The Reaction of Iodine Monochloride with Polycyclic Aromatic Compounds: Polar and Electron Transfer Pathways

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Several polycyclic aromatic hydrocarbons were treated with iodine monochloride. Although iodination is the predominant reaction of benzenoid arenes, chlorination is the sole reaction with anthracene, phenanthrene and naphthalene compounds (except for **5**), whose oxidation half-wave potentials are less than 1.58 V vs Ag/Ag^+ (0.1 M). Arenes with higher potentials are unreactive. Naphthalene (**9**) and its derivatives with mild electron-withdrawing substituents are chlorinated; the exception (**5**) yields the 1-iodo product (**21**). The reaction is first order in substrate and second order in ICl. An electron transfer pathway involving radical cation intermediates is assumed. Ion-pair collapse of the radical cation-ICl intermediates is proposed for the chlorinations and radical-pair collapse for the iodination.

In the past it appeared that the large majority of electrophilic aromatic substitutions proceed by just one mechanism with respect to the substrate,[1] and that its main features are well established. Nevertheless investigations of this reaction continue and a rich mechanistic diversity has been revealed.[2] Particularly noteworthy is the work of Kochi,[3] whose group has investigated the importance of charge transfer complexes and the formation of radical cations of arenes in substitution reactions. Our investigation of the reactions of iodine monochloride with polycyclic aromatic compounds was prompted by an earlier suggestion that iodine monofluoride was an active agent in fluorinations of polyarenes with I_2 and AgF.[4] It was further suggested that radical cations of the organic substrates were intermediates, as with the anodic fluorination of the same polyarenes.[5]

ICl has been used for more than a century as an iodinating agent for benzene derivatives,[6] but despite the extensive literature on this reagent, only a few reactions with polycyclic aromatic compounds have been reported.[7] Contrary to expectations based on electronegativity, chlorination has accompanied iodination of benzene derivatives at times,[8] and has been the principal reaction in some cases. Chlorination of salicylic acid occurred to a significant extent in the absence of a solvent and in a solvent of low dielectric constant, but iodination was the sole reaction in nitrobenzene.[9] Fluorobenzene gave mainly chlorofluorobenzenes without a solvent or in CCl_4, but in the more polar methanol gave only p-fluoroiodobenzene.[10] It was proposed that chlorination resulted from homolytic cleavage of ICl in the absence of a solvent or in solvents of low dielectric constant. It was estimated that, in more polar solvents of dielectric constants greater than 3.8, ICl dissociates heterolytically.[11]

The mechanism of the iodination of benzene derivatives has been described as a typical example of electrophilic substitution,[12] due to the polar nature of the I-Cl bond. Since ICl has been shown to be a Lewis acid catalyst, even in very small amounts,[13] the chlorination reactions with benzene derivatives without solvent or in nonpolar solvents[9,10] may also be described as examples of electrophilic substitution via $Cl_2{\cdot}ICl$. In this work we show that some polycyclic aromatic compounds undergo chlorination rather than iodination, even in the polar solvent acetonitrile, which we attribute to an electron transfer (SET[14]) mechanism.

The earlier results with benzene derivatives[9–11] are cited to indicate their generally different behavior. The explanations offered by others for the occasions when chlorination rather than iodination occurred in non-polar solvents were based on the information available at the time.

The fact that ICl dissociates to the elements in nonpolar solvents, although only to a slight extent, offered a reasonable explanation. Initially we chose to perform the reactions in the polar solvent MeCN in view of that earlier work. When it became necessary in our work to add the non-polar solvent CCl_4 to dissolve the substrate, thus lowering the dielectric constant, chlorination not iodination occurred. Dichloromethane ($\epsilon = 9.18$)[15] was

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Table 1. Reactions of Polycyclic Aromatic Compounds with Iodine Monochloride

