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Perspective

Structure and Dynamics of Reactive Intermediates in Reaction Mechanisms. σ- and π-Complexes in Electrophilic Aromatic Substitutions

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Problem: To develop a comprehensive strategy for the detection, structural characterization, and dynamic behavior of different types of reactive intermediates—despite a huge span (hours to femtoseconds) of their intrinsic lifetimes in solution. This paper illustrates how the judicious combination of X-ray crystallographic, NMR, and time-resolved UV−vis spectroscopic methods can be employed to elucidate the precise structures of π- and σ-complexes, some as highly reactive intermediates in various electrophilic aromatic substitutions.

1. Introduction

The complete description of the mechanism of a chemical reaction requires both the structural characterization of all reactive intermediates from the reactants to the products and the real-time observation of their mutual interconversions. The critical factor for a successful accomplishment of such a dual task is the lifetime of each intermediate, which may cover all time scales from femtoseconds to hours—depending on the surrounding activation energy barriers. Most importantly, the shorter the lifetime of the transient species, the more closely it is structurally and energetically related to the transition state of the reaction.[1,2] As a consequence, ultrashort-lived transients are most critical in understanding the elementary steps in a reaction mechanism. On the other hand, the longer-lived intermediates are generally considered to be energetically and structurally similar to either the reactants or the products, but they are equally important for the complete description of the reaction sequence from the beginning to the end.

A thorough investigation of a reaction mechanism thus includes three tasks, i.e. the generation of each intermediate, its structural characterization, and a detailed kinetic analysis of all reaction steps. The first requires a variety of synthetic approaches (mostly at low temperatures), the ultimate goal being to prepare the desired reactive intermediates in quantitative yields. The ultimate tool for structural investigations is X-ray crystallography which—at low (77 K) temperatures—produces bond lengths with a precision of up to 0.1 pm and bond angles to 0.05°. However, such precise structural determinations require rather long data acquisition times and thus stable single crystals. In addition, the intermediate must be persistent under the conditions of the low-temperature crystallization process to allow a high-quality crystal to grow.

The ultimate tool for the study of the reaction dynamics are spectroscopic methods, and in particular UV/vis spectroscopy, which not only provides ultrafast time resolution (up to femtoseconds), but also the highest accuracy for the determination of concentrations of reactive intermediates. Moreover, UV/vis spectroscopy is most useful to correlate structural data obtained from an intermediate in crystalline form and spectroscopic/

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[1] Eyring, H.; Polanyi, M. *Z. Phys. Chem.* **1931**, *B12*, 279. (b) Glasstone, S.; Laidler, K. J.; Eyring, H. *The Theory of Rate Processes*; McGraw-Hill: New York, 1941.

[2] Polanyi, J. C.; Zewail, A. H. *Acc. Chem. Res.* **1995**, *28*, 119.

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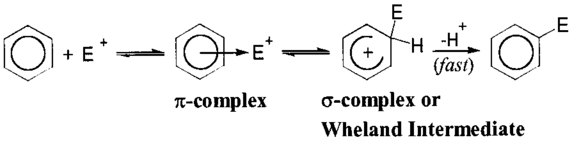
kinetic data collected in the solution phase. Thus, a close match between the UV/vis (diffuse-reflectance) absorption spectra of single crystals and the UV/vis (transient) absorption spectra obtained in solution is the basis for a reliable assignment of the absorption spectra of reactive intermediates. The reaction dynamics can then be monitored in solution using time-resolved spectroscopy, and the resulting concentration/time profiles can be evaluated by standard kinetic methods.

In this paper, the above-described strategies for a successful mechanistic study are applied to the reaction mechanism of electrophilic aromatic substitution as a case in point. Electrophilic aromatic substitution—one of the most investigated reaction in organic chemistry—is commonly considered to occur via the formation of π- and σ-complexes as *sequential* intermediates,[3] i.e.



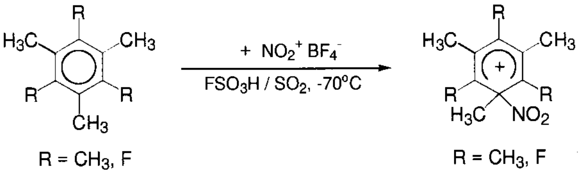
(1)

Interestingly, this reaction sequence is commonly believed to apply to all electrophilic aromatic substitutions despite the fact that in most cases either the π- or the σ-complex or both postulated intermediates are currently still elusive species. For example, only a few π-complexes of arenes with electrophiles have been observed including complexes with nitrosonium cation[4,5] and various metal ions such as thallium(III)[6,7] or mercury(II)[6,8] during aromatic nitrosation and metalation reactions, respectively. Several π-complexes of arenes with silver(I),[9] hydrogen chloride,[10] and triethylsilyl cation ($Si(C_2H_5)_3^+$)[11] have also been reported. Wheland intermediates[3] are even more elusive due to their generally ultrafast deprotonation to form the final substituted arenes (see eq 1). However, a variety of hexasubstituted σ-complexes with no readily abstractable proton (e.g., hexamethylbenzenium ions) have been generated in more or less stable form, and they have been thoroughly characterized by spectroscopic and X-ray crystallographic methods (vide infra).

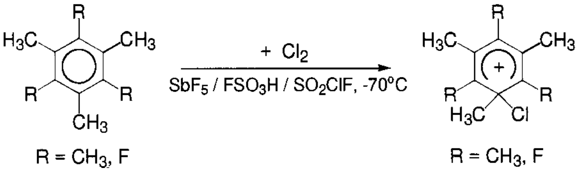
We will describe our methodology to successfully generate and characterize σ- and/or π-complexes of a series of electrophiles with various substituted benzenes. We will demonstrate that—depending on the lifetime—spectroscopic and/or crystallographic techniques can be successfully applied to explore the structures of these intermediates—X-ray crystallography being the slowest but most precise method and NMR and UV/vis spectroscopy being much faster but less informative methods. Moreover, we find that aromatic nitrosations[12] are the only examples of electrophilic aromatic substitutions for which both the π-complexes (arene/nitrosonium ion)[4,5] and the σ-complexes (nitrosoarenium cations)[13] are observed and thoroughly characterized by X-ray crystallography and UV/vis spectroscopy, respectively.

2. The Generation and Stabilization of Reactive Intermediates in Electrophilic Aromatic Substitutions

The earliest reports on the generation of reactive intermediates in electrophilic aromatic substitutions go back to the 1950s and 1960s. For example, Doering et al. prepared the heptamethylbenzenium ion as a relatively stable model of the Wheland intermediate in Friedel–Crafts methylations, and they were the first to utilize ^{1}H NMR spectroscopy to confirm the carbocationic structure based on the 1:2:2:2 intensity ratio of the four distinct proton signals.[14,15] Soon after, various protonated polymethylbenzenes were reported independently by three research groups[16–18] and characterized by IR spectroscopy[16] and by (temperature-dependent) ^{1}H NMR and ^{13}C NMR studies.[17–19] However, long-lived σ-complex intermediates of nitration and chlorination were elusive until the pioneering low-temperature NMR studies of Olah et al. in 1972.[20] Thus, both nitrobenzenium and chlorobenzenium ions were generated at −70 °C and characterized by ^{1}H NMR spectroscopy (see eqs 2 and 3).[21]



(2)



(3)

Moreover, temperature-dependent NMR studies established the migration of the nitronium moiety around the aromatic ring to occur with an activation energy of ca. 17 kcal/mol. In contrast, the NMR spectrum of chlorohexamethylbenzenium ion does not change with temperature (in the range of −70 to −20 °C), which points to rather high activation barriers for Cl^+ migration.[20] All

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(3) (a) For reviews, see: Olah, G. A.; Malhotra, R.; Narang, S. C. *Nitration*; VCH: New York, 1989. (b) Lowery, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd Ed.; Harper and Row Publishers: New York, 1987; p. 623. (c) March, J. *Advanced Organic Chemistry*; John Wiley & Sons: New York, 1992; p. 501. (d) Although generally referred to as the Wheland intermediate (Wheland, G. W. *J. Am. Chem. Soc.* **1942**, *64*, 900.), the arenium σ-complex was originally formulated by Pfeiffer, P. and Winzinger, R. (Liebigs Ann. Chem. **1928**, *461*, 132) as an intermediate in "electrophilic" aromatic bromination. We thank a reviewer for kindly pointing this historical fact out to us.

(4) Kim, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1991**, *113*, 4962.

(5) Bosch, E.; Kochi, J. K. *J. Org. Chem.* **1994**, *59*, 5573.

(6) Lau, W.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 6720.

(7) Lau, W.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7100.

(8) Lau, W.; Kochi, J. K. *J. Org. Chem.* **1986**, *51*, 1801.

