1,3,5-Tris(dialkylamino)benzenes: Model Compounds for the Electrophilic Substitution and Oxidation of Aromatic Compounds

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Anionic \(\sigma\) complexes have been known and extensively studied as intermediates of nucleophilic aromatic substitution since the beginning of the century.1 In a paper that still makes fascinating reading, Meisenheimer describes the formation and isolation of anionic \(\sigma\) complexes by reaction of picryl ethers with potassium alkoxides. Structural proof is derived from the fact that identical complexes are obtained from methyl 2,4,6-trinitrophenyl ether with potassium ethoxide, and from ethyl 2,4,6-trinitrophenyl ether with potassium methoxide.2 Cationic \(\sigma\) complexes (Wheland intermediates), on the other hand, had been characterized or isolated only in a few cases,3 despite the ubiquitous implication of electrophilic aromatic substitution in synthesis. Such cationic \(\sigma\) complexes were expected to be stabilized best by three amino substituents, in meta positions relative to each other,4 in analogy to the stabilization of anionic \(\sigma\) complexes by three meta-oriented nitro groups (Scheme I).

Franz X. Effenberger was born in Goldenstein, Northmoravia, on April 7, 1930. He received his Ph.D. degree in 1959 and his Habilitation in 1964, both from the University of Stuttgart. He spent one year as research associate with P. A. S. Smith at the University of Michigan in Ann Arbor and was appointed full professor at the University of Stuttgart in 1972, succeeding Heimut Brederbeck. In 1977 he spent five months as visiting professor at the Cornell University in Ithaca, NY. Since 1987 he is also rector (president) of the University of Stuttgart.

Neither 1,3,5-triaminobenzene itself nor its N-monosubstituted derivatives can serve as model substrates for arene reactions: these compounds exist, at least in part, in the form of the nonbenzenoid tautomers,5 and

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σ complexes, once formed, are facilely deprotonated to the corresponding quinoid systems.

N-Peralkylated 1,3,5-triaminobenzenes would, by virtue of the high donor potential of the NR₂ substituents, represent ideal model compounds.⁴ Such compounds were not known, though, at the outset of our investigations. We have developed general synthetic routes for this class of compounds and have studied the stabilization of cationic and as well as radical intermediates in the reactions of tris(dialkylamino)benzenes with electrophiles and oxidants.

**Synthesis and Physical Properties of 1,3,5-Tris(dialkylamino)benzenes**

N-Alkylation of aminobenzenes provides the usual access to (N,N-dialkylamino)benzenes. This synthetic procedure is not applicable to 1,3,5-triaminobenzene (Scheme 11). We have prepared N-peralkylated triaminobenzenes in good yield by two alternative routes. When chlorogluclidine is simply heated with secondary amines at 180–300 °C in an autoclave, triaminobenzenes 1 are obtained with three identical NR₂ substituents. Reaction of (dialkylamino)halobenzenes with lithium dialkylamides allows for the stepwise introduction, via arylene intermediates, of various dialkylamino groups, affording triaminobenzenes 2 with different NR₂ substituents (Scheme II).

The extent to which NR₂ substituents influence the electronic state and the reactivity of an arene σ system strongly depends on the relative π-donor potential of the individual dialkylamino group and on the hybridization of its N atom. The graduated effect of dialkylamino groups on π systems is well-known from the chemistry of enamines.⁸ A quantification of the resonance interaction between individual NR₂ groups and a C=C π system appeared highly desirable, considering the widespread preparative employment of enamines.

The relative donor potential of NR₂ substituents with respect to an acceptor π system in the uncharged ground state should be reflected in the different π-electron density of the β-carbon. The chemical shift of β-protons in enamines has indeed been employed successfully for probing C₆ σ-electron density.¹⁰ In the case of enamines of cyclic ketones, however, it is difficult to assess the influence of conformational and buttressing effects on chemical shifts. The 1,3,5-tris(dialkylamino)benzenes, in contrast, have a rigid planar structure. This makes them better suited for a quantification of the donor potential of the different NR₂ moieties on the basis of aromatic ring proton chemical shifts.