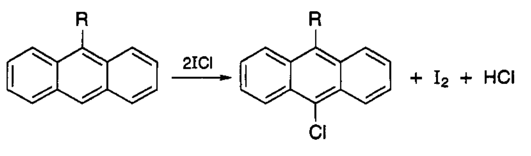
no.	compd	$E_{1/2}$[a] (V)	products	yield (%)
1	9-methylanthracene	0.66	9-chloro-10-methylanthracene (**14**)	61.3
			1,2-dianthrylethane[c] (**15**)	15.5
			anthraquinone (**16**)	12.8
2	anthracene	0.84	9-chloroanthracene (**17**)	98.1
2	anthracene[b]		9-chloroanthracene (**17**)	66.8
			9,10-dichloroanthracene (**18**)	4.52
3	9-phenanthracene	0.98	9-chloro-10-phenylanthracene (**19**)	89.7
4	9-bromoanthracene	0.99	9-bromo-10-chloroanthracene (**20**)	43.4
5	2,7-dimethoxynaphthalene	1.14	1-iodo-2,7-dimethoxynaphthalene (**21**)	81.1
6	phenanthrene	1.23	9-chlorophenanthrene (**22**)	55.7
			9,9′-biphenanthryl (**23**)	6.0
7	9-nitroanthracene	1.25	9-chloro-10-nitroanthracene (**24**)	86.0
8	9-anthracenecarbonitrile	1.32	10-chloro-9-anthracenecarbonitrile (**25**)	62.8
9	naphthalene	1.34	1-chloronaphthalene (**26**)	72.0
10	1-iodonaphthalene	1.53	1-chloro-5-iodonaphthalene (**27**)	16.9
11	1-bromonaphthalene	1.55	1-bromo-5-chloronaphthalene (**28**)	48.8
12	1-chloronaphthalene	1.58	no reaction	
13	1-nitronaphthalene	1.62	no reaction	

used as a solvent for the synthesis of **24** and the kinetics of **7** with ICl. In this work the range of dielectric constants does not influence the results. In general, the ease of oxidation of the substrate is the important factor. In the elegant work on the collapse of complexes of aromatic cation radicals, Sankararaman, Haney and Kochi[16] reported not only examples of the two pathways of collapse, but also the effect of solvent polarity on the pathway, Based on their studies the ion-pair collapse of the complex is favored by low polarity.

Results

Product Identification. The results of the reactions of polycyclic compounds with ICl are summarized in Table 1. Except for **5**, the more easily oxidized polycyclic compounds, as indicated by the voltammetric half-wave potentials, Table 1, are chlorinated, while those with higher potentials fail to react. For comparison, the values of a few arene compounds are: Benzene, 2.00 V, Toluene, 1.93 V, o-xylene, 1.57 V;[17b] anisole, 1.76 V, veratrole 1.45 V.[17c]

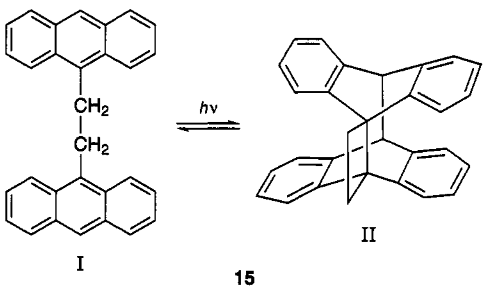
The anthracene compounds and phenanthrene are chlorinated. Naphthalene itself and its derivatives with weakly deactivating, ortho, para-directing substituents (**10**,**11**) are chlorinated; **12** does not react, **13** with an electron withdrawing substituent fails to react. In contrast **5**, which contains strong electron releasing substituents, is iodinated. The chlorinations are accompanied by the formation of elemental iodine.



(1)

R = H, Br, CN, Me, C_6H_5, NO_2

It should be noted that the photoisomer of 1,2-dianthrylethane (**15 II**)[18] is a product of the reaction of **1** with ICl. The same by-product was obtained from the anodic fluorination[4] of **1** and the reaction of **1** with I_2 and AgF.[4] While the formation of **15 II** may seem to be formally analogous to a $4\pi + 4\pi$ cycloaddition reaction, the likelihood that it is initiated by intramolecular electrophilic attack of a radical cation in one ring upon the other, neutral, ring appears to make this classification tenuous.



(2)

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Kinetic Studies. The chlorination reactions of compounds **7** and **9** were investigated by a series of kinetic experiments in order to determine the rate law. Studies of the rate of chlorination of both **7** and **9** as a function of substrate concentration in the presence of a large excess of ICl, established the reaction to be first order with respect to arene. While it was not possible to study the rate of chlorination of **7** as a function of ICl concentration in the presence of a large excess of **7**, analogous experiments on **9** showed the reaction to be second-order with respect to ICl. Thus, the rate law for the chlorination of **9** is found to be

$$\text{rate} = k[\mathbf{9}][\text{ICl}]^2$$

where k, the third order rate constant is 5.70×10^{-3} $L^2 \cdot mol^{-2} \cdot s^{-1}$ at 25 °C.