(9) The following reviews discuss Ag(I)/arene complexes in detail: (a) Beverwijk, C. D.; van der Kerk, G. M. J.; Leusink, A. J.; Noltes, J. G. *Organometal. Chem. Rev.* **1970**, *A5*, 215. (b) Hubig, S. M.; Lindeman, S. V.; Kochi, J. K. *Coord. Chem. Rev.*, in press. (c) Lindeman, S. V.; Rathore, R.; Kochi, J. K. *Inorg. Chem.* submitted for publication.

(10) Deeg, A.; Mootz, D. *Z. Naturforsch.* **1993**, *48b*, 571. See also: Taylor, R. in ref 3.

(11) The controversy about the π- or σ-character of the toluene/$SiEt_3+$ complex will be discussed later (see Section 5).

(12) Williams, D. L. H. *Nitrosation*; Cambridge University Press: Cambridge, 1988.

(13) Hubig, S. M.; Kochi, J. K. *J. Am. Chem. Soc.*, in press.

(14) Doering, W. v. E.; Saunders: M.; Boyton, H. G.; Earhart, H. W.; Wadley, E. F.; Edwards, W. R.; Laber, G. *Tetrahedron* **1958**, *4*, 178.

(15) The heptamethylbenzenium tetrachloroaluminate salt was prepared by exhaustive methylation of mixed trimethylbenzenes by methyl chloride in the presence of dry aluminum trichloride at 37 °C. Heptamethylbenzenium cation was also generated by adding hexamethylbenzene to methanol in concentrated sulfuric acid at 97 °C.[14]

the above-mentioned conclusions based on ^{1}H NMR results have been confirmed by low-temperature ^{13}C NMR studies carried out by Koptyug et al. in 1973,[22,23] which establish the carbocationic character of chloro-, nitro-, bromo-, methyl-, and sulfonic acid-substituted hexamethylbenzenium σ-complexes as well as protonated hexamethylbenzene.

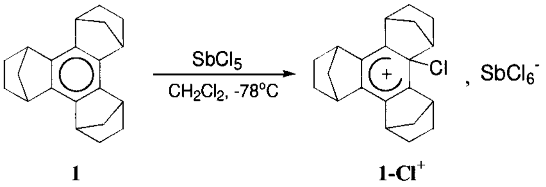
The above-mentioned findings prompted us to examine the following questions about the generation of reactive intermediates in electrophilic aromatic substitution:

(a) Can the list of stable σ- and/or π-complexes be extended to other electrophiles such as iodonium, nitrosonium, etc.?

(b) Can we generate long-lived intermediates under conditions that are more closely related to typical reaction conditions of electrophilic aromatic substitutions? In other words, are superacids or magic acid[17−23] really necessary to stabilize intermediates in electrophilic aromatic substitution sufficient for observation?

(c) Is it possible to obtain single crystals of such reactive intermediates which are suitable for X-ray crystallography?

In fact, about 30 years after Olah's pioneering NMR studies[17] the first isolation of a chlorobenzenium σ-complex in crystalline form and its thorough structural characterization by X-ray crystallography were successfully carried out in our laboratory in 1994.[24] Thus, the sterically crowded aromatic donor **1** forms a bright yellow precipitate when mixed with the chlorinating agent $SbCl_5$ in dichloromethane at −78 °C, i.e.



(4)

X-ray crystallography of single crystals grown at −20 °C from a hexane/dichloromethane mixture establishes the structure of **1**−Cl$^+$ as shown in the ORTEP diagram in Figure 1.[24]

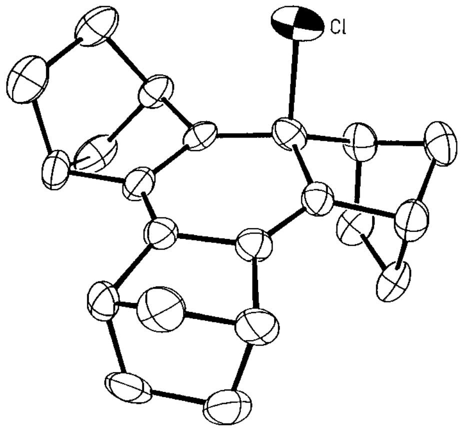


Figure 1. ORTEP diagram of the chloroarenium cation **1**−Cl$^+$ with the hydrogens omitted for clarity.

The attachment of a chlorine atom to the aromatic ring with a C−Cl bond distance of $d = 1.86$ Å generates a cyclohexadienyl ring system which clearly confirms the σ-complex character of this chlorobenzenium ion.

The successful generation of **1**−Cl$^+$ $SbCl_6^-$ in dichloromethane under such mild reaction conditions has encouraged us since to prepare other reactive intermediates in various electrophilic aromatic substitutions under similar conditions, to examine them by spectroscopic techniques, and to grow single crystals suitable for X-ray crystallography. In fact, we now know that the generation of stable σ- and π-complexes with various electrophiles in dichloromethane is not restricted to crowded arenes such as **1** (**TMT**) or its ethano analogue (**TET**), but can also be achieved with the prototypical hexamethylbenzene (**HMB**, see Chart 1). On the other hand, other alkylbenzenes such as mesitylene (**MES**) and pentamethylbenzene (**PMB**, see Chart 1) undergo the corresponding substitution reactions in dichloromethane too fast under the same conditions to produce the Wheland intermediate in sufficiently high (steady-state) concentration for observation.

As cationic electrophiles, we choose $E^+ = H^+, CH_3^+, Cl^+, Br^+, I^+, NO_2^+$, and NO^+, which are employed in various forms using different E^+ carriers such as Cl_2 for Cl^+ or ICl for I^+, etc. The generation of σ- and π-complexes of these electrophiles with arenes in dichloromethane are carried out under a variety of different reaction conditions as follows:

Method A: The E^+ carrier and the arene are codissolved in dichloromethane (in most cases at low temperatures) in the presence of low (1−5 vol %) concentrations of acids of different strength including methanesulfonic acid (CH_3SO_3H), trifluoromethanesulfonic acid (CF_3SO_3H), fluorosulfonic acid (FSO_3H), and tetrafluoroboric acid (HBF_4)/ether mixture. Whereas the first three acids are used to vary the acidity of the medium, tetrafluoroboric acid is used to provide an effective counteranion (BF_4^-) for the isolation of benzenium σ-complexes in crystalline form. Method A has been successfully applied to various E^+ carriers including chlorine (Cl_2), bromine (Br_2), iodine (I_2), nitrous (HNO_2) and nitric (HNO_3) acid (generated in situ from Bu_4N^+ NO_2^- and Bu_4N^+ NO_3^-, respectively), isoamyl or *n*-octyl nitrite, *n*-octyl nitrate, and N-substituted succinimides

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(16) Perkampus, H.-H.; Baumgarten, E. *Ber. Bunsen-Ges. Phys. Chem.* **1964**, *68*, 70.

(17) (a) Olah, G. A. *Abstracts*, 138th National Meeting of the American Chemical Society, New York, New York, 1960; p 3P. (b) Olah, G. A. *J. Am. Chem. Soc.* **1965**, *87*, 1103. (c) Olah, G. A.; Schlosberg, R. H.; Porter, R. D.; Mo, Y. K.; Kelly, D. P.; Mateescu, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 2034. The reports are for arenium ions of relevance to hydrogen−deuterium exchanges as electrophilic processes.

(18) (a) MacLean, C.; Mackor, E. L. *Mol. Phys.* **1961**, *4*, 241. (b) MacLean, C.; Mackor, E. L. *Discuss. Faraday Soc.* **1962**, *34*, k65.

(19) Protonations were carried out with (a) HCl or HBr in the presence of aluminum halides,[16] (b) with HF/SbF_5 or $AgSbF_6$/HCl in SO_2 or $HF/SbF_5/SO_2ClF/SO_2F_2$,[17] or (c) in neat HF.[18]

(20) Olah, G. A.; Lin, H. C.; Mo, Y. K. *J. Am. Chem. Soc.* **1972**, *94*, 3667.

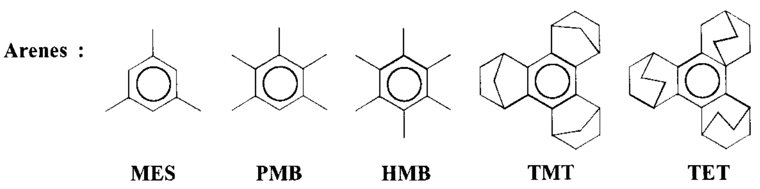
(21) The structural assignment as hexamethylbenzenium ion is based on the four distinct proton signals in the ^{1}H NMR spectrum with relative intensities of 1: 2: 2: 1 for the ipso, meta, ortho, and para protons, respectively.

