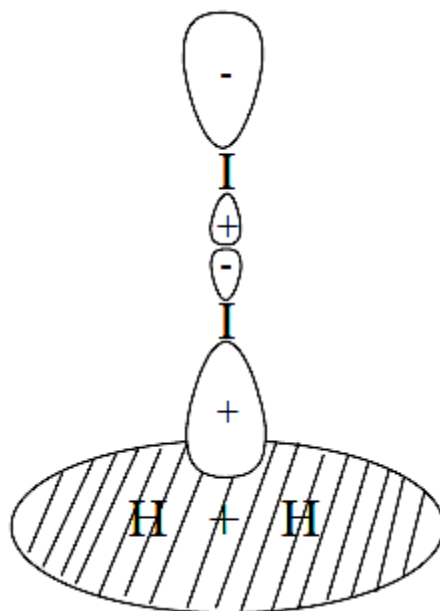

Figure 8. Endwise positive overlap of the σ*-antibonding LUMO of I_2 with the σ-bonding HOMO of H_2 leading to cleavage of the I_2 bond and formation of a 3c-2e H_2I+ intermediate. (Shading indicates a filled orbital, no shading indicates an empty orbital).

7. Supporting Calculations

Since most of the above reactions are believed to occur by a mechanism involving an endwise interaction with the

σ*-antibonding orbital of the dihalogen molecule and its eventual heterolytic cleavage, it is instructive to examine the polarization of the dichlorine molecule by its various reaction partners during the early stages of their interaction. To do this, we carried out DFT calculations for the intermolecular interactions of the molecules in question (Antle *et al*., 2022). The Gaussian calculations were carried out remotely at the Ohio Supercomputer Center with the B3LYP functional and the 6-311G++(*d*, 2*p*) basis set. Note that in the laboratory the reactions in question are typically carried out in the solution phase, *i.e.*, reaction 12 in water and reactions 7-9 in benzene. However, in this computational study, we examined the interactions of the isolated (*i.e.*, gas-phase) molecules in order to assess the pure stabilization effects of each intermolecular interaction without the influence of a dielectric solvent.

Table 2. Results of the DFT study of the interaction of water and dichlorine

Associated Molecules	ΔE (kcal/mol)	d (O $\rightarrow$ Cl) (Å)	d (Cl $\rightarrow$ H) (Å)	d (Cl $\rightarrow$ Cl) (Å)	$\tilde{\nu}$ (Cl—Cl) (cm^{-1})
Cl_2	-	-	-	2.05	516
$H_2O \rightarrow Cl_2$	-3.11	2.68	-	2.07	481
$Cl_2 \rightarrow H_2O$	-0.76	-	2.76	2.05	516
$H_2O \rightarrow Cl_2 \rightarrow H_2O$	-4.61	2.62	2.64	2.08	473

The arrows indicate the direction of electron flow from the EPD to the EPA. The bond frequencies are given in wave numbers.

As a test case, the results for reaction 12 between dichlorine and water are summarized in Table 2 and Figure 9. As may be seen, the interaction in which water acts the EPD and dichlorine as the EPA (data row 2) leads to a lowering of the energy (column 2), a lengthening of the Cl-Cl bond distance (column 5), and a lowering of its vibrational frequency (column 6), all of these changes being consistent with an incipient cleavage of the Cl-Cl bond as assumed above. In contrast, exploration of the reverse situation in which dichlorine acts as the EPD and water as the EPA (data row 3) leads to a much smaller interaction energy and little to no effect on either the Cl-Cl bond length or its vibrational frequency.
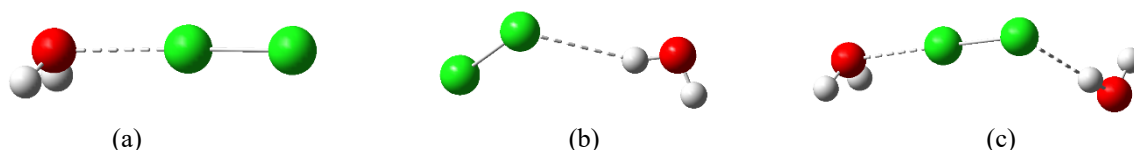

Figure 9. The interaction of water (oxygen is red and hydrogen is light grey) with chlorine (green)

(a) water is the EPD (Lewis base) and Cl_2 is the EPA (Lewis acid). (b) Cl_2 is the EPD (Lewis base) and water is the EPA (Lewis acid). (c) Cl_2 is an EPA for one water and an EPD for a second water.

