Acc. Chem. Res. **1984,** *17,* 243–250 **243**

Reaction Pathways of the Cation Radicals of Aromatic Compounds Related to the Anthracenes

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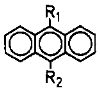
Received December 2, 1982 (Revised Manuscript Received June 8, 1983)

By virtue of their dual functionality, cation radicals in general are highly reactive entities. However, the ease with which the reactive intermediates undergo reactions with nucleophiles or form dimeric products can be moderated by suitable structural modification. The reactions of cation radicals of anthracene derivatives (1) or the related heterocycles (2) are very slow compared to those of the cation radicals of benzene derivatives. The diminished reactivity of $1^{+}\cdot$ and $2^{+}\cdot$ has been exploited to establish the reaction pathways of cation radicals with nucleophiles. In this Account, the kinetics and mechanism studies of these systems, which have contributed to the understanding of the complex reaction pathways of these intermediates, will be discussed.



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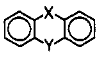

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My own interest in these systems dates back to a brief stay in the laboratory of Professor Ralph Adams. This was in 1968 shortly after cation radicals had been proven to be the primary intermediates of the anodic oxidation of anthracene and related compounds by three independent studies.[1-3] During the same time, the first kinetic study of these intermediates was published.[4]

The reaction of 9,10-diphenylanthracene (DPA) cation radical with pyridine was chosen as a model system for the study of cation radical–nucleophile reactions.[5] One of our primary goals in this work was to establish the nature of the primary intermediate that undergoes reaction with the nucleophile. At the time, it was not obvious that the reaction should be viewed as the direct attack of pyridine on the cation radical, generated in electrode reaction 1 to give the open-shell intermediate as indicated in reaction 2. One possible

$$\mathrm{DPA \rightleftarrows DPA^{+}\cdot + e^{-}} \tag{1}$$

$$\mathrm{DPA^{+}\cdot + C_5H_5N \rightarrow DPA\cdot{-}^{+}NC_5H_5} \tag{2}$$

alternative was that the nucleophile participates in the transition state for electron transfer as in reaction 3 and

$$\mathrm{DPA + C_5H_5N \rightarrow DPA^{+}{-}^{+}NC_5H_5 + 2e^{-}} \tag{3}$$

the process involves a two-electron transfer of which the cation radical is not a discreet intermediate. The latter mechanism was, at that time, favored by some as the most probable mechanism of the anodic acetoxylation of aromatic compounds.[6]

Our rotating disc electrode (RDE) studies of the reaction eliminated mechanism 3 from consideration.[5] Mechanism 3 predicts that two electrons/molecule of DPA will be transferred during RDE experiments regardless of the conditions. We found that the apparent number of electrons transferred could be controlled, ranging from one to two, by suitable adjustment of the rotation rate.[5] Our results led to the proposal of a mechanism consisting of reactions 1, 2, 4, and 5. The nature of the electron-transfer step 4 was not considered in detail with the view of Adams[7] that this is not the primary question.

$$\mathrm{DPA\cdot{-}^{+}NC_5H_5 \rightleftarrows DPA^{+}{-}^{+}NC_5H_5 + e^{-}} \tag{4}$$

$$\mathrm{DPA^{+}{-}^{+}NC_5H_5 + C_5H_5N \rightarrow DPA(NC_5H_5)_2^{2+}} \tag{5}$$

At the same time kinetic studies were being carried out on a related reaction, the hydroxylation of the thianthrene (structure 2, X = Y = S) cation radical.[8,9] These studies resulted in rate law 6 and the proposal of the disproportionation mechanism (reactions 7 and 8), with $k_{\mathrm{obsd}} = 2k_8K_7$.

$$-\mathrm{d}[\mathrm{Th}^{+}\cdot]/\mathrm{d}t = k_{\mathrm{obsd}}[\mathrm{Th}^{+}\cdot]^2[\mathrm{H_2O}]/[\mathrm{Th}] \tag{6}$$

$$2\mathrm{Th}^{+}\cdot \overset{K_7}{\rightleftarrows} \mathrm{Th}^{2+} + \mathrm{Th} \tag{7}$$

$$\mathrm{Th}^{2+} + \mathrm{H_2O} \xrightarrow{k_8} \mathrm{ThO} + 2\mathrm{H}^{+} \tag{8}$$