(22) (a) Mamatyuk, V. I.; Rezvukhin, A. I.; Detsina, A. N.; Buraev, V. I.; Isaev, I. S.; Koptyug, V. A. *Zh. Org. Khim.* **1973**, *9*, 2429. (b) Koptyug, V. A. *Topics Curr. Chem.* **1984**, *122*.

(23) (a) These studies were carried out in fluorosulfonic acid or in HSO_3F/SO_2ClF mixtures, except for the chlorohexamethylbenzenium tetrachloroaluminate which was generated in dichloromethane. (b) The signals for both the aromatic carbons and the methyl carbons in the ^{13}C NMR spectra exhibit the same 1: 2: 2: 1 intensity patterns as observed in the ^{1}H NMR spectra.[22]

(24) (a) Rathore, R.; Loyd, S. H.; Kochi, J. K. *J. Am. Chem. Soc.* **1994**, *116*, 8414. (b) Rathore, R.; Hecht, J.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 13278.

Chart 1



Electrophiles : H^+, CH_3^+, Cl^+, Br^+, I^+, NO_2^+, NO^+

(X = Cl, Br, I, and NO_2). In a typical experiment, a prechilled (−78 °C) solution of hexamethylbenzene (5−10 mM) in dichloromethane is mixed with 1 equiv of bromine (Br_2) and treated with excess Brønsted acid (e.g., $HBF_4 \cdot Et_2O$, 5 vol %). The resulting dark-orange solution is analyzed by UV/vis and NMR spectroscopy (vide infra) to confirm the formation of bromohexamethylbenzenium cation. This bromoarenium ion is isolated in crystalline form (as tetrafluoroborate salt) by carefully layering the dichloromethane solution with an equal volume of hexane and keeping this dual-layer mixture in a low-temperature bath at −78 °C for an extended period of time.

Method B: The E^+ carrier and the arene are codissolved in dichloromethane (in most cases at low temperature), and silver(I) hexafluoroantimonate ($Ag^+ SbF_6^-$) is added in excess. This method is successfully applied to E^+ carriers such as chlorine (Cl_2), bromine (Br_2), iodine monochloride (ICl), nitrosyl chloride (NOCl), and methyl iodide (CH_3I). Under these experimental conditions, the silver salt accomplishes a dual task: (i) The silver cation forms an insoluble precipitate with the anionic part of the E^+ carrier, e.g.

$$Br_2 + Ag^+ \longrightarrow AgBr\downarrow + Br^+ \qquad (5)$$

(ii) Similar to tetrafluoroborate, the hexafluoroantimonate anion represents an effective counterion for the isolation of arenium σ-complexes in crystalline form (e.g., bromohexamethylbenzenium hexafluoroantimonate).

In a typical experiment, a cold (−78 °C) solution of hexamethylbenzene (10 mM) in dichloromethane is treated with 1 equiv each of bromine (Br_2) and silver hexafluoroantimonate (Ag SbF_6) dissolved in dichloromethane (10 mM). The color of the mixture immediately turns dark orange. At the same time, a voluminous precipitate of AgBr (see eq 5) forms, which is removed by low-temperature filtration. Upon analysis by UV/vis and NMR spectroscopy (vide infra) to confirm the formation of bromohexamethylbenzenium ion, the dark-orange solution is carefully topped with anhydrous hexane and stored in a cold bath which is diligently kept at −85 °C.[28] After about 3 days, a crop of dark-orange single crystals is formed, and the identity of bromohexamethylbenzenium hexafluoroantimonate is confirmed by X-ray crystallography.

Other methods: Besides the two principal preparation methods for σ- and π-complexes mentioned above, several other methods have been successfully applied in certain cases. For example, chloroarenium σ-complexes can be obtained in dichloromethane at low temperature using antimony pentachloride ($SbCl_5$)[24] or molybdenum pentachloride ($MoCl_5$)[25] as chlorinating agent, e.g.

$$ArH + 2\,SbCl_5 \xrightarrow[-78^\circ C]{(CH_2Cl_2)} Ar(H)Cl^+\,SbCl_6^- + SbCl_3 \qquad (6)$$

A third method C is based on the chlorination in eq 6, in which Cl^+ from an isolated chloroarenium salt is directly transferred to another arene donor.[24b] This is an attractive general method for the preparation of a family of chloroarenium salts since the only byproduct is the original (readily soluble) arene, and various (noncoordinating) counteranions can be easily introduced. In principle, it is applicable to the preparation of a wide variety of E-substituted arenium salts.[26] Another special example is the nitronium ion (NO_2^+) which can be used as the commercially available tetrafluoroborate salt, to generate nitrohexamethylbenzenium ion in a sulfur dioxide/fluorosulfonic acid mixture at −70 °C (see eq 2).[20]

Nitrosations can be carried out with nitrous acid generated in situ in acidic milieu[12]—protonated nitrous acid and the nitrosonium cation (NO^+) being the nitrosating agents—or with nitrosonium ion as a pure salt (e.g., $NO^+ BF_4^-$) in acetonitrile solution.[5] Under the latter (nonaqueous) reaction conditions, the formation of transient electron-donor/acceptor complexes between the arenes and nitrosonium cation have been observed.[4,5] This complex can be isolated in crystalline form at −20 °C using slow-diffusion techniques. X-ray crystallographic studies with several different single crystals uniformly establish the π-character of all arene/NO^+ complexes examined.[4,27] On the other hand, all attempts to generate stable σ-complexes in nitrosation, viz. nitrosoarenium ions, by similar (thermal) methods as described above for nitration and chlorination, have been unsuccessful. However, nitrosoarenium σ-complexes can be efficiently generated by an alternative photochemical method based on the charge-transfer activation of arene/NO^+ π-complexes in dichloromethane.[13] Time-resolved absorption spectroscopy reveals that these transient σ-complexes exhibit lifetimes that are extremely temperature-dependent and vary from nanoseconds (T = 298 K) to hours (T = 77 K, vide infra).[13]

In summary, the development and application of a variety of preparation methods for reactive intermediates in electrophilic aromatic substitution serve two purposes: First, it provides a flexibility in the methodology necessary to develop the most efficient synthetic proce-

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[25] Nugent, W. A. *J. Org. Chem.* **1980**, *45*, 4534.

[26] For example, as a synthetic methodology, *transfer chlorination* has been applied to other donors (compare: Mori, T.; Rathore, R.; Lindeman, S. V.; Kochi, J. K. *J. Chem. Soc. Chem. Commun.* **1998**, 927, and *transfernitration* has been described by Olah et al. in ref 3a.

[27] (a) Rathore, R.; Lindeman, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 9343. (b) Rathore, R.; Lindeman, S. V.; Kochi, J. K. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1585. (c) Rathore, R.; Kochi, J. K. *J. Org. Chem.* **1998**, *63*, 8630.

[28] Bromohexamethylbenzenium cation shows only three signals due to insufficient resolution of the proton signals at δ = 2.80 (9H). However, all signals are fully resolved in the ^{13}C NMR spectrum (see text).

Table 1. ^{1}H NMR Spectral Data for σ-/π-Complexes of Hexamethylbenzene with Various Electrophiles[a]

	E^+	1-Me[b]	3,5-Me[b]	2,6-Me[b]	4-Me[b]
1	H^+	1.53	2.23	2.55	2.70
2	CH_3^+	1.54	2.35	2.60	2.83
3	Cl^+	1.78	2.30	2.71	2.87
4	Br^+	1.77	2.29	2.80[c]	
5	NO_2^+	1.98	2.34	2.56	2.98
6	NO^+	2.48[d]			
7	I^+	2.35[d]			
8	*e*	2.18[d]			

[a] In deuterated dichloromethane at -80 °C using CH_2Cl_2 as reference. The chemical shifts are given in ppm. [b] The numbering of the methyl groups refers to the hexamethylbenzenium σ-complexes (1 = ipso, 3,5 = meta, 2,6 = ortho, and 4 = para position). [c] Only one signal observed for *o*- and *p*-methyl protons together (9H). [d] Only one signal obtained for all methyl protons (18H). [e] Pure (uncomplexed) hexamethylbenzene as reference.