We have derived a consistent set of HMO parameters for the dimethylamino and pyrrolidino groups by correlating HMO π-electron densities with aryl proton chemical shifts for a series of methoxy-, (dimethylamino)-, and pyrrolidinobenzenes.¹¹ In this procedure, it was essential to scrupulously account for specific steric and/or anisotropic effects on protons in ortho positions to the substituents, which are different for each group, and also to exclude protons in meta positions which may principally not be incorporated into a Hückel-type correlation.¹² The parameters k₁⁻⁻, thus derived describe, in a quantitative manner, the different overlap integral (β) = R₀(ΣNR₂) of the lone electron pairs of the respective NR₂ moieties with the sp²-carbon π orbitals. For the piperidino and morpholino groups, the respective k₁⁻⁻ values were determined from a comparative study of the C(1)–NO rotation barriers in 2,4,6-tris(dialkylamino)-1-nitrosobenzenes.¹³

<table>
<thead>
<tr>
<th>-benzene</th>
<th>E₃₀⁰/β</th>
<th>ν₃₀⁰/cm⁻¹ (TNB complex)</th>
<th>E₁/²/β</th>
<th>δ ppm</th>
<th>δ ppm</th>
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<tr>
<td>1a, 1,3,5-trimorpholino-</td>
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<td>16000</td>
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<tr>
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<tr>
<td>1d, 1,3,5-trimorpholino-</td>
<td>-0.711⁴</td>
<td>20900</td>
<td>0.35</td>
<td>6.10</td>
<td></td>
</tr>
</tbody>
</table>

* Only longest wavelength CT band. * For the heteroatom parameters, the h and k values were used as described in the text and in ref 11a.

¹ In CH₂Cl₂ (UVASOL Merck), rounded to the nearest 100 cm⁻¹. * Measured at a rotating platinum electrode in CH₂CN against Ag/Ag⁺ (10⁻⁴ M in CH₂CN) as reference, supporting electrolyte 10⁻¹ M LiClO₄. ¹ In CDCl₃, TMS internal standard. ¹ Doubly degenerate HOMOs.


Chemical shifts, however, reflect upon the electronic properties of the (neutral) ground state. The (positively charged) transition state for electrophilic attack of the aromatic π system is better approximated by charge-transfer (CT) complexes with strong electron acceptors,
or by the relative stability of the radical cations formed in oxidation. Still, the CT transition energies for complexes of 1a-d with trinitrobenzene are well correlated with the HOMO energies, calculated with the chemical shift derived $\delta_{C-N}$ parameters. For the first polargraphic oxidation potentials, the correlation likewise holds. The physical properties of the symmetrical tris(dialkylamino)benzenes 1a-d are collected in Table I.

Formation, Structure, and Reactivity of Aromatic $\sigma$ Complexes

Aminobenzenes, as ambident nucleophiles, may be attacked by electrophiles both at the amino group and at the aromatic ring. Attack at the amino function, though kinetically more favorable, is often reversible. Reaction at a ring position, on the other hand, may be followed by irreversible deprotonation, i.e., re-aromatization. So, C-substitution products are as a rule isolated from the reactions of aminobenzenes with electrophiles.

A mixture of C- and N-monoprotonation products has been established spectroscopically for the protonation of 1,3,5-triaminobenzene itself,12a,b Protonation of the triaminobenzenes 1a-d likewise affords C- and N-protonation products 3 and 4, depending on the NR$_2$ substituent, which in this case are stable and isolable in dilute solution (Scheme III).

N-Protonation to 3 is favored by high basicity of the amino nitrogen, which may be approximated by the basicity of the respective secondary amines. Increasingly higher donor potential of the NR$_2$ substituent toward the aromatic $\pi$ system tips the scale in favor of C-protonation to 4. The donor potential of the pyrrolidino group is significantly higher than that of the piperidino group, which may be approximated by the donor potential of the pyrrolidino group. The donor potential of the pyrrolidino group is significantly higher than that of the piperidino group.