The studies of the reactions of DPA[5] and Th[8,9] cation radicals with nucleophiles set the stage for a lively discussion of the mechanisms of these reactions that has not yet concluded. Within 2 years both of the proposed mechanisms were challenged. On the basis of voltammetric studies,[10] $\mathrm{Th}^{+}\cdot$ was proposed to be the reactive intermediate in the hydroxylation reaction and mechanism 9–11 was suggested. This sequence, termed the

$$\mathrm{Th}^{+}\cdot + \mathrm{H_2O} \rightarrow \mathrm{Th}\cdot{-}\mathrm{OH} + \mathrm{H}^{+} \tag{9}$$

$$\mathrm{Th}\cdot{-}\mathrm{OH} + \mathrm{Th}^{+}\cdot \rightleftarrows \mathrm{Th}^{+}{-}\mathrm{OH} + \mathrm{Th} \tag{10}$$

$$\mathrm{Th}^{+}{-}\mathrm{OH} \rightarrow \mathrm{ThO} + \mathrm{H}^{+} \tag{11}$$

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(2) J. Phelps, K. S. V. Santhanam, and A. J. Bard, *J. Am. Chem. Soc.*, **89**, 1752 (1967).

(3) M. E. Peover and B. S. White, *J. Electroanal. Chem.*, **13**, 93 (1967).

(4) R. E. Sioda, *J. Phys. Chem.*, **72**, 2322 (1968).

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(7) R. N. Adams, *Acc. Chem. Res.*, **2**, 175 (1966).

(8) H. H. Shine and Y. Murata, *J. Am. Chem. Soc.*, **91**, 1872 (1969).

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half-regeneration mechanism, had previously been proposed for the hydroxylation of DPA[4] and phenothiazine[11] cation radicals. Chronoamperometric data for the pyridination of $DPA^{+\cdot}$ were found to be most consistent with the disproportionation scheme, and mechanism 12–13 was proposed[12] in contradiction to the earlier study.[5]

$$2DPA^{+\cdot} \rightleftarrows DPA^{2+} + DPA \qquad (12)$$

$$DPA^{2+} + C_5H_5N \rightarrow DPA^{+}\text{–}^{+}NC_5H_5 \qquad (13)$$

Thus, one of the most important questions in ion radical chemistry had emerged: what is the reactive intermediate in the reactions, ion radical or doubly charged ion? The same question later played a dominating role in studies on the protonation of anion radicals of aromatic hydrocarbons.[13–15]

Disproportionation of Cation Radicals

Disproportionation to doubly charged ions (DI) and neutral parent compounds is always a distinct possibility during ion radical (IR) reactions. The DI will invariably be more reactive toward nucleophiles (dications) or electrophiles (dianions) than the corresponding IR. The likelihood that such reactions will follow the disproportionation pathway depends on three factors: (a) k_{DI}/k_{IR}, the relative rate constants for the reactions of the two species; (b) the magnitude of K_{disp}, the disproportionation equilibrium constant; and (c) the magnitude of k_{disp}, the rate constant for disproportionation. For cation radical $A^{+\cdot}$, K_{disp} (eq 16) can be calculated from the difference in standard potentials for electrode reactions 14 and 15 according to relationship 17, which reduces to eq 18 at 298 K.

$$A^{+\cdot} + e^- \overset{E_1°}{\rightleftarrows} A \qquad (14)$$

$$A^{+\cdot} \overset{-E_2}{\rightleftarrows} A^{2+} + e^- \qquad (15)$$

$$2A^{+\cdot} \overset{K_{disp}}{\rightleftarrows} A^{2+} + A \qquad (16)$$

$$-\Delta G° = RT \ln K_{disp} = F(E_1° - E_2°) \qquad (17)$$

$$\log K_{disp} = (E_1° - E_2°)/0.0591 \qquad \text{(at 298.1 K)} \qquad (18)$$

In general, K_{disp} for cation radicals of aromatic compounds in solvents such as acetonitrile will be exceedingly small. In 1970, no reliable K_{disp} for pertinent aromatic cation radicals were available. This was because of the fact that the dications are so reactive that it had not been possible to obtain reversible electrode potentials for reaction 15, and it was commonly believed that the dications react with the solvents. We observed that the reversible potentials could be obtained in solvents containing strong mineral acids[16] or even in neutral solvents if nucleophilic impurities were effectively removed.[17] The values of $-(E_1° - E_2°)$ for the oxidations of substrates of structures 1 and 2 in acetonitrile were observed to be of the order of 500 mV or greater and, in general, $K_{disp} < 10^{-9}$.