Finally, in data row 4 we explored the effect of a synergic push-pull polarization in which the negative end of the incipient Cl_2 dipole produced by its EPA interaction with a water molecule simultaneously acts as an EPD toward a second water molecule, leading to incipient hydrogen bonding. As can be seen, the energy change (column 2) and the perturbations of both the Cl_2 bond length (column 5) and vibrational frequency (column 6) are even greater than those produced by a single water molecule alone. At the same time both the O-Cl and Cl-H distances (columns 3 and 4) decrease relative to those reported for the interaction with a single water molecule. Also of note is that the calculated orientations of the reactants show that when Cl_2 is the EPA, it approaches the oxygen atom of water endwise, but when it acts as the EPD it approaches cornerwise, both orientations being in keeping with the predictions of frontier orbital theory (recall Figure 4).

Table 3 and Figure 10 show the results of a similar calculation for reaction 7 between benzene and dichlorine. Once again, when benzene acts as the EPD and dichlorine as the EPA (data row 2) we see a lowering of the energy (column 2) and a perturbation of both the bond length (column 5) and vibrational frequency (column 6) consistent with an incipient weakening of the Cl-Cl bond, though the energy change is less than that for water, as might be expected for the difference between an n-EPD versus a π-EPD. Predictably, reversing the roles and allowing Cl_2 to be the EPD and benzene the EPA (data row 3) produces a significantly smaller interaction energy (column 2) and a negligible effect on the Cl_2 bond distance (column 5) and vibrational frequency (column 6).

Table 3. Results of the DFT study of the interaction of benzene and dichlorine

Associated Molecules	ΔE (kcal/mol)	d (C → Cl) (Å)	d (Cl → H) (Å)	d (Cl → Cl) (Å)	$\tilde{v}$ (Cl—Cl) (cm^{-1})
Cl_2	-	-	-	2.05	516
$C_6H_6 \rightarrow Cl_2$	-1.72	3.03	-	2.08	463
$Cl_2 \rightarrow C_6H_6$	-0.54	-	3.41	2.05	517
$C_6H_6 \rightarrow Cl_2 \rightarrow C_6H_6$	-2.38	3.02	3.32	2.08	461

The arrows indicate the direction of electron flow from the EPD to the EPA. The bond frequencies are given in wave numbers.
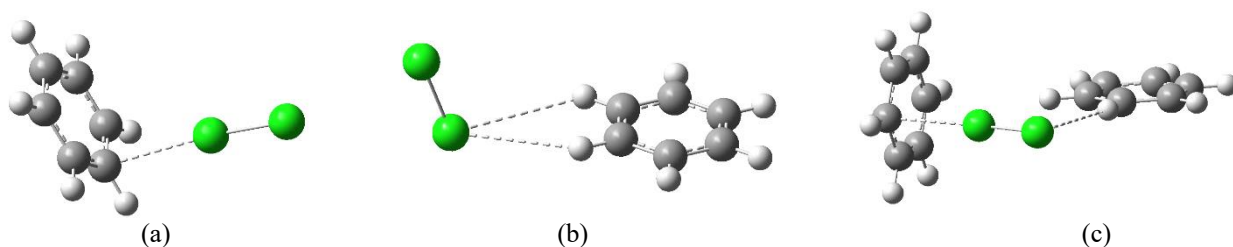

(a)   (b)   (c)

Figure 10. The interaction of benzene (carbon is dark gray and hydrogen is white) with chlorine (green)

(a) benzene is the EPD (Lewis base) and Cl_2 is the EPA (Lewis acid). (b) Cl_2 is the EPD (Lewis base) and benzene is the EPA (Lewis acid). (c) Cl_2 is an EPA for one benzene and an EPD for a second benzene.