The problem of competitive N- and/or C-reaction arises for the reaction of 1a-d with all electrophiles. For model investigations, the pyrrolidino compound 1a represents the most suitable substrate since it reacts with electrophiles preferentially at a ring carbon, and since well-established $\sigma$ complexes 5 are isolated from the alkylation,14,15 sulfonation,16 acylation,16 and halogenation17,18 of 1a. The halo $\sigma$ complexes are much less stable, though, and will be discussed separately (see below) (Scheme IV).

The activation of 1a, by three pyrrolidino groups, is sufficient to allow for reactions with a wide variety of electrophiles in inert organic solvents without the addition of catalysts. The $\sigma$ complexes 5 crystalize directly from the reaction mixture. Especially stable $\sigma$ complexes with nonnucleophilic anions, e.g., BF$_4^-$ and ClO$_4^-$, are obtained by straightforward anion exchange. As a rule, re-aromatization of Wheland intermediates occurs spontaneously. Deprotonation of the $\sigma$ complexes 5, i.e., formation of the substituted tris(diaklylamino)benzenes 6, requires base.

The stability of the $\sigma$ complexes 5 allows for a facile crystal structure determination. By combining such experimentally determined geometries with MO calculations, a deeper understanding may be obtained of how electronic and steric influences combine to affect the stability and reaction behavior of Wheland intermediates in general.19 One planar (B) and two bent conformations (A, C) are theoretically possible for Wheland intermediates. Earlier CNDO calculations had predicted a planar structure for $\sigma$ complexes with $R'=H$ and a bent one for $R'=R''=\text{CH}_3$.20 $\sigma$ complexes with unlike substituents indeed are bent, as determined spectrosopically in solution21 heptamethyloclobadhydrium tetrachloroaluminate, on the other hand, has been found by X-ray crystallography to be more or less planar (Scheme V).

![Scheme III](image)

![Scheme IV](image)

![Scheme V](image)

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(c) Knoche, W.; Schoeller, W. W.; Schomäcker, R.; Vogel, S. Accepted for publication in J. Am. Chem. Soc.
(21) (a) Mackor, E. L.; MacLean, C. Pure Appl. Chem. 1964, 8, 393.
We have determined the crystal structure of 2,4,6-tripyrrolidinocyclohexadienyl bromide (5a: E = H, X = Br), 1-methyl-2,4,6-tripyrrolidinocyclohexadienyl perchlorate (5b: E = CH₃, X = ClO₄), and 1-bromo-2,4,6-tripyrrolidinocyclohexadienyl bromide (5c: E = X = Br). The protonated σ complex 5a in fact is basically planar, but 5b and 5c are definitely bent, with the CH₃ and Br substituents in axial positions. The deviation from planarity, as given by the experimentally determined dihedral angle α, is 15.4° for 5b and 15.0° for 5c (Table II). This dihedral angle, in conjunction with the length of the bond between C(1) and the incoming substituent E, plays a crucial role in correlating the stability and reactivity of σ complexes with theoretical calculations.

For σ complexes with identical ligands, R = R′, and hence equivalent C–R and C–R′ bonds, the planar conformation is expected to be electronically most stable since the cyclohexadienyl π system favors a planar geometry, and hyperconjugative stabilization is at a maximum in this conformation. With unlike ligands, R ≠ R′, conformations A and C no longer are energetically degenerate, and the conformation that has the ligand with the better donor σ orbital in the axial position is better stabilized. This electronic effect is expected to be reinforced if the ligand with the better σ donor bond also is the sterically more demanding one. The markedly different degree of hyperconjugation weakens the axial and strengthens the equatorial bond in the bent conformation. MNDO results show that σ complexes that are unsubstituted in the pentadienyl moiety are not very susceptible to steric effects of the ligands R and R′ at C(1) and that hyperconjugation effects dominate for these σ complexes. To test the validity of the MNDO calculations, the σ complexes 7 with unlike ligands were optimized with MNDO methods. The geometries thus obtained are in reasonable agreement with the crystal structures determined for 5a–c (see Table II). The MNDO results in particular confirm the planar conformation to be more stable for σ complexes with identical ligands, and a nonplanar conformation to be more stable for σ complexes with unlike ligands. Due to the above-mentioned steric and hyperconjugative effects, a big energy difference results between the stable conformation with R = CH₃ or Br in a quasi-axial position (α = +20°, see Table II) and the inverted conformation with a quasi-axial hydrogen