Discussion

The high dielectric constant of CH_3CN (38.8)[15] precludes homolytic cleavage of ICl[11] when it is used as the solvent. The presence of positive iodine species in acetonitrile solutions has been inferred from its moderate conductivity,[19] which may be due to a partial ionization

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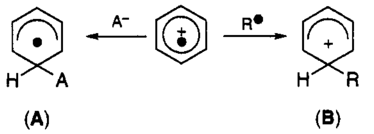
yielding $[(CH_3CN)]_2I^+$ ions.[20] The dissociation increases slowly, however, as demonstrated by an examination of the UV-Vis spectrum of ICl in acetonitrile.[21] We do not believe that the prior formation of an independent positive iodine species was significant in this work, since some reactions described here occurred more rapidly than the ionization reaction of ICl with the solvent. It is also unlikely that the chlorinations occurred by electrophilic attack by Cl in the $I^{\delta+}$-$Cl^{\delta-}$ molecule. The chemistry of ICl[22] reveals that the Cl is consistently weakly basic, whereas the I is strongly acidic.

The reactions of ICl with aromatic compounds in polar solvents may be described in a traditional manner as examples of electrophilic aromatic substitution with benzene derivatives to give iodinated products or as examples of oxidative substitution with some polycyclic aromatic compounds to give chlorinated products. Which of the two pathways is followed appears to depend upon the relative oxidation potentials of the substrates. Since the formation of elemental iodine accompanies chlorination of polycyclic aromatic compounds by ICl, an oxidative process occurs. An oxidative mechanism may be more accurately described in terms of electron transfer with the formation of radical cations. A mechanism involving radical cations has been proposed for the heterogeneous chlorination of anthracene compounds by copper(II) chloride,[23] based on the relative oxidation potentials of the substrates. The similarity of the results found here (Table 1) leads to an analogous conclusion.

The reactions of radical cations of polyarenes have been extensively investigated,[24] especially by electrochemical procedures. Examples of direct attack by chloride ions on several species of radical cations are known.[25] However, the formation of independent radical cations, as occurs by anodic oxidation, is not assumed here. It is in the context of recent studies of aromatic substitution that we believe the explanation for the behavior of ICl lies. The formation of π-complexes between electrophiles and aromatic compounds has been known for a long time, but their importance in the electrophilic mechanism has been debated.[26] More recently, intensive investigations have been made which indicate that electron donor-acceptor (EDA) complexes may be of significant importance in the mechanism,[3] e.g., aromatic mercuration, bromination and chlorination[27] and nitration.[28] It is proposed that substitution reactions may occur via the transient charge transfer (CT) complex:

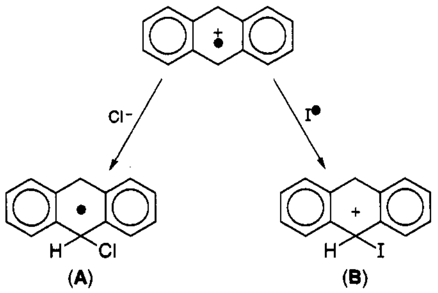
$$\mathrm{ArH{\cdot}ICl} \rightleftarrows \mathrm{ArH^{\bullet+}ICl^{\bullet-}} \qquad (3)$$

Aromatic substitution can occur when the CT complex collapses by either an ion-pair (**A**) or a radical-pair (**B**) interaction.[16]



(4)

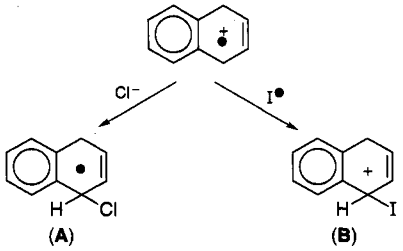
Because of the low ionization energies of polycyclic aromatic hydrocarbons their EDA complexes with electron acceptors form charge transfer (CT) complexes, in which a transient radical cation of the arene is present.[29] ICl readily forms EDA complexes with aromatic compounds.[30] Because of the relatively low oxidation energies of the polycyclic arenes, electron transfer leading to the CT complex $ArH^{+}{\cdot}ICl^{-}$ occurs.



(5)

The chlorination of the anthracene compounds can occur by the ion-pair route (**A**) followed by the removal of the second electron by ICl and the loss of a proton to the chloride ion.