In contrast to the case of reaction 12, a push-pull mechanism involving a simultaneous interaction with two benzene molecules (data row 4), though giving an improved interaction energy (column 2), produces only negligible perturbations of both the Cl_2 bond distance (column 5) and vibrational frequency (column 6) relative to that for only one benzene molecule, probably because of the low polarity of benzene and its negligible ability to function as an EPA in hydrogen bonding. Once more, in keeping with the predictions of frontier orbital theory, the computed orientations show that the Cl_2 molecule, when acting as a σ*-EPA, approaches the benzene molecule endwise, but when acting as a so-called π*-EPD, it approaches cornerwise.

Finally, Table 4 and Figure 11 show the results of the calculations for the interactions of dichlorine with both the aluminum trichloride (data row 3) and iron trichloride (data row 5) monomers, where we have also repeated the data for both the unperturbed Cl_2 molecule (data row 1) and that of its interaction with benzene alone (data row 2) for ease of comparison. In both cases there is a much greater interaction energy (column 2) than with benzene alone, with that for $FeCl_3$ being slightly over five times larger than the value for $AlCl_3$. In both cases calculated orientations show that the Cl_2 molecule approaches the metal chloride monomer cornerwise as might be expected from use of its π*-antibonding HOMO (Figure 12). However, there is no evidence of the Cl_2 bonding distance shortening (column 5) or of its vibrational frequency increasing (column 6), as predicted by simple frontier orbital theory. Indeed, in both cases, the exact opposite occurs, though to a lesser extent than the changes reported for the interaction of Cl_2 with benzene alone. We have no ready explanation for this anomaly using simple frontier orbital theory.

Table 4. Results of the DFT study of the interaction of benzene and dichlorine with both the $AlCl_3$ and $FeCl_3$ catalysts

Associated Molecules	ΔE (kcal/mol)	d (C → Cl) (Å)	d (Cl → M) (Å)	d (Cl → Cl) (Å)	$\tilde{v}$ (Cl—Cl) (cm^{-1})
Cl_2	-	-	-	2.05	516
$C_6H_6 \rightarrow Cl_2$	-1.72	3.03	-	2.08	463
$Cl_2 \rightarrow AlCl_3$	-3.18	-	2.65	2.06	488
$C_6H_6 \rightarrow Cl_2 \rightarrow AlCl_3$	-9.89	2.48	2.41	2.24	299
$Cl_2 \rightarrow FeCl_3$	-15.66	-	2.46	2.07	466
$C_6H_6 \rightarrow Cl_2 \rightarrow FeCl_3$	-23.72	2.65	2.52	2.16	331

The arrows indicate the direction of electron flow from the EPD to the EPA. The bond vibrational frequencies are given in wave numbers.
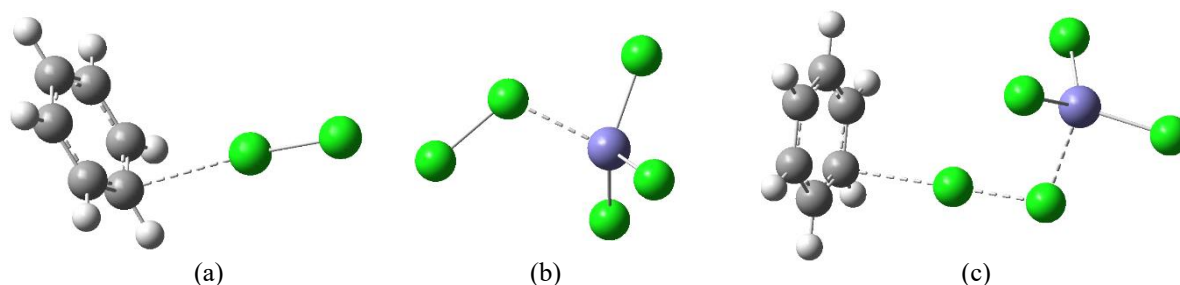