(α = 20°). Population of this inverted conformation consequently is likely to be very low indeed.

Two limiting situations may be envisaged on the basis of the theoretical and experimental results outlined so far for the reactivity of nonplanar σ complex intermediates: (i) the most stable conformation of the σ complex has the potential leaving group R′ in a quasi-axial position; (ii) the most stable conformation is that with R′ in a quasi-equatorial position (see C and A, respectively, in Scheme V). Re-aromatization via elimination of R′⁺ is kinetically favored for i. In the case of ii, an energetically highly unfavorable conformation, close to C with quasi-axial R′, has to be adopted prior to dissociation.

Figure 1 illustrates this concept graphically. The circle at the reaction coordinate represents, in comparison to C, the less stable conformation A, which as a result of calculations is not a minimum in the energy profile. It follows that if the attacking electrolyte prefers the axial position in a nonplanar σ complex, the second energy barrier represents the rate-determining step (Figure 1: reaction from left to right). If, under otherwise constant conditions, the entering group goes preferentially into the equatorial position, the leaving group is needed in an axial position, and the first activation barrier is rate-determining (Figure 1: reaction from right to left). These results also suggest that a σ complex may be stabilized with respect to re-aromatization by purely sterical effects in addition to the well-known electronic stabilization. The 2,4,6-tri-tert-butyl σ complex 8a (Scheme VI), with a poor leaving group R in an axial position, may well represent an example for this situation.

Experimental results that were hitherto hard to understand now became explicable in terms of the out-

Figure 1. Simplified hypersurface of the electrophilic substitution on aromatics with nonplanar intermediate σ-complexes.

Scheme VII

Scheme VIII

Scheme IX

There is general consent that the first step is the formation of a radical cation. Dimeric σ complexes likewise are intermediates common to all the mechanisms proposed, their deprotonation giving the biaryls as the first oxidation products isolated. It remains undecided, though, whether the dimeric σ complexes arise from direct dimerization of radical cations, from electrophilic attack upon unreacted arene by dicationic free radicals, or from a secondary oxidation step from the radical cations, or...
from oxidation of the 1:1 adducts of radical cation and arene.

Dimeric σ complexes 14 were isolated for the first time, as stable products, from the oxidation of tris(di-alkylamino)benzenes. Of the wealth of complexes 14 that could thus be obtained in crystalline form, the two σ complexes that are formed by oxidation of 1a and of 1-ethyl-2,4,6-tripyrrolidinobenzene (6a, R = C6H5) were selected for an X-ray structure determination, and for an in-depth study of the mechanism of their formation and their follow-up reactions (Scheme IX).

While the monomeric σ complexes 5 are characterized by simple three-band electron spectra, the longest wavelength absorption of the dimers 14 is split and/or shifted due to through-space as well as through-bond interaction. The relative orientation of the two cyclohexadienyl rings in 14a and 14b differs widely; the torsional angle θ is 65° in 14a and 163.3° in 14b. The crystal structures provide some insight into the probable arrangement of the two arene moieties which combine in the transition state of the oxidative dimerization. The endo conformation found for the dimer 14a is very similar to the geometry derived from calculations. This orientation is favored by considerable charge-transfer interaction between the two π systems. Severe steric interaction in the endo arrangement, on the other hand, between the ethyl group of one and a pyrrolidino group of the other arene ring makes the exo approach more favorable for the dimerization of 6a. This closely resembles the structure determined for the final product 14b.