Naphthalene and two of its derivatives with weakly deactivating substituents, **10** and **11**, are chlorinated,-while **13** with a strongly deactivating substituent fails to react (Table 1). Although chlorine is a weakly deactivating substituent, **12** also fails to react, but it has the highest oxidation potential of the three halogen derivatives of naphthalene. Surprisingly **5** is iodinated, as are other methoxy derivatives observed earlier.[7] The electron-releasing substituents lower the oxidation potential of naphthalene, which might be expected to lead to electron transfer and radical cation formation, but the same substituents activate the ring in the traditional sense, which would be expected to lead to electrophilic attack, which may appear to be the case. By the mechanism described for the anthracene compounds, however, the CT complex may undergo ion-pair or radical-pair collapse.



(6)

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Ion-pair collapse followed by electron and proton loss would lead to chlorination (**A**), while iodination would result from radical-pair collapse by reaction with an iodine atom (**B**) and loss of a proton to a chloride ion. *The remarkable result of all of the reactions in the solvents used is that in no case were the rates of iodination and chlorination competitive.* The following mechanism is consistent with the results for the chlorinations based on the observations made. However, other, kinetically equivalent, mechanisms are possible.

$$\mathrm{ArH} + \mathrm{ICl} \overset{K_1}{\rightleftharpoons} \mathrm{ArH{\cdot}ICl}$$

$$\mathrm{ArH{\cdot}ICl} \overset{K_2}{\rightleftharpoons} \mathrm{ArH^{\bullet+}{\cdot}ICl^{\bullet-}}$$

$$\left.\begin{array}{l} \mathrm{ArH^{\bullet+}{\cdot}ICl^{\bullet-}} \xrightarrow{k_3} \mathrm{ArHCl^{\bullet}} + \mathrm{I^{\bullet}} \\ \mathrm{ArHCl^{\bullet}} + \mathrm{ICl} \xrightarrow{k_4} \mathrm{ArHCl^{+}} + \mathrm{I^{\bullet}} + \mathrm{Cl^{-}} \\ \mathrm{ArHCl^{+}} + \mathrm{Cl^{-}} \xrightarrow{\text{fast}} \mathrm{ArCl} + \mathrm{HCl} \end{array}\right\} \text{chlorination}$$

$$\left.\begin{array}{l} \mathrm{ArH^{\bullet+}{\cdot}ICl^{\bullet-}} \xrightarrow{k_5} \mathrm{ArHI^{+}} + \mathrm{Cl^{-}} \\ \mathrm{ArHI^{+}} + \mathrm{Cl^{-}} \xrightarrow{\text{fast}} \mathrm{ArI} + \mathrm{HCl} \end{array}\right\} \text{iodination}$$

Molecular Orbital Calculations on Radical Cations. In order to understand how the electron distribution in the radical cations might influence the relative preference for chlorination or iodination, we carried out a series of restricted Hartree-Fock calculations on the radical cations of **1**, **2**, **6**, **8**, **9**, and **11**.[31] In every case except that of the radical cation of **11**(1-bromonaphthalene) chlorination was found to have occurred at the position of greatest electron deficiency (C-1 in **9**, C-9 in both **2** and **6**, and C-10 in both **1** and **8**, as measured by both total and π-electron densities). In 1-bromonaphthalene, although C-4 is predicted to be the most electron deficient carbon, chlorination occurs at C-5 (the second most electron deficient position in the radical cation) to give **30**.[32] These facts are generally consistent with a mechanism in which the radical cation is attacked by a nucleophilic chlorine species (e.g., Cl^- or ICl_2^-) at its most electron-deficient position. However, our results with 2,7-dimethoxynaphthalene (**5**) indicate that the mere ability to form radical cations easily is not in itself a guarantee of eventual chlorination.

The observation that 2,7-dimethoxynaphthalene (**5**) does not undergo chlorination, but gives only iodinated product, cannot be ascribed to lack of formation of a radical cation, since the methoxy groups markedly stabilize the radical cation of naphthalene, as indicated by its low value of $E_{1/2}$. Rather,we suspected that methoxy-induced charge redistribution might be responsible for the shift in reaction product. To test this possibility, we performed molecular orbital calculations on the radical cation of 2,7-dimethoxynaphthalene. Our calculations showed that π-electron donation by the methoxyl group (0.174 π-electron per methoxyl) leads to a significant reduction (35%) of the positive charge within the ring and a concomitant stabilization of the radical cation, as indicated by its calculated ionization potential of 13.16 eV (compared to 13.49 and 13.41 eV for naphthalene and 1-bromonaphthalene, respectively). It is thus possible that the transfer of a large fraction of the positive charge out of the rings would lead to a greatly lowered reactivity toward chloride ion and, by default, increased reactivity toward iodine atoms.