Table 2. ^{13}C NMR Spectral Data for σ-/π-Complexes of Hexamethylbenzene with Various Electrophiles[a]

	E^+	C_1[b]	$C_{3,5}$[b]	$C_{2,6}$[b]	C_4[b]
1	CH_3^+	56.7	139.2	197.7	191.1
2	Cl^+	67.0	137.4	187.3	196.8
3	Br^+	58.7	137.9	187.1	197.3
4	NO_2^+	98.4	141.8	181.5	204.7
5	NO^+	150.8[c]			
6	*e*	133.2[c]			

	E^+	1-Me[b]	3,5-Me[b]	2,6-Me[b]	4-Me[b]
1	CH_3^+	21.5	14.9	23.9	23.7
2	Cl^+	24.6	15.2	22.5	26.1
3	Br^+	20.5	14.6	21.5	24.9
4	NO_2^+	23.6	14.6	19.7	26.2
5	NO^+	17.8[d]			
6	*e*	17.0[d]			

[a] In deuterated dichloromethane at -80 °C. The chemical shifts are given in ppm. [b] The numbering of the carbon atoms and methyl groups refers to the hexamethylbenzenium σ-complexes (1 = ipso, 3,5 = meta, 2,6 = ortho, and 4 = para position. [c] Only one signal obtained for all aromatic carbon atoms (6H). [d] Only one signal obtained for all methyl carbon atoms (18C). [e] Pure (uncomplexed) hexamethylbenzene as reference.

dure for each particular electrophile. Second, the generation of a particular arene/electrophile σ- or π-complex by more than one synthetic procedure provides additional evidence for the validity of the assignment. In fact, we emphasize that all σ- and π-complexes of arenes with electrophiles described in this article have been generated via at least two independent synthetic procedures, and their NMR and UV/vis spectra are found not to be affected by the preparation method.

3. Identification of σ- and π-Complexes by NMR Spectroscopy

Historically, NMR spectroscopy is the first method successfully employed to observe and identify reactive intermediates in electrophilic aromatic substitutions.[14,17−23] Among all spectroscopic techniques, NMR spectroscopy provides the most detailed information on the structure of the investigated substrates within a short data acquisition time. More precise structural data can only be obtained by X-ray crystallography which however requires the preparation of single crystals. Thus, NMR spectroscopy is the practical method for a general comparison of all intermediates (including metastable complexes) in the reactions of electrophiles with arenes.

To compare our synthetic methods under mild conditions (see the previous section) with the published procedures (in superacids or magic acid),[17,18,22] we first examine the ^{1}H NMR spectra in deuterated dichloromethane at low (-80 °C) temperature. Table 1 summarizes the ^{1}H NMR data for σ- and π-complexes of various electrophiles with hexamethylbenzene.

We note that the low-temperature NMR spectra for electrophiles **1** through **5** in deuterated dichloromethane are quite similar to those recorded previously in superacids or magic acid.[17−21] Thus, four proton signals are observed with well-separated chemical shifts between $\delta = 1.5$ and 3.0.[28] Integration of the four proton signals results in relative intensities of 2:2:2:1 and 1:2:2:1 for electrophile **2** and electrophiles **1**, **3**, and **5**, respectively. This splitting of the proton signals with invariant intensity ratios, which is to be contrasted with the single proton signal of hexamethylbenzene (δ 2.18, 18H), is taken as strong evidence for the formation of hexamethylbenzenium σ-complexes.[14−21] Thus, the positive charge of the σ-bonded electrophile is delocalized over the carbon atoms of the six-membered ring with increasing partial positive charge going from the ipso (1) to the meta (3,5) to the ortho (2,6) and to the para (4) carbon atoms, which results in increasing downfield chemical shifts. Interestingly, there is also an increasing downfield shift of the ipso and the para signals on going from the protonated hexamethylbenzene to the nitrohexamethylbenzenium ion. Obviously, nitronium cation generates a significantly stronger positive charge on the ipso and the para carbon atoms than a proton.

In contrast to the electrophiles **1** through **5**, the ^{1}H NMR spectra of nitrosonium (**6**) and iodonium (**7**) complexes recorded in deuterated dichloromethane at -80 °C exhibit only one single proton signal at δ 2.48 (18H) and δ 2.35 (18H), respectively (see Table 1). The downfield shifts of both signals as compared to pure hexamethylbenzene (δ 2.18) indicate substantial positive charge on the aromatic ring, however this charge is equally distributed over all aromatic carbon atoms which suggests both electrophiles to be located in a central position over the aromatic ring as observed in π-(η^6-)complexes.

The ^{13}C NMR data compiled in Table 2 (also recorded in deuterated dichloromethane at -80 °C) confirm our conclusions based on the ^{1}H NMR data (vide supra). Thus, the electrophiles CH_3^+, Cl^+, Br^+, and NO_2^+ form σ-complexes with hexamethylbenzene under our experimental conditions (see previous section) which is evidenced by the 1:2:2:1 splitting of the signals of both the aromatic and the methyl carbon atoms. The downfield chemical shifts of the aromatic carbon signals indicate increasing positive charge and thus suggest their assignment in the order of ipso, meta, ortho, and para positions with increasing downfield shift. The downfield chemical shifts of the methyl carbon signals are less pronounced and show a slightly different order with the *m*-methyl groups showing the least downfield shifts (see Table 2). Moreover, the downfield shifts of the aromatic carbon atoms in ipso and para position increase from methyl to nitro substitution, which parallels the trend observed in the ^{1}H NMR spectra and thus confirms our conclusion that nitrohexamethylbenzenium ion bears more positive charge on the aromatic ring than heptamethylbenzenium ion.

In contrast, the complex of nitrosonium cation with hexamethylbenzene exhibits a ^{13}C NMR spectrum that is very different from those obtained with the other electrophiles.[29] Thus, the spectrum consist of only two signals at δ 150.8 (6C) and δ 17.8 (6C), which are assigned to the aromatic and the methyl carbon atoms, respectively. The lack of the 1:2:2:1 splitting as observed with the other electrophiles points to the π-(η^6-)character of this complex (vide supra), and the downfield shift of the aromatic carbon atoms (δ 150.8) as compared to uncomplexed hexamethylbenzene (δ 133.2) reveals a sizable positive charge equally distributed over the entire six-membered ring.

In summary, both the ^{1}H NMR and the ^{13}C NMR spectra recorded in dichloromethane closely match those recorded previously in strong acids. Moreover, all NMR data consistently reveal a significant difference between the complexes of nitrosonium or iodonium ion with hexamethylbenzene and those of the other electrophiles. Thus, the single proton or carbon signals observed with NO^+ and I^+ suggest a π-complex to be formed between the arene and either electrophile, whereas the splitting of the proton and carbon signals observed with the other electrophiles is indicative of the formation of σ-complexes. To substantiate these conclusions, UV/vis spectroscopic evidence is presented in the following section; and for selected complexes X-ray crystallographic results are reported (vide infra).

4. UV/Vis Spectra of σ- and π-Complexes

UV/vis spectroscopy represents the fastest method for the detection and identification of chemical intermediates. For example, the new generation of diode-array spectrophotometers allows the complete UV/vis spectra to be recorded within milliseconds. Fast mixing/detection methods such as the stopped-flow technique exhibit even better time resolution and enable us to monitor reactive intermediates in bimolecular thermal reactions that occur on the microsecond time scale. If the lifetime of the transient species is shorter than the time scale of the fastest mixing techniques, photochemical techniques can be utilized for the generation and detection of the ultrashort-lived transients. Thus, laser-flash photolysis techniques with a time resolution solely limited by the laser pulse width makes it possible to detect reactive intermediates with ultrashort lifetimes even in the femtosecond regime.

Despite the ultimate time resolution of UV/vis spectroscopy, the data on electronic absorption spectra of reactive intermediates pertinent to electrophilic aromatic substitution are heretofore quite limited and mainly include protonated alkylbenzenes, heptamethylbenzenium cation, and various substituted hydroxy- or aminobenzenium ions.[30] For example, protonated hexamethylbenzene in HF[31] and heptamethylbenzenium cation in hydrochloric acid[14] both show narrow absorption bands centered at 395 and 397 nm, respectively. Chlorohexamethylbenzenium cation exhibits an absorption maximum at 410 nm in dichloromethane.[25] In contrast, the hexamethylbenzene/nitrosonium (π-) complex in dichloromethane shows two (charge-transfer) absorption bands, viz. one narrow intense band centered at 337 nm and one broad weak band around 500 nm.[4,5] Since electronic absorption spectra are strongly solvent-dependent, we have recorded a series of UV/vis spectra of various arene/electrophile complexes in dichloromethane solution under similar (low-temperature) conditions (see Table 3). Most importantly, the UV/vis spectra are recorded under the same conditions as the NMR spectra described in the previous section, and they are thus assigned to the same intermediates.