Dimeric σ complexes 14 are obtained as sole products from the oxidation of 1a and 6a only if the oxidant is added rapidly, and if light and atmospheric oxygen have been painstakingly excluded. Without these precautions, the complexes 14 are formed together with the σ complexes 15, arising from hydrogen abstraction of the solvent, and the quinone immonium compounds 16 and diaryl peroxides 17, respectively, arising from reaction with O2 (Scheme X).

Continuous-flow ESR has unequivocally established the radical cations 1a⁺⁺ and 6a⁺⁺ as intermediates in the oxidation of 1a and 6a. Spectra simulated for these structures are in good agreement with the experimental ESR spectra. The long-wavelength absorption band of the radical cations at λ > 800 nm constitutes an ideal probe for following both their formation and secondary reactions. Photochemical dissociation of the dimeric σ complexes 14 is a very fast and highly efficient process. The complexes 14 may also be thermally dissociated into two radical cations. By UV/vis-spectroscopically monitoring the different, competitive reactions of 6a⁺⁺, formed from flash photolysis of 14b, the following rates have been determined for the individual processes: dimerization (→14b), k = 2.3 × 10⁴ L M⁻¹ s⁻¹; H abstraction (→15b), k = 2.5 × 10⁵ s⁻¹; reaction with O₂ (→17), k = 9 × 10⁶ L M⁻¹ s⁻¹. Half-life times have been determined for the two radical cations in the same manner; surprisingly, τ₁/₂ ≥ 1 s for 6a⁺⁺ and only ~1 ms for 1a⁺⁺.

All these experimental results may be rationalized theoretically. Qualitative arguments, which are confirmed by quantitative methods (extended Hückel, MNDO), show that interaction between the HOMOs of the two cyclohexadienyl subunits, π₂ and π', respectively, in the dimeric σ complexes is confined basically to through-space interaction. The two resulting combinations, π₂ ± π', are energetically degenerate and nonbonding for a dimeric σ complex with a torsional angle θ of 60° and almost degenerate for θ > 160°. For the interaction between the two lowest unoccupied orbitals, π₃ and π₃', of the two subunits, through-bond coupling prevails over through-space coupling for all torsional angles. Hence, the combination [π₃ - π₃' + σ] is energetically lower than [π₃ + π₃' - σ] for all conformations and thus represents the LUMO of the dimeric σ complex. The doubly occupied combination [π₃ + π₃' + σ], corresponding to [π₃ + π₃' - σ], denotes a significant electron transfer from the σ bond into the a priori vacant orbitals π₄ and π₄'; this, in terms of the MO formalism, is the reason for the severe hyperconjugative weakening of the central C(1)/C(1') bond in the dimeric σ complex.

The "photochemical dogma" demands that photoreactivity in the condensed phase be governed, as a rule, by the first electronically excited state. This may be represented in terms of the simplest one-determinant model by promotion of one electron from the HOMO [which has no contribution from the central σ bond] into the LUMO, [π₃ - π₃' + σ*], which is antibonding between C(1) and C(1'). Hence, the central σ bond is weakened even more than in the ground state and thus becomes predestined for photodissociation. Both the thermal and photochemical dissociation of the dimeric σ complexes are symmetry-allowed processes, with the photoreaction being kinetically slightly more favored.

This argument holds for 14a ($\beta = 65^\circ$) as well as for 14b ($\beta = 163^\circ$) since MO theory does not differentiate, in either the ground or the first excited state, between complexes with varying conformation about the central \( \sigma \) linkage. This picture changes drastically, however, when one compares the two radical cations, formed either by dissociation of 14a and 14b or by oxidation of 1a and 6a.