Table 2. Calculated SOMO and LUMO Values of Radical Cations

compd	SOMO (eV)	LUMO (eV)
1	−9.69	−5.12
2	−9.81	−5.20
8	−10.05	−5.59
6	−10.20	−5.00
5	−10.37	−4.87
9	−10.70	−5.28
11	−10.71	−5.42
iodine atom	−10.45[a]	
chloride ion	−16.58[a]	

[a] Experimental.

We believe that both the preference for iodination over chlorination in the case of 2,7-dimethoxynaphthalene and the observed positional selectivity can be explained in terms of Klopman's and Salem's perturbation theory.[33] In this approach, the energetics of reactions with early (i.e., reactant-like) transition states are modeled in terms of the perturbation interaction between the orbitals of the substrate (here taken to be the radical cation of the aromatic) and the attacking reagent (either chloride ion or iodine atom). The perturbation energy is given by the expression

$$\Delta E = -\sum_{ab}(q_a + q_b)\beta_{ab}S_{ab} + \sum_{k<l}\frac{Q_kQ_l}{\epsilon R_{kl}} - 2\sum_{s}^{occ}\sum_{r}^{unocc}\frac{\sum_{ab}(C_{ra}C_{sb}\beta_{ab})}{E_r - E_s}$$

The first term represents the interaction between filled orbitals in substrate and reagent and is overall repulsive, accounting for the bulk of the activation energy. The second term represents the coulombic interaction between charged atoms in the substrate and those in the attacking reagent (the "charge" term); for the case of a radical cation interacting with an anion, the summation will be negative. The third term accounts for the interaction between filled or half-filled orbitals in one reactant and empty or singly-occupied orbitals in the other. Since the energy gap between orbitals (E_r-E_s)-appears in the denominator, the dominant contributions are expected to be due to interactions between frontier orbitals, i.e., HOMO—LUMO (highest occupied MO—lowest unoccupied MO) or SOMO—SOMO (singly—occupied MO) interactions. In such cases, this corresponds to the "frontier" term, and will be negative. Thus, both terms reduce the interaction energy, facilitating reaction. Reactions may be either charge controlled or frontier controlled, depending on the relative importance of the second and third terms.

Charge-Controlled Chlorination. The calculated SOMO and LUMO energies for the radical cations of several compounds investigated in this work are summarized in Table 2, along with the HOMO energies of chloride ion and iodine atom.

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[31] The calculations were done on a CAChe computer system using the MOPAC package of programs (CAChe MOPAC version 94; QCPE program # 455, version 6.0) at the AM1 computational level, with full geometry optimization.

[32] The reason for this is not understood.

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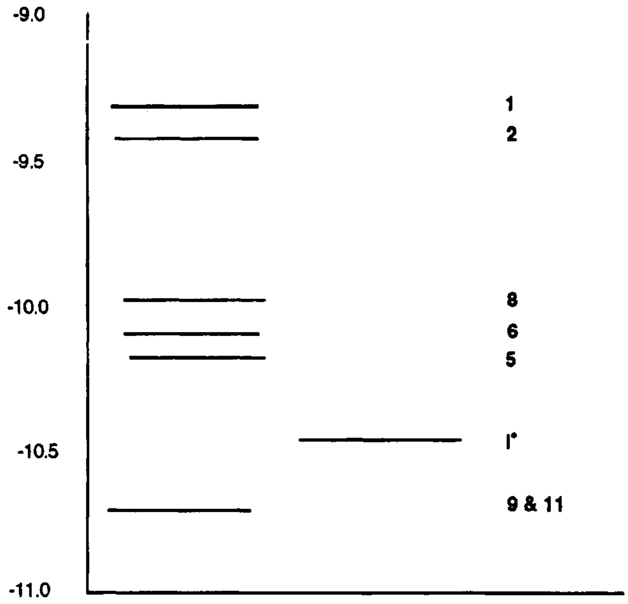

Figure 1. SOMO–LUMO gaps for radical cations and iodine atom.

The large energy gap between the HOMO of Cl^- and either the LUMO's or the SOMO's of the radical cations ensures that the third term will be insignificant. On the other hand, the second term is expected to make a large stabilizing contribution to the interaction energy. Thus, to a reasonable approximation

$$\Delta E_{Cl} \approx -\sum_{ab}(q_a + {}_{qb})\beta_{ab}S_{ab} + \sum_{k<l}\frac{Q_kQ_l}{\epsilon R_{kl}}$$

and attack of chloride ion on the radical cations is expected to be be charge-controlled, with attack occurring preferentially at the site of highest positive charge density. The structures of the chlorination products generally support this prediction.