Table 3. UV/Vis Spectral Data for σ-/π-Complexes of Hexamethylbenzene with Various Electrophiles[a] (λ_{max} (nm), fwhm (cm^{-1}), log ϵ (M^{-1} cm^{-1}))

	E^+	HMB	TMT	TET	PMB	MES
1	$H^{+\,b}$	395	395	395	377	
		3600	3900	3600	3300	
		3.87	3.66	6.78	3.72	
2	$CH_3^{+\,b}$	398	432	428		
		3600	3300	3300		
		3.94		3.91		
3	Cl^+	410	510	500		
		3400	3800	3300		
		4.01	3.67	3.72		
4	Br^+	460	530	520		
		3500	4100	3800		
		4.04	3.97	3.87		
5	NO_2^+	430	498	480		
		3400	3500	3200		
		3.96	3.87	3.90		
6	I^+	390/466				
		2400/–				
7	$NO^+(\pi)^b$	337/500	352/510	355/508	340/490	337/480
		2200/–	2300/–	2300/–		
		3100/–	3500/–	3400/–		
8	$NO^+(\sigma)^c$	430	430	430	430	430
		2900	4800	4600		

[a] In dichloromethane at −78 °C unless stated otherwise. [b] At room temperature. [c] Generated by photochemical means (see text).

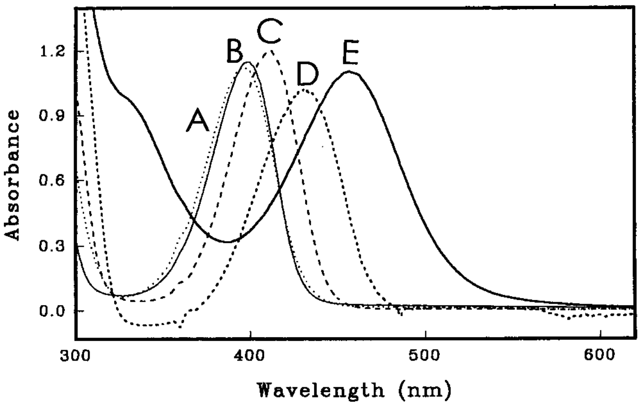

Figure 2. UV/vis absorption spectra of σ-complexes of hexamethylbenzene with various electrophiles (A = H^+, B = CH_3^+, C = Cl^+, D = NO_2^+, E = Br^+) in dichloromethane at −78 °C.

Let us first compare the complexes of hexamethylbenzene (**HMB**) with electrophiles **1** through **5,** which is illustrated in Figure 2. Thus, all these ArH/E^+ complexes show similar absorption spectra featuring one narrow absorption band with a bandwidth of ≈ 3500 cm^{-1} full width at half-maximum (fwhm). The position of the absorption maximum shifts slightly from 395 to 460 nm on proceeding from the protonated hexamethylbenzene to the bromohexamethylbenzenium ion (see Figure 2).

In contrast, both the complex of hexamethylbenzene with nitrosonium cation and that with iodonium ion exhibit two absorption bands of different intensity and bandwidth (see Figure 3). Thus, we observe a strong narrow band at 337 or 390 nm and a weak broad band

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[29] With the corresponding iodonium complex, no ^{13}C NMR signals are obtained in deuterated dichloromethane at −80 °C due to the highly labile nature of the complex which leads to the formation of paramagnetic species presumably arising from decomposition.

[30] For a comprehensive compilation of UV/vis data of benzenium ions, see ref 22b, pp 96−103.

[31] Kilpatrick, M.; Hyman, W. H. *J. Am. Chem. Soc.* **1958**, *80*, 77.

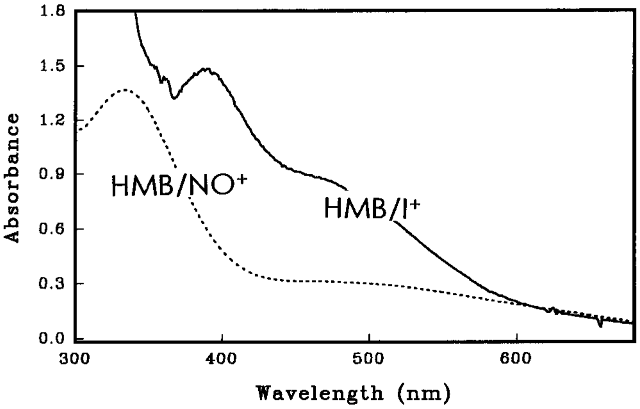

Figure 3. UV/vis absorption spectra of π-complexes of hexamethylbenzene (**HMB**) with nitrosonium (NO^+) and iodonium (I^+) in dichloromethane at 25 and −78 °C, respectively.

centered at 500 or 466 nm for the nitrosonium and the iodonium complex, respectively. In the case of arene/nitrosonium complexes, the double absorption bands have been assigned to charge-transfer transitions from the arene donor to the nitrosonium acceptor within a donor/acceptor (π-) complex.[4,5] The similarity of the UV/vis spectra of nitrosonium and iodonium complexes on one hand and those of the other electrophiles on the other hand parallels the distinction made earlier with the NMR spectra and thus strongly supports our conclusion about the formation of two different types of complexes, viz. σ- and π-complexes, depending on the electrophile (vide supra). Moreover, the narrow absorption band of the σ-complexes around 400 nm is ascribed to the cyclohexadienyl chromophore in which the positive charge is delocalized over the six-membered ring.

The UV/vis spectra of complexes of hindered arene donors **TMT** and **TET** with various electrophiles show qualitatively the same effects as those of hexamethylbenzene (see Table 3). Thus, electrophiles **1**−**5** form σ-complexes with one narrow absorption band. On the other hand, the spectra of the corresponding NO^+ (π-) complexes show the typical double absorption band as observed with hexamethylbenzene. Interestingly, the absorption bands of the σ-complexes (entries **1**−**5**) vary more strongly with the electrophile as compared with the hexamethylbenzene complexes. Thus, the chloro-, bromo-, and nitroarenium cations derived from **TMT** or **TET** exhibit orange to red colors with absorption maxima up to 530 nm as compared to the yellow color of all hexamethylbenzenium ions (see Figure 4).

This significant difference in color between the yellow hexamethylbenzenium ions and the orange/red **TMT** σ-complexes is clearly related to the structural differences of the two chromophores (see section 5).

Despite the fast response of UV/vis spectroscopy, most attempts to record electronic spectra of Wheland intermediates with pentamethylbenzene or mesitylene have been unsuccessful. Thus, protonated pentamethylbenzene and the photochemically generated (vide infra) nitrosopentamethylbenzenium and nitrosomesitylenium ions (see Table 3) are the only examples for which UV/vis spectral data are presently available. For all other electrophiles in Table 3, we note that—under the same conditions under which σ-complexes are observed with hexamethylbenzene, **TMT**, and **TET**—aromatic substitution products are obtained that are derived from pentamethylbenzene or mesitylene, respectively. For example, mixing of pentamethylbenzene or mesitylene with $SbCl_5$ in dichloromethane at −50 °C leads to a rapid formation of chloro-pentamethylbenzene or chloromesitylene, respectively, in nearly quantitative yield.[25] This result leads to our conclusion that all the arenium ions listed in Table 3 are excellent prototypes for Wheland intermediates in electrophilic aromatic substitutions. Moreover, the chloroarenium ion derived from **TMT** has been successfully used as Cl^+ carrier to either transfer the chloronium ion to other aromatic[24] and olefinic[32] substrates (see Figure 5) or to achieve efficient electrophilic transfer chlorination of aromatic compounds such as polymethylbenzenes or methoxybenzenes;[24,33] i.e., see Scheme 1.

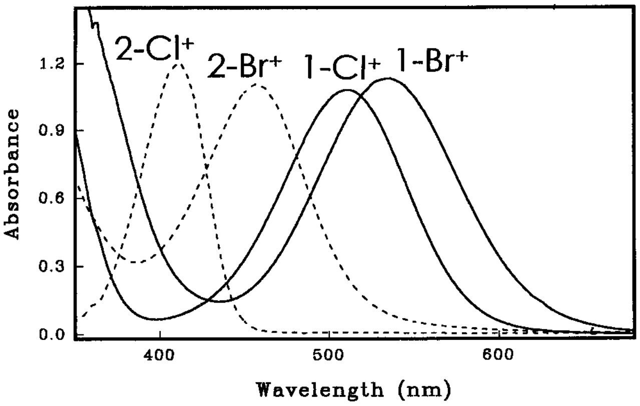

Figure 4. UV/vis spectral comparison of **HMB**- and **TMT**-derived σ-complexes.