The radical cation 1a'' does not exist in the highly symmetrical \( D_{3h} \) structure, but rather in two, energetically very close, Jahn–Teller distorted structures 1a''-I and 1a''-II (Scheme XI). The respective charge densities and orbital coefficients can be approximated by the MNDO data for the simplified model structure shown in Figure 2.

Both the Jahn–Teller distorted forms of 1a'' are planar. In structure I, the overall highest coefficient and thence spin density of the SOMO \( \sigma_s \) is located at C(1) (conjoined with a negligible charge density, not unexpected for a positively charged alternating hydrocarbon structure). Moreover, C(1) is freely accessible in structure I and, thus, the predesigned point of attack in dimerization with a second radical cation, as well as in other radical reactions. Structure II is characterized by a relatively high coefficient and consequently low charge density at C(3)/C(5). These two ring positions are freely accessible and, hence, likely targets for radical attack. MNDO calculations demonstrate that, upon introduction of an alkyl substituent into the radical cation at C(1), the two neighboring dialkylamino groups are twisted almost 90° relative to the ring plane.

Structure 6a''-I thus remains as the only energy minimum for 6a++. The electronic configuration \( \pi_1^2 \pi_2^2 \pi_3 \) again is characterized by an extremely high coefficient and concomitant low charge density at the alkyl-substituted ring carbon. This reactive center, though electronically favored, yet appears extremely shielded by the alkyl substituent itself as well as by the two, nearly orthogonal NR\(_2\) groups in the \( \alpha \)- and \( \alpha' \)-positions.

On the basis of these theoretical arguments, and with the assumption of kinetic control, the following predictions can be made for regioselectivity and relative reactivity of the two tris(dialkylamino)benzene radical cations 1a++ and 6a++; all of them have been experimentally validated (see above). Reaction of 1a++ with a sterically demanding second radical cation which would directly yield the dimeric \( \sigma \) complex, H abstraction from a much less bulky solvent molecule, and reaction with the sterically least demanding \( O_2 \) are all equally facilitated at either C(1) in structure 1a++-I or C(3)/C(5) in structure 1a++-II. Compound 6a++, on the other hand, where electronic direction allows for reaction only at the extremely well shielded carbon C(1), may be attacked at this site by sufficiently small reagents only. H abstraction from the solvent and \( O_2 \) addition are still practical and indeed are observed solely at the alkyl-substituted ring carbon. Dimerization at this site is sterically impossible, however, and is thus restricted to a nonalkylated ring position. This site, though sterically much less hindered, is electronically very unfavorable. Consequently, dimerization of 6a++ is kinetically severely impeded relative to that of 1a++, and its half-lifetime is therefore 1000 times longer.

Reactions of Halo \( \sigma \) Complexes

As pointed out above, halo \( \sigma \) complexes are comparably much less stable. In their reactions with bases, product formation strongly depends on the nature of the base, the reaction temperature, and the re-
action time. This is exemplified in Scheme XII by the reactions of the bromo σ-complex 5e with a variety of bases/nucleophiles.

Deprotonation exclusively is effected by strong bases, e.g., alkoxides, giving 1-bromo-2,4,6-tripyrrolidino-phenylbenzene. With triethylamine in chloroform, the bipheryl 18 is obtained. Sulfides, on the other hand, and likewise hydrogen sulfite react as reducing agents only, 5c being dehalogenated to 1a. With potassium cyanide in methanol, the dimeric σ complex 14a is formed in almost quantitative yield within 20 min. The reaction of 5c with potassium rhodanide in methanol at ambient temperature illustrates most strikingly how product formation with a halobenzenium σ complex depends on the actual reaction time. If the reaction is quenched after 1 min, one finds the bromo substituent having been exchanged quantitatively, yielding the rhodano σ complex 5a. After 20 min, a mixture is obtained of the rhodano, the dimeric, and the protio σ complexes 19, 14a, and 5a, respectively (Scheme XIII).