Frontier-Controlled Iodination. Charge-controlled reactions of radical cations with iodine atoms are expected to be unimportant, owing to negligible coulombic attraction between the carbons of radical cation and the uncharged iodine atom, so that

$$\Delta E_I \approx \sum_{ad}(q_a + q_d)\beta_{ad}S_{ad} - 2\sum_{s}^{occ}\sum_{r}^{unocc}\frac{\sum_{ad}(C_{ra}C_{sd}\beta_{ad})}{E_r - E_s}$$

(Note that the lead term in this expression is not identical to that in the expression for ΔE_{Cl}). In consequence, only when frontier control becomes important should iodination be able to compete effectively with chlorination, and this will depend critically upon the size of the energy gap between the SOMO of iodine atom and the SOMO's of the radical cations. When the SOMO-SOMO energy gap is large, iodine reactivity will be low, leading to charge-controlled chlorination. If the SOMO-SOMO energy gap becomes sufficiently small (or, in the limit, if the SOMO's become degenerate) frontier-controlled iodination may become the dominant reaction pathway. Data for the SOMO(radical cation)-SOMO(iodine) energy gaps for the compounds we studied, shown graphically in Figure 1, along with the observed reaction type, clearly support this expectation.

Among the compounds in this study, only 2,7-dimethoxynaphthalene, whose SOMO energy is only 0.1 eV above that of iodine, undergoes iodination. Moreover, frontier control should lead to preferential substitution at the protonated carbon which makes the major contributor to the SOMO. For 2,7-dimethoxynaphthalene, this carbon is C-1, again in agreement with experiment.

The dichotomy between charge and frontier control we observed in the reactions of arenes with iodine monochloride parallels similar observations made by King and O'Malley on electrochemical fluorination of aromatic hydrocarbons.[4] Radical cations, generated by anodic oxidation, can react either with fluoride ion to give fluoroarenes, or with a second molecule of arene, affording dimers. Fluorination occurred in radical cations with pronounced positive charge buildup (e.g., 9-methylanthracene), and is the result of charge control. By contrast, radical cations with strongly delocalized positive charges (e.g., perylene) were found to be unreactive toward fluoride ion. Instead, since the SOMO of the radical cation and the HOMO of the arene have very similar energies, frontier control occurs and the dominant products are dimers.

Conclusions

The conclusions drawn from this work are limited to the reaction of ICl with polycyclic aromatic hydrocarbons, whose radical cations are characterized by a positive charge localization, at the 9- and 10- positions in anthracene and the 1- and 5- positions in naphthalene. Our observations are consistent with a model in which the radical cation intermediate can undergo either nucleophilic attack to give chlorinated products, or radical attack to give iodinated products. Radical attack becomes most likely when strongly electron-releasing substituents can assume a significant fraction of the positive charge.

Experimental Section

Apparatus and instruments used for identification were: Mel-Temp. mp (uncorr.); Hitachi Perkin Elmer R-24 or Varian FT 80A NMR; Hitachi Perkin Elmer 599-B IR; Carey 14, UV; Hitachi-Perkin Elmer RMS-4, mass spec.; Varian 5000, HPLC, IBM C-18 column, 4.5 × 15 mm. Elemental analyses were provided by Galbraith Laboratories. The medium pressure chromatography apparartus for separations was as described previously.[4] A BAS Electrochem Analyzer was used for cyclic voltammetry. Acetonitrile (Burdick & Jackson or Baker Analyzed Reagent HPLC) was passed through a column of alumina[34] (80 mesh, Brickman Basic Activity I) activated by heating to 350°. Aldrich Gold label compounds were used without further purification, the other Aldrich aromatic compounds were purified by column chromatography and/or recrystallization.

ICl was prepared from Cl_2 (Matheson High Purity) and I_2 (Bradford Scientific 99.9%) by the literature method[35] and purified by crystallization from the melt four times, mp 26–27° (lit. 27.2°). It was stored in sealed glass ampules and dispensed with a syringe through a glass capillary needle. Alternatively, Cl_2 was bubbled through a solution of I_2 in MeCN until the color of I_2 was replaced by that of ICl, then purged with nitrogen. Both methods of preparation led to chloro derivatives in subsequent reactions with polycyclic aromatic compounds. All glassware was flame-dried under a

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stream of nitrogen. Transfers were made and reactions run also under nitrogen. Aldrich solutions of ICl in CH_2Cl_2 were also used. Unless otherwise noted the reactions with ICl were carried out by one or both procedures described for **1** or **2**. The products were identified by IR, UV and NMR spectroscopy and, where necessary, elemental analysis.