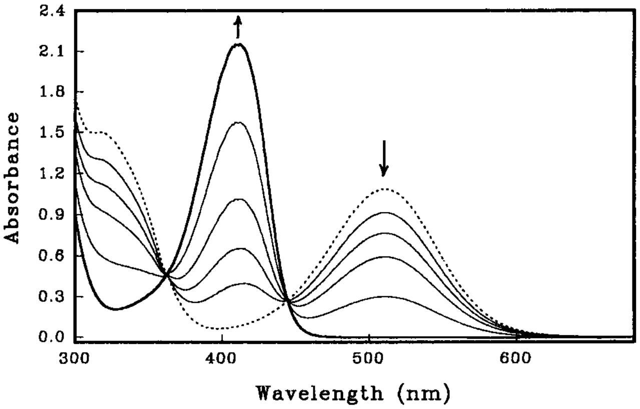

Figure 5. Chloronium (Cl^+) transfer from **TMT** to **HMB** in dichloromethane at −78 °C as monitored by the increase in absorption at 410 nm and the decrease at 510 nm in the UV/vis spectra.

The UV/vis and NMR spectral data of arene/nitrosonium complexes (see entries **6** in Table 1, **5** in Table 2, and **7** in Table 3) clearly establish their π-character. All attempts to generate the corresponding nitrosoarenium σ-complexes by the general methods described in Section 2 have been unsuccessful—even in the case of mesitylene,

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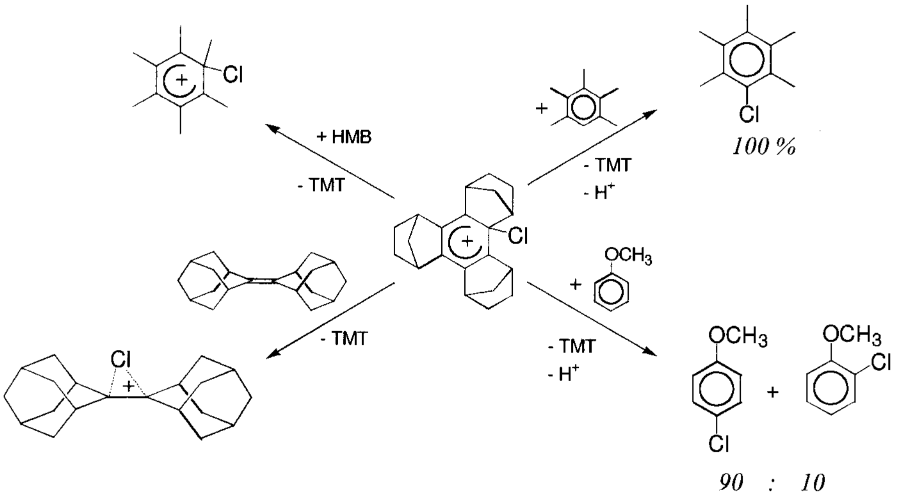
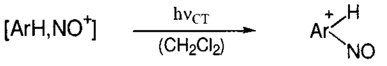
(32) Mori, T.; Rathore, R.; Lindeman, S. V.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1998**, 927.

(33) (a) Note that the electrophilic transfer-chlorination of anisole with chloroarenium leads to *p*- and *o*-chloroanisoles in quantitative yield in a 90: 10 isomer distribution as obtained in conventional electrophilic aromatic chlorinations.[24] (b) Similarly, the nitronium ion (NO_2^+) is transferred (at low temperature) from nitrohexamethylbenzenium cation to benzene or mesitylene; and it results in the formation of nitrobenzene and nitromesitylene, respectively.[20]

Scheme 1



which is efficiently nitrosated by nitrosonium cation in acetonitrile solution.[5] However, recent time-resolved spectroscopy experiments carried out in our laboratory have led to the real-time observation of various nitrosoarenium σ-complexes when they are photochemically generated by charge-transfer photoexcitation of the corresponding arene/nitrosonium π-complexes in dichloromethane solution,[13] i.e.



$$[\mathrm{ArH,NO^{+}}] \xrightarrow[(\mathrm{CH_2Cl_2})]{h\nu_{\mathrm{CT}}} \mathrm{Ar}\overset{+}{<}^{\mathrm{H}}_{\mathrm{NO}} \qquad (7)$$

At room temperature, these nitrosoarenium σ-complexes are very short-lived and can only be observed by nanosecond time-resolved spectroscopy. However, steady-state photolysis of the same arene/nitrosonium complexes in n-butyl chloride glass at $T = 77$ K leads to nitrosoarenium ions which persist for hours.[13] Most interestingly, the UV/vis absorption spectra of all nitrosoarenium ions in Table 3 (entry **8**) —obtained either at −78 °C by laser flash photolysis experiments or at $T = 77$ K by using a dewar-equipped spectrophotometer—uniformly show one narrow absorption band centered at 430 nm (see Figure 6).

Most importantly, the photochemical generation of the nitrosoarenium σ-complexes by charge-transfer photoexcitation of the corresponding π-complexes not only represents an elegant preparative method, but also provides mechanistic insight as to how the interconversion from π- to σ-complexes can occur. Thus, femtosecond time-resolved laser experiments clearly establish that nitrosoarenium σ-complexes are formed by ultrafast ($k \approx 10^{11}$ s^{-1}) radical/radical coupling of arene cation radicals with nitric oxide.[13] This finding represents the first, unambiguous experimental evidence of an electron-transfer mechanism that is applicable not only for aromatic nitrosations, but may also be applicable for other electrophilic aromatic substitutions.[34] In other words, the transformation of the ArH/E$^+$ π-complexes into σ-complexes occurs via an intermediate radical pair [ArH$^{\bullet+}$, E$^\bullet$] which is formed by electron transfer from the arene to the electrophile E$^+$.

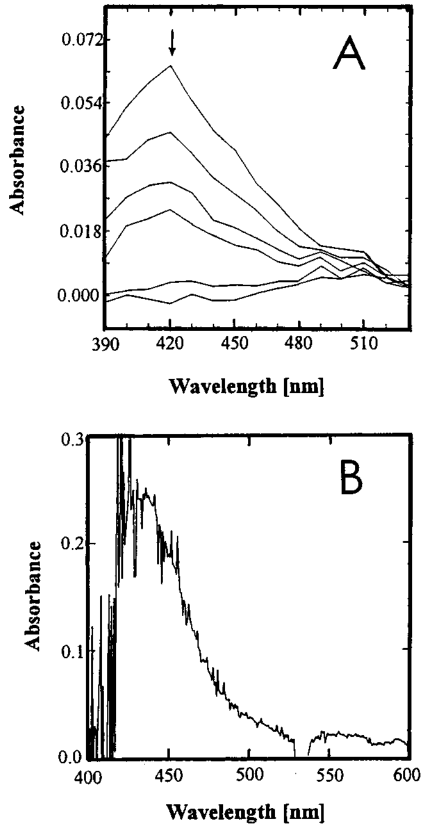


Figure 6. UV/vis absorption spectrum of nitrosohexamethylbenzenium σ-complex obtained (**A**) in dichloromethane solution at $T = 195$ K and (**B**) in n-butyl chloride glass at $T = 77$ K. The spectra in (**A**) are recorded at (top-to-bottom) 0.77, 1.2, 1.4, 2.5, and 4.6 μs upon 10-ns laser excitation of the hexamethylbenzene/nitrosonium π-complex.

In summary, the UV/vis spectroscopic results reported in this section give important insight into the nature of various arene/electrophile complexes as well as into the mechanism of their formation. First, the electronic absorption spectra provide a clear distinction between π-

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[34] (a) For example, chloroarenium σ-complexes may form by coupling of arene cation radical with chlorine atom. This conclusion is based on the observation of the reverse process, viz. the decomposition of chloroarenium ion to arene cation radical and chlorine atom,[24] i.e., Ar(H)Cl$^+$ → ArH$^{\bullet+}$ + Cl$^\bullet$. (b) Rathore, R.; Kochi, J. K. *Adv. Phys. Org. Chem.* **2000**, *35*, 193.

and σ-complexes and thus confirm our conclusions on the basis of the NMR spectral data. Second, the ultrafast time resolution of UV/vis spectroscopy allows us to observe and characterize transient intermediates that are too short-lived to be examined by NMR spectroscopy. Finally, the ultrafast formation dynamics of σ-complexes in electrophilic aromatic substitutions can be readily monitored by this spectroscopic technique. As a result, all intermediates in electrophilic aromatic nitrosations from the beginning to the end are clearly identified and their reaction dynamics are observed in real time.

5. Structural Analysis of σ- and π-Complexes by X-ray Crystallography

The ultimate tool to investigate the molecular structure of a chemical compound is X-ray crystallography, which provides precise coordinates for all atoms of the molecule and thus important information on the bond lengths and angles. The latter data are crucial for gaining information on the electronic properties of the atoms such as hybridization, bond orders, location of positive or negative charges, etc. Most critical for the investigation of reactive intermediates in electrophilic aromatic substitutions are precise results on the relative location and orientation of electrophile (E^+) and arene (ArH) in the ArH/E^+ complex and on the distribution of the positive charge between electrophile and arene ring. Thus, the crystallographic data ultimately lead to a clear determination of the π- versus σ-character of the ArH/E^+ complexes, their hapticity ($\eta^1-\eta^6$), and the degree of charge transfer between electrophile and arene.[35] However, the structural features that reveal the nature of the arene/electrophile complexes are extremely subtle and can only be reliably observed on high-quality single crystals utilizing low-temperature (77 K) X-ray crystallography.