One way in which the reliable K_{disp} can be used to test for the feasibility of the disproportionation mechanism is to compare the observed rate constants (k_{obsd}) with the maximum possible values predicted for eq 16 and 19.[18] Reactions such as the pyridination of $DPA^{+\cdot}$ and

$$A^{2+} + \text{nucleophile} \rightarrow \text{products} \qquad (19)$$

the hydroxylation of $Th^{+\cdot}$ had been observed to be first order in the nucleophiles. This requires that, if the disproportionation mechanism were operative, forward reaction 16 must be at least 10 times more rapid than reaction 19. Thus, the observed pseudo-second-order rate constant ($k_{obsd} = 2k_{19}K_{16}$) could be no greater than $10^{-1}\ k_f$, where k_f refers to forward reaction 16.[18] The maximum possible value of k_f can be estimated from equation 20, where $(k_b)_{diff}$ refers to a diffusion-controlled

$$(k_f)_{max} = (k_b)_{diff}K_{disp} \qquad (20)$$

rate constant for back-reaction 16. For example, if K_{disp} is 10^{-9} and $(k_b)_{diff}$ is 10^{10} M^{-1} s^{-1}, $(k_f)_{max}$ is 10 M^{-1} s^{-1} and the maximum value of k_{obsd} consistent with the disproportionation mechanism is 1 M^{-1} s^{-1}.

Reactions Occurring at the Dication Stage

The reactions of cation radicals with nucleophiles either have been or are considered to take place by one of the three mechanisms shown in Scheme I. The mechanisms are illustrated for the reaction between $Th^{+\cdot}$ and anisole (AnH) and are designated disproportionation, complexation, and half-regeneration. The most important difference between the disproportionation mechanism and the other two is that the dication, rather than the cation radical, is the species reacting with the nucleophile. The primary difference between the complexation and the half-regeneration mechanisms is that in the former, the initial interaction results in the formation of a π complex and covalent bonding does not occur until the dication stage, whereas in the latter, the bond formation takes place in the first step. Thus, the complexation mechanism is a compromise between disproportionation where the dication is the electrophile and half-regeneration where only ions with a single charge are involved.

Reactions of Thianthrene Cation Radical with Arene Nucleophiles. The value of K_{disp} for $Th^{+\cdot}$ in acetonitrile was observed to be equal to 2.3×10^{-9}, which results in a value of 2.3 M^{-1} s^{-1} for $(k_{obsd})_{max}$ for the reactions of $Th^{+\cdot}$ going through the disproportionation mechanism with rates directly dependent upon the nucleophile concentration.[17] Values as high as 0.2 and 3 M^{-1} s^{-1} were observed for the reactions with water[8,9] and anisole,[19] respectively. Thus, it was conceivable on the basis of the available kinetic and equilibrium[17] data that both of these reactions follow the disproportionation mechanism. The only conflicting evidence at this point came from the voltammetric study,[10] which indicated that $Th^{+\cdot}$ was indeed the species undergoing reaction with the nucleophiles.

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(11) C. Barry, G. Cauquis, and M. Maurey, *Bull. Chim. Soc. Fr.*, 2510 (1966).

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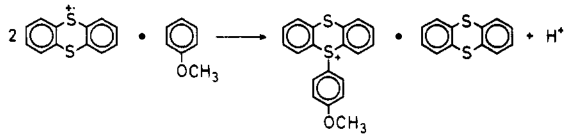
The reaction studied initially was that of $Th^{+\cdot}$ with anisole.[20] Reaction 21 is very similar with respect to kinetics and the products[19] to the hydroxylation reaction. All three of the mechanisms in Scheme I were considered to be feasible. For clarity, the rate expressions for each of the mechanisms are given in Scheme I. Under conditions where [AnH] and [Th] are large relative to $[Th^{+\cdot}]$, these quantities can be considered to be constant, and useful relationships involving $1/k_{app}$, the apparent second-order rate constants, can be derived for the three mechanisms. This analysis serves to differentiate between the disproportionation mechanism (eq 24) and the other two mechanisms (eq 29 and 34). The distinguishing feature is the intercepts of plots of $1/k_{app}$ vs. [Th].[20] Disproportionation requires that the intercept be a constant independent of [AnH], whereas the intercepts for the other two mechanisms are predicted to be directly proportional to $[AnH]^{-1}$. The kinetic study[20] resulted in a linear relationship (eq 35), where a and b are constants, for the reactions of