From the reaction of 19 with sodium bromide, only the protio σ complex 5a (E = H, X = Br) is isolated after 60 min of reaction time. These reactions all show light dependence and are accompanied by drastic color changes of the reaction mixtures. The rapidity of the exchange of Br vs SCN renders a straightforward nucleophilic substitution, whether S,N1 or S,N2, highly unlikely. The formation of 14a and 15a has rather to be rationalized in terms of radical intermediates, via a one-electron charge-transfer mechanism.

The halo σ complex 21 is reduced by the nucleophile Nu-, via electron transfer, to the radical intermediate 22 whence, by cleavage of a halide ion, the radical cation 1a** is formed. Compound 1a** now undergoes all the follow-up reactions outlined in Scheme X, e.g., dimerization to 14a and H abstraction from the solvent to 15a. The substitution product 23 may be formed by radical recombination of Nu* and 1a** or by addition of the nucleophile Nu- to 1a**, and subsequent electron transfer from 24 to unreacted substrate 21 under formation of 22 in conjunction with 23. This second mechanism would constitute a radical chain process. The rate of the electron transfer depends both on the relative redox potential of the different reactive intermediates, which compete with each other in the mechanism outlined in Scheme XIV, and on the leaving tendency of the halides or other leaving groups. The experimentally determined reduction potentials of some halo σ complexes and of the σ complexes 19, 14a, and 5a are collected in Table III, together with the oxidation potentials of the respective anions (nucleophiles) and of triethylamine. The relative reactivity of the halo σ complexes 21 with rhodanide, halides, or tertiary amines shows good qualitative agreement with the gradation derived for the corresponding donor–acceptor charge-transfer interaction. The protio σ complex 5a is formed more and more with prolonged reaction time, since it has the most negative reduction potential (see Table III) and since the negligible leaving tendency of the hydroxide ion makes formation of 5a virtually irreversible.

There is no stringent proof possible for the radical chain mechanism, outlined in Scheme XIV for the nucleophilic substitution of halo σ complexes, since halide

![Diagram](image_url)

**Table III**

<table>
<thead>
<tr>
<th>Potential of Nucleophiles (A) and Reductive Potentials of σ Complexes (B) (vs Ag/AgNO₃, 0.1 M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
</tr>
<tr>
<td>E₁/₂, mV</td>
</tr>
<tr>
<td>(B)</td>
</tr>
<tr>
<td>E₁/₂, mV</td>
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</table>

* Determined for the tetrabutylammonium salts in CH₃CN/THAP, 0.1 M. Determined as the perchlorate.

ions set free in the course of the reaction may function as electron donors. The fact, however, that the reaction is accelerated by light and is incubated by radical inhibitors strongly argues in favor of a radical chain mechanism.

**Summarizing Remarks**

1,3,5-Tris(dialkylamino)benzenes are exceptionally well suited model substrates for the electronic substitution as well as the oxidation of arenes. From both types of reaction, Wheland intermediates, which still retain one hydrogen at the sp\(^3\) carbon atom, could be isolated for the first time in crystalline form and their structure determined by X-ray crystallography. When these structural data are combined with the results of MO calculations, a deeper insight may be gained into the energy profile of electrophilic attack on aromatic substrates. Thence, experimental results that so far were inexplicable can be interpreted satisfactorily. The follow-up reactions of radical cations, formed primarily in triaminobenzene oxidation, can likewise be rationalized. Triaminobenzenes are comparable in their reaction behavior to enamines and thus can be employed successfully as model compounds also for enamine reactions.\(^{14,34,36}\) This mechanistic parallel might prove both practically and theoretically important in future investigations.

Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. To all my co-workers who have contributed to this work over the years and whose names are given in the respective references, I want to express my heartfelt thanks for their enthusiastic collaboration. Among these, I want to emphasize the names of R. Niess, who was the first to prepare N-peralkylated triaminobenzenes; W.-D. Stohrer, who did almost all the calculations on these systems; J. J. Stezowski, who determined the crucial crystal structures; and P. Fischer, who was responsible for the NMR spectroscopic part and also did the translation of this contribution.