Reaction of 9-Methylanthracene (1). To **1** (0.614 g, 3.19 mmol) in 90 mL of MeCN, 0.421 g, 2.59 mmol of ICl was added. After 24 h the reaction was stopped by bubbling ethylene through the solution to remove excess ICl. The solid remaining after evaporation was taken up in ether, washed twice with 10% $Na_2S_2O_3$, once with water and twice with brine before removal of the ether and vacuum desiccation. The solid products were separated by medium pressure chromatography on silica yielding the desired product (**14**) 0.181 g (61.3% yield) of yellow crystals: mp 181–183.5° (lit.[36] 180–181°). Also obtained was 0.077 g (15.5% yield) of a white solid that darkened at 240° and melted with decomposition at 260–270° (lit.[18] 278–284°) identified as **15** by comparison with an authentic sample and 0.069 g (12.8% yield) of **16**, formed from **14** during chromatography.

Reaction of Anthracene (2). To a solution of ICl (1.51 g, 9.30 mmol) in 25 mL of MeCN, 1.76 g, 9.89 mmol of **2** in 75 mL of $CHCl_3$ was added. After 3 h the solvent was removed and the product mixture dissolved in ether. The ether solution was poured into 0.5 M $Na_2S_2O_3$ producing a yellow precipitate, which was extracted with petrolem ether. The removal of the solvent gave 0.972 g, (98.1% yield) of **17**. In a second experiment, ICl (0.162 g, 1.00 mmol) in 100 mL of MeCN, was added to 0.224 g (1.26 mmol) of **2**. After 2.5 h at ambient temperature, the solvent was removed and the residue dissolved in ether and the solution added to 0.5 M $Na_2S_2O_3$ solution to remove I_2. The yellow precipitate that formed was dissolved in petroleum ether and separated by medium pressure chromatography on alumina giving **17** (0.0711 g, 66.8% yield) yellow crystals (EtOH): mp 105° (lit.[37] 104.5–105.5°). Also recovered was **18** (0.028 g, 4.52% yield) yellow crystals (EtOH): mp 209° (lit.[37] 209.5–211°).

Reaction of 9-Phenylanthracene (3). A mixture of **3** (0.470 g, 1.85 mmol) and ICl (0.5237 g, 4.13 mmol) was stirred in 100 mL of MeCN for 24 h. The usual treatment gave 0.421 g (89.7% yield) of **19**; mp 172–174° (twice from MeOH and pet. ether) (lit.[36] 173–174°).

Reaction of 9-Bromoanthracene (4). A solution of **4** (1.49 g, 5.78 mmol) in 75 mL of CCl_4[38] was added to ICl (2.09 g, 12.9 mmol) in 25 mL of MeCN, giving **20** (1.63 g, 43.4% yield)), yellow crystals (EtOH): mp 210° (lit.[39] 210–212°).

Reaction of 2,7-Dimethoxynaphthalene (5). A mixture of **5** (0.809 g, 4.30 mmol) and ICl (0.618 g, 3.81 mmol) was stirred in 80 mL MeCN. The separation of the product mixture required a C-18 reverse phase medium in a 50 × 1 cm column by MPLC, yielding 0.171 g (72.7% yield) of **21**: mp 38–41°; ^{1}H NMR ($CDCl_3$, 80 MHz), 7.68 (d, 1 H, $J_{3,4} = 8$ Hz), 7.57 (d, 1 H, $J_{5,6} = 8$ Hz), 7.41 (d, 1 H, $J_{6,8} = 2$ Hz) 7.00 (d 1 H $J_{3,4} = 8$ Hz); 6.98 (dd, 1H, $J_{5,6}$ = 6.98 (dd 1 H $J_{5,6} = 8$ Hz, $J_{6,8} = 2$ Hz); ^{13}C NMR ($CDCl_3$, 77.3 MHz), 5 protonated carbons [d 57.8, 55.9 (str)]; IR (KBr) ν 3020 (weak), 2940 (weak), 1628 (str), 1510 (str), 1266 (str), 1223 (str), 1069 (str), 1027 (str), 832 (str); mass spectrum, m/z (rel intensity) 157 (27.4),271 (11.6), 314 (100.0, M^+), 315 (13.4, M+1), 316 (1.6 M+2).