These challenging technical requirements have severely limited the number of successful structural analyses of reactive intermediates in electrophilic aromatic substitutions. In fact, the few crystal structures of arenium σ-complexes available to date have all been obtained within the past decade. For example, the **TMT**-based chloroarenium ion (see eq 4 and Figure 1)[24] exhibit a carbon−chlorine bond distance of $d = 1.86$ Å, which is only slightly longer that of a chlorine atom σ-bonded to a quaternary carbon atom in other chlorocarbons.[36] Furthermore, the bond angles of the ipso carbon, which clearly reveal its sp^3 hybridization, and the significantly altered bond lengths in the aromatic ring, which result in a cyclohexadienyl structure, represent unambiguous evidence for the σ-character of this arene/electrophile complex.

The successful isolation of this chloroarenium ion as a single-crystal prompted us to attempt the crystallization of other σ-complexes. For example, the isolation of the chlorohexamethylbenzenium salt in crystalline form demonstrates that successful (low-temperature) crystallizations leading to suitable single crystals are not restricted to crowded arene donors (such as **TMT**). Importantly, the crystal structure of chlorohexamethylbenzenium hexafluoroantimonate[25] exhibits a chlorine−carbon bond distance of $d = 1.81$ Å, which is even closer to the sum of the single-bond covalent radii of chlorine and carbon, and $C_{ortho}-C_{ipso}-Cl$ bond angles of about 106°, which are very close to the tetrahedral bond angles of sp^3-hybridized carbon atoms. In addition, the structure of chlorohexamethylbenzenium ion, a good model for the Wheland intermediate in electrophilic aromatic chlorinations (vide supra), is in remarkable agreement with that of heptamethylbenzenium ion,[37] which represents a model for the Wheland intermediate in Friedel−Crafts methylations. First, both structures show similar bond lengths in the six-member ring with shortened **b** bonds that reveal the common cyclohexadienyl structure of both σ-complexes (see Table 4). Second, the methyl group and the chlorine atom are located at about the same angle relative to the aromatic plane (see Figure 7 and Table 4).

The crystal structure of bromohexamethylbenzenium cation[38] also shows more or less the same bond lengths in the aromatic ring with a shortened **b** bond that points to a cyclohexadienyl structure (see Table 4). The only difference as compared to the isostructural chlorohexamethylbenzenium[25] and heptamethylbenzenium[37] ions lies in the angle (α) between the electrophile, the *ipso*-carbon, and the plane of the cyclohexadienyl ring. Thus, bromohexamethylbenzenium ion exhibits an angle α of 68°, which is significantly greater than that for chlorohexamethylbenzenium ion ($\alpha = 56°$) and heptamethylbenzenium ion ($\alpha = 55°$, see Table 4). This increase in the angle α on going from the chlorohexa-methylbenzenium ion to the bromohexamethylbenzenium ion, which is accompanied by a decrease in the β angle between the *ipso*-methyl group and the aromatic plane (see Table 4), is illustrated in Figure 8 in which all three X-ray structures are superimposed.

Figure 8 also includes a cationic silyl/arene complex based on the X-ray structural data of toluene/$Si(C_2H_5)_3^+$ BPh_4^- which were obtained by Lambert et al.[39] in 1993.[40] Lambert's data and his conclusions have triggered a vigorous discussion over the charge distribution between triethylsilyl cation and toluene as well as the π- vs σ-character of this unique complex.[41−43] The discussion focuses on the existence of free silyl cation and its stabilization as a π-complex as opposed to the formation of a silyl-substituted arenium σ-complex. Thus, the rather long distance between silicon and the para carbon atom of toluene of $d = 2.18$ Å (which is 0.24 Å greater than

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[35] For a detailed discussion of the effects of charge-transfer bonding on the structure of arene donors as revealed by low-temperature X-ray crystallography, see ref 9b.

[36] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.

[37] Borodkin, G. I.; Nagi, S. M.; Gatilov, Y. V.; Shakirov, M. M.; Rybalvo, T. V.; Shubin, V, G. *Zh. Org. Khim.* **1992**, *28*, 1806.

[38] Dhanasekaran, T.; Lindeman, S. V.; Kochi, J. K. Unpublished results.

[39] Since the ipso carbon center lies in the nodal plane, the α- and β-tilt angles will play a minimal role on the cyclohexadienyl chromophore (see Table 4 and Figure 2). However distortion from planarity has important consequences (see Figures 4 and 9).

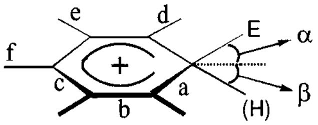
[40] (a) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1917. See also: (b) Lambert, J. B.; Zhang, S.; Ciro, S. M. *Organometallics*, **1994**, *13*, 2430 and (c) Reed, C. A.; Xie, Z.; Bau, R.; Benesi, A. *Science*, **1993**, *262*, 402. The cationic triethylsilyl/toluene complex exhibits the silyl moiety to be closest to the para carbon. The position of the *ipso*-methyl group in the silyl/hexamethylbenzene complex in Figure 9 is thus calculated. See: Hubig, S. M.; Lindeman, S. V.; Kochi, J. K. *Coord. Chem. Rev.*, in press.

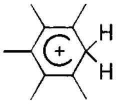
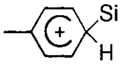
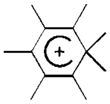
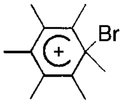
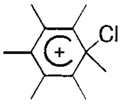
[41] Pauling, L. *Science* **1994**, *263*, 983.

[42] (a) Olah, G. A.; Rasul, G.; Li, X.-Y.; Buchholz, H. A.; Sandford, G.; Prakash, G. K. *Science* **1994**, *263*, 983. (b) Lambert, J. B.; Zhang, S. *Science* **1994**, *263*, 984.

[43] (a) Reed, C. A.; Xie, Z. *Science* **1994**, *263*, 985. (b) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 325 has pointed out the continuum of π- and σ-complexes. See also: (c) Hair, G. S.; Cowley, A. H.; Jones, R. A.; McBurnett, B. G.; Voigt, A. *J. Am. Chem. Soc.* **1999,** *121*, 4922.

Table 4. Bond Lengths[a] and Angles in Various σ-Complexes



	σ-Complexes	a	b	c	d	e	f	α	β
1		1.453	1.357	1.425	1.499	1.503	1.498	50°	50°
2		1.41	1.37	1.38	-[b]	-[b]	1.50	76°	-
3		1.493	1.375	1.423	1.499	1.510	1.495	55°[c]	55°[c]
4		1.496	1.375	1.428	1.493	1.507	1.488	68°	42°
5		1.493	1.369	1.431	1.505	1.510	1.501	56°	50°

[a] In Å with esd <0.5 pm, except for entry 2 (esd ≅ 1 pm).[40b] [b] No *o*- and *m*-methyl groups. [c] Average over two chemically equivalent methyl groups.

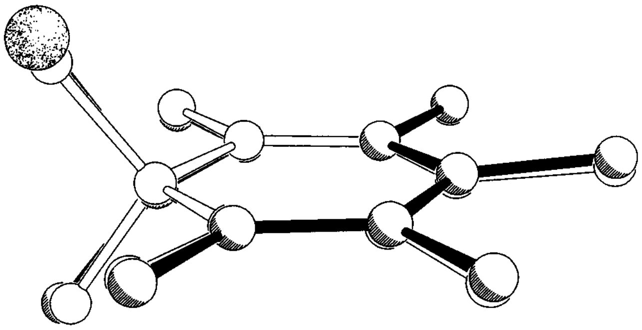


Figure 7. Superposition of the isostructural chlorohexamethylbenzenium (dark bonds) and heptamethylbenzenium σ-complexes.

the sum of the single-bond covalent radii of carbon and silicon),[41] the α angle of 76°, and the C−Si−C bond angle of 114° in the pyramidal silyl group illustrate convincingly that there is no clear-cut distinction between π- and σ-complexes.[44] Indeed, there is most likely to be a continuum of complexes of various degrees of π-/σ-character—with the silyl complex obviously exhibiting a rather high degree of π-character.