$$1/k_{app} = a[Th]/[AnH] + b/[AnH] \qquad (35)$$

$Th^{+\cdot}$ in the presence of excess Th and AnH. This analysis ruled out the disproportionation mechanism.



(21)

Scheme I

disproportionation

$$2Th^{+\cdot} \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} Th^{2+} + Th$$

$$Th^{2+} + AnH \xrightarrow{k_{22}} Th^{+}\text{–}An + H^{+} \qquad (22)$$

$$-d[Th^{+\cdot}]/dt = 2k_7k_{22}[Th^{+\cdot}]^2[AnH]/(k_{-7}[Th] + k_{22}[AnH]) \qquad (23)$$

$$1/k_{app} = [Th]/(2k_{22}K_7[AnH]) + 1/(2k_7) \qquad (24)$$

complexation

$$Th^{+\cdot} + AnH \underset{k_{-25}}{\overset{k_{25}}{\rightleftarrows}} (Th/AnH)^{+\cdot} \qquad (25)$$

$$(Th/AnH)^{+\cdot} + Th^{+\cdot} \underset{k_{-26}}{\overset{k_{26}}{\rightleftarrows}} (Th/AnH)^{2+} + Th \qquad (26)$$

$$(Th/AnH)^{2+} \xrightarrow{k_{27}} Th^{+}\text{–}An + H^{+} \qquad (27)$$

$$-d[Th^{+\cdot}]/dt = 2k_{26}k_{27}K_{31}[Th^{+\cdot}]^2[AnH]/(k_{-26}[Th] + k_{27}) \qquad (28)$$

$$1/k_{app} = [Th]/(2k_{27}K_{25}K_{26}[AnH]) + 1/(2k_{26}K_{25}[AnH]) \qquad (29)$$

half-regeneration

$$Th^{+\cdot} + AnH \underset{k_{-30}}{\overset{k_{30}}{\rightleftarrows}} Th\cdot\text{–}(AnH)^{+} \qquad (30)$$

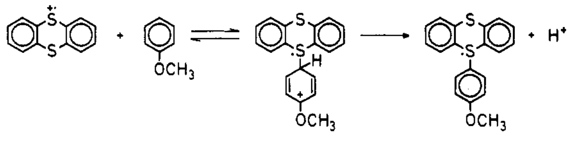
$$Th\cdot\text{–}(AnH)^{+} + Th^{+\cdot} \underset{k_{-31}}{\overset{k_{31}}{\rightleftarrows}} Th^{+}\text{–}(AnH)^{+} + Th \qquad (31)$$

$$Th^{+}\text{–}(AnH)^{+} \xrightarrow{k_{32}} Th^{+}\text{–}An + H^{+} \qquad (32)$$

$$-d[Th^{+\cdot}]/dt = 2k_{31}k_{32}K_{30}[Th^{+\cdot}]^2[AnH]/(k_{-31}[Th] + k_{32}) \qquad (33)$$

$$1/k_{app} = [Th]/(2k_{32}K_{30}K_{31}[AnH]) + 1/(2k_{31}K_{30}[AnH]) \qquad (34)$$