Reaction with Phenanthrene (6). A mixture of **6** (0.162 g, 0.909 mmol) and ICl (0.139 g, 0.863 mmol) was stirred in 30 mL of MeCN for 24 h. The usual procedure produced 0.51 g of **22** (55.7% yield): mp 49–50° (lit[40] 51–51.5°) and 0.009 g **23**[41] (6% yield): mp 107–113°; mass spectrum, m/z (rel intensity) 354 (0.6, M^+), 254 (36, 9-(Ph)phen.$^+$), 178 (100,phen.); IR (KBr) ν 3020, 2950, 1457, 1231, 738, 668; ^{1}NMR ($CDCl_3$, $(CH_3)_4Si$, 80 MHz) 7.94–7.43 (m, 9), 5.36 (s 1 H).

Reaction of 9-Nitroanthracene (7). A quantity of **7** (2.0 g, 9.0 mmol) was added to 1.30 g, 8.0 mmol,ICl in 150 mL of MeCN and let stand with stirring for 41 h. The usual treatment provided 0.719 g of **24**(86.0% yield): mp 221–223.5° (d) (lit.[42] 220–221°). A sample was also prepared by the reaction of **7** with a 1.0 M solution of ICl in CH_2Cl_2. The product was **24**.

Reaction of 9-Anthracenecarbonitrile (8). A solution of **8** (0.388 g, 1.91 mmol) in 75 mL CCl_4 was added to 0.292 g, 1.80 mmol, ICl in 25 mL of MeCN giving **25** (0.134 g, 62.8% yield)) yellow crystals (HOAc): mp 253° (lit.[43] 255°). 1H NMR ($CDCl_3$, Me_4Si, 90 MHz) 7.8 (m 4H), 8.5 (m, 4H) ppm; IR (KBr wafer) ν 2210, 2620, 1550, 1480, 1435, 1330, 1250, 930,750 cm^{-1}.

Reaction of Naphthalene (9). A quantity of **9** (1.15 g, 8.97 mmol) was stirred with 29 g, 7.94 mmol ICl in 120 mL MeCN for 24 h. The usual treatment gave 0.466 g of an oily liquid, **26**[44] (72.0% yield). Anal. Calcd for $C_{10}H_7Cl$: C, 73.86; H, 4.34; Cl, 21.80. Found: C, 74.00; H, 4.52; Cl, 21.59. IR (neat) ν 3060,1508, 1473,1205, 973, 794,767; UV (cyclohexane) 226 (4.86), 276 (3.73), 287 (3.80), 293 (3.59).

Reaction of 1-Iodonaphthalene (10). A mixture of **10** (1.40 g, 5.51 mmol) and ICl (0.815 g, 5.02 mmol) was stirred in 50 mL of MeCN. The usual treatment gave 0.122 g **27** (16.9% yield): mp 87.5–89° (lit.[45] 89°).

Reaction of 1-Bromonaphthalene (11). A mixture of **11** (1.22 g, 5.91 mmol) and 0.782 g (4.83 mmol) ICl was stirred in 50 mL of MeCN for 27.5 h. The usual treatment gave 0.285 g **28** (48.8% yield): mp 116–116.5° (lit.[46] 115–116°).

Kinetics Measurements. The kinetics of the chlorination with ICl were studied using naphthalene as a representative compound because of its invisibility in the visible region and the absence of other reactions. The progress of the reaction with an excess of naphthalene was measured by monitoring the rate of formation of I_2 by its absorbance at 499 nm. Varying amounts of acetonitrile were added to aliquots of stock solutions of ICl and **9** and 4-mL solutions in cuvettes were prepared, which were kept in the dark at 25.3°. They were withdrawn periodically for absorbance measurements in a Perkin-Elmer 21 spectrophotometer. In experiments using an excess of ICl, small aliquots were quenched periodically and the relative amounts of **9** and **26** determined by GC/MS. Stock solutions of ICl and **9** were added to MeCN in polystyrene test tubes and maintained at 24.9°. Every 5 min aliquots were withdrawn and quenched in another test tube containing Et_2O, 2% $Na_2S_2O_3$ and sat. NaCl solution. The products in the ether phase were determined by GC/MS measurements.

The rate of the reaction of **7** was determined in CH_2Cl_2 by observing the increase in absorbance due to the formation of **24** and I_2. A sample of **7** was added to a solution of an excess of ICl in CH_2Cl_2 in a closed cuvette. The progress of the reaction was followed by observing the growth of **24** at 394 nm and I_2 at 499 nm in a Perkin-Elmer Lambda 3b UV/Vis spectrophotometer.

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