There are only a few structures of pure arene/electrophile π-complexes known. The best examples include the crystal structures of arene/nitrosonium complexes,[4,9b,27] which uniformly show the nitrosonium cation to be located in a more or less central position above the absolutely planar arene ring ($\beta = 0°$, vide supra) indicating a π-(η^6-)complex. The expansion of all bond distances in the planar aromatic ring that is observed with nitrosonium complexes of strong donors such as hexamethylbenzene, indicates degrees of charge transfer close to unity, which makes these complexes structurally indistinguishable from complexes of nitric oxide (NO) with arene cation radicals ($ArH^{•+}$).[35]

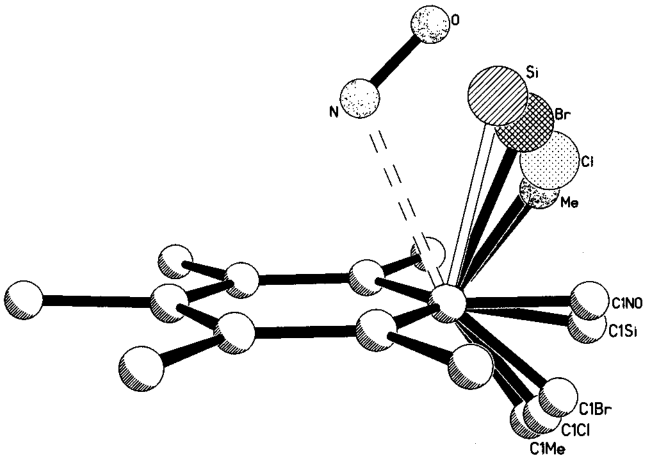


Figure 8. Superposition of the X-ray structures of hexamethylbenzene complexes with various electrophiles showing the continuous transition from the heptamethylbenzenium σ-complex to the hexamethylbenzene/nitrosonium π-complex depending on the electrophile.

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(44) All attempts to isolate single crystals of the hexamethylbenzene complex of trimethylsilyl cation have as yet been unsuccessful. (b) In an analogous vein, we have UV−vis data on the hexamethylbenzene complex of *tert*-butyl cation, but have been unable to grow an X-ray-quality single crystal.

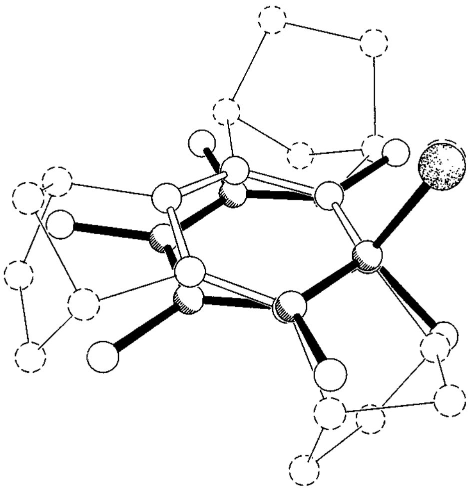

Figure 9. Superposition of the chloroarenium cations derived from hexamethylbenzene and **TMT** showing the planar versus bent structures of the two cyclohexadienyl chromophores.

Despite the fact that protonated aromatic hydrocarbons are readily prepared in solution in the presence of various acids, their isolation in crystalline form and the preparation of single crystals suitable for X-ray crystallographic studies has been accomplished only very recently by Reed et al. using perfluorinated tetraphenylborate and carborane anion as counteranions.[45] As a result, the structure of protonated pentamethylbenzene has been determined, and it clearly reveals the unmethylated carbon atom as the site of protonation. Moreover, the angles of the two hydrogen atoms relative to the aromatic plane of $\alpha = \beta = 50°$ and the shortened **b**-bond (see Table 4) provide additional evidence that this pentamethylbenzenium cation is a true σ-complex.

All X-ray crystallographic results are in excellent agreement with predictions on the basis of UV/vis and NMR spectral data. For example, the uniform 1:2:2:1 splitting of the carbon or proton signals in the NMR spectra as well as the similarity of the UV/vis spectra of all σ-complexes—featuring one narrow absorption band centered at 400 or 500 nm for the hexamethylbenzene and the **TMT** or **TET**-based complexes, respectively—parallels the similarity of the cyclohexadienyl structure of the chromophore. On the other hand, the significant difference in color between the yellow hexamethylbenzenium ions and the orange/red σ-complexes derived from **TMT** is clearly related to a structural difference between the two chromophores. Thus, in the hexamethylbenzenium ion the cyclohexadienyl chromophore exhibits a planar structure, whereas in **TMT**-derived σ-complexes the annelation of the norbornyl rings causes the cyclohexadienyl chromophore to be bent out of plane. This structural difference is illustrated in Figure 9 by superimposing the chloroarenium ions derived from **HMB** and **TMT** with an arbitrary overlap of the chlorine atom and the carbon atoms C_1, C_2, and C_6.

In contrast, π-complexes with η^6 hapticity such as the nitrosonium/arene complexes show only one single carbon or proton signal in the NMR spectra, and the UV/vis spectra show absorption bands that are assigned to charge-transfer transitions as observed in other electron donor−acceptor (π-) complexes.[46] Accordingly, on the basis of its UV/vis spectrum, which is very similar to that of nitrosonium π-complexes, we speculate on the elusive structure of the hexamethylbenzene/iodonium complex[47] which most likely exhibits the iodine atom located somewhere between the silyl and the nitrosonium cation in Figure 8.

In summary, although the number of crystal structures of arene/electrophile complexes is still limited (owing to the extreme experimental difficulties), the few examples available clearly demonstrate the continuous transition between π- and σ-complexes among the reactive intermediates in electrophilic aromatic substitution (see Figure 8). Depending on the electrophile, either the π- or the σ-complex is more stable and thus more easily detected and characterized. However, the critical parameters in the correlation between thermodynamic and structural properties are not yet clearly understood.

6. Concluding Remarks

In this paper, we utilize three methods for the observation, identification, and structural characterization of reactive intermediates in electrophilic aromatic substitutions, viz. time-resolved UV/vis spectroscopy, NMR spectroscopy, and X-ray crystallography. X-ray crystallography provides the most precise structural information, but it also requires high-quality single crystals. On the other hand, UV/vis spectroscopy is the fastest method to detect transient species with lifetimes as short as femtoseconds. However the UV/vis spectra contain limited structural information. Both the time scale and the structural information provided by NMR spectroscopy are intermediate between those of UV/vis spectroscopy and X-ray crystallography. As a consequence, the method of choice for the detection and identification of an intermediate species critically depends on its lifetime.

Most σ- or π-complexes in electrophilic aromatic substitutions encompass a rather wide range of different lifetimes, and they cannot be characterized by a single technique. In fact, X-ray crystallographic studies on σ- or π-complexes are still rather rare. However, all known crystal structures strongly support the conclusions drawn from the analyses of NMR and UV/vis spectroscopic data and confirm the assignments of the spectral absorption bands. We can thus utilize time-resolved (UV/vis) spectroscopy as the general technique for the identification of *all* reactive intermediates in electrophilic aromatic substitutions. Moreover, the fast time scale of UV/vis spectroscopy allows us to obtain information on the dynamics of the interconversion between various short-lived intermediates. Nitrosation is found to be the only example of an electrophilic aromatic substitution for which both the π- and the σ-complexes are observed and identified.[48] Furthermore, the transformation from π- to the σ-complex (which can be monitored in real time) is found to occur via the formation of an ultrashort-lived

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(45) Reed, C. A.; Fackler, N. L. P.; Kim, K.-C.; Stasko, D.; Evans, D. R.; Boyd, P. D. W.; Rickard, C. E. F. *J. Am. Chem. Soc.* **1999**, *121*, 6314.

(46) Foster, R. F. *Organic Charge-Transfer Complexes*; Academic Press: London, 1969.

(47) All our attempts to isolate the hexamethylbenzene/iodonium complex in crystalline form and to grow single crystals suitable for X-ray crystallography have as yet been unsuccessful.

(48) In addition, see Hubig et al.[13] for the role of paramagnetic (electron-transfer) intermediates in electrophilic aromatic nitrosation.

radical pair (consisting of arene cation radical and nitric oxide), which is taken to be structurally and energetically close model of the transition state in electrophilic aromatic nitrosation.

Critical to the success of these studies is the synthetic methodology for the generation of reactive intermediates in high yields under representative (typical) reaction conditions. Knowing this, we envision a time soon when X-ray diffraction requires much less time and UV−vis spectroscopy provides much more structural information,[49] both sufficient to routinely allow the complete mapping out the course of many organic reactions; and theoretical insight will provide quantitative information on the role of E^+ electrophiles in $\pi \rightarrow \sigma$ transformations of predictive value.

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(49) Particularly with the aid of theoretical calculations.