Since the kinetics do not distinguish between the complexation and the half-regeneration mechanisms, it is necessary to rely on other considerations to assign a mechanism. If the reaction involved the formation of the covalently bonded intermediate **3** (= $Th\cdot$–$(AnH)^{+}$), proton loss would be expected to intervene before involvement of the second $Th^{+\cdot}$ moiety. Further evidence regarding this point was obtained from a comparable study of the reaction of $Th^{+\cdot}$ with phenol (PhOH),[21] a reaction of general features very similar to reaction 21.[22] If **5** were a common intermediate in all cases and undergoes competing electron transfer (eq 37) and proton loss (eq 38), the nature of R (H or CH_3) in **5** would have a profound effect on the partitioning between reactions 37 and 38. The rate of reaction 37 should be more or less independent of R, whereas reaction 38 would be expected to be several orders of magnitude faster when R is H. This follows from the fact that proton transfer (eq 38) can be from oxygen when R is H but must be from carbon in the other case. Under nearly identical conditions in CH_2Cl_2 containing TFA (trifluoroacetic acid), reactions involving both AnH[20] and PhOH[21] were observed to go nearly exclusively by pathways second order in $Th^{+\cdot}$ when $[Th^{+\cdot}]$ ranged from 10^{-4} to 10^{-3} M. At lower $[Th^{+\cdot}]$ the reaction became first order in $Th^{+\cdot}$ when the other reactant was AnH but not in the PhOH case. This appears to be inconsistent with competing reactions 37 and 38 since reaction 38 is far more favorable when R is H and would be expected to compete at higher $[Th^{+\cdot}]$. Furthermore, the deprotonation of dication **6**, especially when R is H, would be expected to be so rapid that reverse reaction 37 could not compete effectively.



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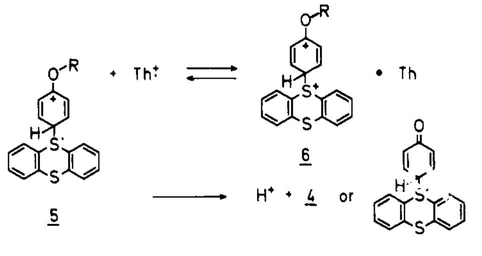

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Thus, it appears that reactions between $Th^{+\cdot}$ and the arene nucleophiles, AnH and PhOH, follow the complexation mechanism under conditions where the ki-

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[20] U. Svanholm, O. Hammerich, and V. D. Parker, *J. Am. Chem. Soc.*, **97**, 101 (1975).

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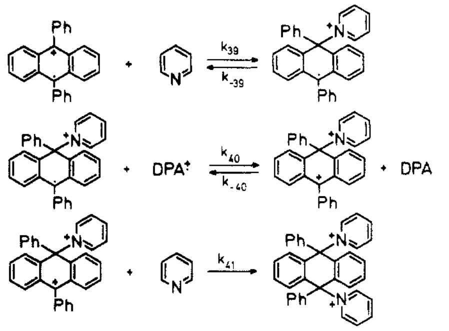
netics are second order in $Th^{+}\cdot$.

Reactions of Anthracene Cation Radicals. The cation radicals of anthracene and 9-phenylanthracene (PA) were observed to undergo arylation reactions in the presence of a number of benzene derivatives including AnH.[23] The reaction between $PA^{+}\cdot$ and AnH was studied in most detail, and the kinetics were observed to be similar to those of the reactions of $Th^{+}\cdot$. The complexation mechanism was proposed for these reactions as well.[23]

The pyridination of $DPA^{+}\cdot$ is a related reaction. The most important difference between the nucleophilic action of pyridine and that of the other arene nucleophiles is that bonding takes place to nitrogen in the pyridine case and C–C bonding is involved with the other nucleophiles. All of the early studies appeared to leave no doubt that the mechanism of the reaction of $DPA^{+}\cdot$ with pyridine consists of reactions 39–41.



(39)

(40)

(41)

The cation radical was shown to be the species undergoing nucleophilic attack,[5] the disproportionation mechanism was ruled out,[18] and the final product of the reaction was characterized.[24] The kinetic studies resulted in rate law 42,[5,25–27] and a reasonably good

$$-d[DPA^{+}\cdot]/dt = 2k_{39}[DPA^{+}\cdot][pyridine] \quad (42)$$

Hammett correlation was found with 4-substituted pyridines.[5] Thus, it appeared that only reaction 39 contributed to controlling the rate.