Figure 11. The interaction of benzene (carbon is dark gray and hydrogen is white), Cl_2 (green), and $AlCl_3$ (aluminum is purple and chlorine is green)

(a) benzene is the EPD (Lewis base) and Cl_2 is the EPA (Lewis acid). (b) Cl_2 is the EPD (Lewis base) and $AlCl_3$ is the EPA (Lewis acid). (c) Cl_2 is an EPA for benzene and an EPD for $AlCl_3$.
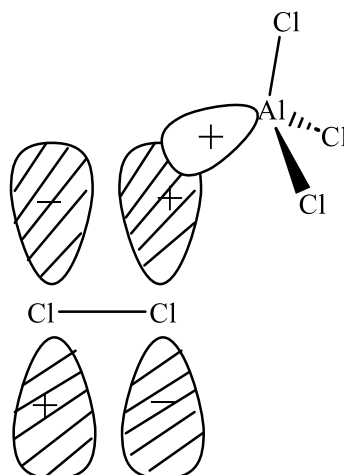

Figure 12. Cornerwise positive overlap of the filled π^*-antibonding HOMO of Cl_2 with the empty n-bonding LUMO of the $AlCl_3$ monomer

(Shading indicates a filled orbital, no shading indicates an empty orbital).

When we apply a push-pull mechanism in which the Cl_2 molecule simultaneously interacts with both benzene and a metal chloride monomer (data rows 4 and 6), as postulated in equation 8, there is an even greater enhancement of the interaction energies (column 2), with that for the $AlCl_3$ case almost tripling over the value in the absence of benzene, and that for the $FeCl_3$ case increasing by about half the value for its interaction with Cl_2 alone. In both cases there is a greatly enhanced lengthening of the Cl_2 bond (column 5) and a lowering of its vibrational frequency (column 6), in keeping with the bond's impending heterolytic cleavage. These effects are more pronounced for $AlCl_3$ than for $FeCl_3$, as they apparently reflect the relative increases in their interaction energies with respect to Cl_2 alone rather than their absolute values.

Our final calculated ΔE values for the reactions 7, 8, and 9 in benzene solvent are -1.45, -21.94, and -7.84 kcal/mol, respectively. The overall calculated energy for the net reaction was -31.23 kcal/mol, which compares favorably with the net reaction enthalpy of -29.37 kcal/mol computed from the literature values for the enthalpies of formation of the reactants and products in the gas phase (Pedley, 1994). In benzene, the chloronium cation and tetrachloroaluminate anion formed in equation 8 were found to exist as an ion pair rather than as free ions.

8. Summary

Based on the extended MO definitions of the Lewis acid-base concepts and the application of simple frontier orbital theory, an anomaly in the traditional textbook mechanism for Friedel-Crafts chlorination of benzene was detected and an alternative mechanism consistent with these concepts proposed. This was compared with similar past suggestions for revision and with several analogous halogenation reactions in which the dihalogen acts as the σ^*-EPA (a Lewis acid and

not a Lewis base). Reasons were also given for retaining the $AlCl_3$ monomer rather than the Al_2Cl_6 dimer as the active catalyst. These suggestions were then compared with the results of DFT calculations on the systems in question. Though this alternative mechanism probably requires further experimental justification, there is no doubt that it is far more consistent than the currently accepted mechanism with what is known about both the donor and acceptor properties of dichlorine. It also avoids the highly unlikely formation of a free Cl^+ cation in a nonpolar solvent like benzene. This new mechanism can, of course, be applied to Friedel-Crafts catalyzed halide substitution on benzene by the other dihalogens as well.

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