However, more recent studies have resulted in conflicting results. While only rate law 42 was found at $[DPA^{+}\cdot]$ of the order of 10^{-4} M,[26] rate law 43 was pro-

$$-d[DPA^{+}\cdot]/dt = 2k_{40}K_{39}[DPA^{+}\cdot]^2[pyridine] \quad (43)$$

posed for the data obtained at $[DPA^{+}\cdot]$ of the order of 10^{-5} M.[28] Linear sweep voltammetry (LSV) studies[29,30] resulted in rate law 44. Difficulty is encountered in

$$-d[DPA^{+}\cdot]/dt = k_{obsd}[DPA^{+}\cdot]^2[pyridine]/[DPA] \quad (44)$$

attempting to relate rate law 44 to mechanism 39–41. The reaction orders 2 in $DPA^{+}\cdot$ and −1 in DPA are consistent with reactions 39 and 40 being in equilibrium followed by irreversible product-forming reactions. However, if the product-forming reaction is (41), the reaction order in pyridine would be 2.

Mechanism 39–41 must be modified in order to be consistent with the kinetics and the complexation mechanism 45–47 provides a rationale for all of the rate data. Under conditions where the reaction is first order

$$DPA^{+}\cdot + C_5H_5N \underset{k_{-45}}{\overset{k_{45}}{\rightleftharpoons}} (DPA/C_5H_5N)^{+}\cdot \quad (45)$$

$$(DPA/C_5H_5N)^{+}\cdot + DPA^{+}\cdot \underset{k_{-46}}{\overset{k_{46}}{\rightleftharpoons}} (DPA/C_5H_5N)^{2+} + DPA \quad (46)$$

$$(DPA/C_5H_5N)^{2+} \xrightarrow{k_{47}} DPA^{+}\text{–}NC_5H_5^{+} \quad (47)$$

in $DPA^{+}\cdot$, forward reaction 45 could be rate determining, and rate law 42 can be modified by replacing k_{39} by k_{45}. When rate law 43 is applicable, equilibrium 45 could be followed by rate-determining electron transfer 46 and $k_{obsd} = 2k_{46}K_{45}$. The final case arises when both (45) and (46) are at equilibrium, and internal reorganization of the dication–pyridine complex (47) becomes rate determining, resulting in rate law 44 with $k_{obsd} = 2k_{47}K_{45}K_{46}$. Naturally, kinetic data cannot be considered as proof for mechanism 45–47. On the other hand, it is the only one proposed to now that is consistent with all of the data. Considering the number of species involved in these reactions, it is not surprising that the observed rate laws and mechanisms depend strongly upon the reaction conditions. The fact that the kinetic data and mechanism 45–47 conform to the patterns observed for the reactions of $Th^{+}\cdot$ strengthens the concept of π-complex formation as the initial cation radical–nucleophile interaction. Initial π-complex formation has also been proposed in order to explain kinetic data for some ion radical dimerization reactions.[31,32]

Further Comments on the Complexation Mechanism. Attempts in the author's laboratory to obtain spectral evidence for the cation radical–nucleophile complexes have not been successful. The equilibrium concentrations of the complexes could be very low. This would preclude their observation by UV–visible spectroscopy since their presence is masked by the absorption bands of the more abundant uncomplexed cation radical. It is conceivable that the complexes could be detected by ESR spectroscopy. This has not yet been attempted.

In order for the complexation mechanism to be favorable relative to disproportionation, the formation of the complexed cation radical must be accompanied by a significant lowering of the oxidation potential. A rough estimate of the relative rate constants for electron transfer can be made by assuming that the reverse reaction is diffusion controlled, which would give rise to a decade change in the forward rate constant for a 60-mV change in the oxidation potential. If the ratio of complexed to uncomplexed cation radical concentrations is 10^{-2}, an oxidation potential shift of about 180 mV would be required for the rate of the complexation

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(23) U. Svanholm and V. D. Parker, *J. Am. Chem. Soc.*, **98**, 2942 (1976).

(24) D. T. Shang and H. N. Blount, *J. Electroanal. Chem.*, **54**, 305 (1974).

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(26) J. F. Evans and H. N. Blount, *J. Am. Chem. Soc.*, **100**, 4191 (1978).

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(28) J. F. Evans and H. N. Blount, *J. Phys. Chem.*, **83**, 1970 (1979).

(29) E. Ahlberg and V. D. Parker, *Acta Chem. Scand., Ser. B*, **34**, 97 (1980).

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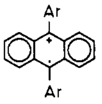
(32) V. D. Parker and D. Bethell, *Acta Chem. Scand., Ser. B*, **35**, 691 (1981).

reaction to be 10 times that of disproportionation.

There are no really pertinent data to use in making predictions of the effect of complex formation on the oxidation potentials of the cation radicals. However, we can consider the extreme of complex formation to be covalently bonded adduct formation. The nucleophile adducts **9** of 9,10-diarylanthracene cation radicals **8**, where Nu is CF_3CO_2, CH_3O, or HO, are oxidized at



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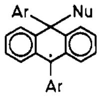

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potentials about 1.0 and 1.2 V less positive than the corresponding cation radicals.[33] The oxidation potentials of the cation radical–nucleophile complexes would be expected to be intermediate between those of **8** and **9**. The ease of oxidation of the complexes would depend upon the identity of the nucleophile as well as the strength of the interactions in the complex.

Since the favorable effect of lowering the oxidation potential brought about by complex formation is counteracted by a low equilibrium concentration of the complex, the complexation mechanism passing through the dication is not very favorable. If the initial complex has another favorable reaction pathway, this will be expected to compete. In the case of the reaction between $Th^{+\cdot}$ and AnH, the complex apparently dissociates (48) and oxidation products of AnH are formed

$$(Th/AnH)^{+\cdot} \xrightarrow{k_{48}} AnH^{+\cdot} + Th \qquad (48)$$

when $[Th^{+\cdot}]$ is too low for (26) to compete.[20] This reaction was not observed when the nucleophile was PhOH, but in CH_2Cl_2 in the absence of TFA the reaction is first order in $Th^{+\cdot}$ and can be formulated as in (49), where C_6H_5O is an oxocyclohexadienyl group.[21]

$$(Th/PhOH)^{+\cdot} \xrightarrow{k_{49}} Th\cdot\text{–}C_6H_5O + H^+ \qquad (49)$$

Thus, loss of the proton allows the covalent bonding to take place at the cation radical stage. In general, if the nucleophile has an easily expelled proton or is negatively charged, rearrangement of the initially formed π complex to the covalently bonded adduct would be expected to be more favorable than further oxidation to the dication.

Reactions Occurring at the Cation Radical Stage

Shortly after the initial papers in our series on homogeneous kinetic studies of the reactions of aromatic cation radicals were published,[20,21,23,25,34-36] a series of papers by Evans and Blount appeared[26,28,37-40] that deal with the same or similar systems. McCreery and coworkers[41-44] have published a series of studies dealing with phenothiazine derivative (X = S, Y = NR) cation radicals reacting with anionic nucleophiles. The half-regeneration mechanism was favored by both of these groups.

Reaction of Thianthrene Cation Radical with Water. The mechanism studies on this reaction have attracted the most attention.[45,46] The hydroxylation of $Th^{+\cdot}$ in acetonitrile was observed to be second order in $Th^{+\cdot}$, third order in H_2O, and inhibited by acid.[38] These observations led to the proposal of mechanism 50–52 and rate law 53. However, mechanism 50–52 is

$$Th^{+\cdot} + H_2O \overset{K_{50}}{\rightleftharpoons} Th\cdot\text{–}{}^{+}OH_2 \qquad (50)$$

$$Th\cdot\text{–}{}^{+}OH_2 + H_2O \overset{K_{51}}{\rightleftharpoons} Th\cdot\text{–}OH + H_3O^+ \qquad (51)$$

$$Th\cdot\text{–}OH + Th\cdot\text{–}{}^{+}OH_2 \xrightarrow{k_{52}} \text{products} \qquad (52)$$

$$-d[Th^{+\cdot}]/dt = 2k_{52}K^2{}_{50}K_{51}[Th^{+\cdot}]^2[H_2O]^3/[H_3O^+] \qquad (53)$$

inconsistent with rate law 53 and the analysis[38] involved the improper use of the equilibrium approximation on reaction 50.[47] The mechanism predicts reaction orders in H_2O either 1 or 2 depending upon the magnitude of K_{50}. If K_{50} is large, the predominant cation radical species will be $Th\cdot\text{–}{}^{+}OH_2$, a condition necessary for reaction 52, and a first-order dependence upon $[H_2O]$ will result from reaction 51. On the other hand, if K_{50} is small, the stronger oxidant $Th^{+\cdot}$ will participate in reaction 52 and a second-order dependence on $[H_2O]$ is expected to arise from reactions 50 and 51.

The inconsistencies noted above led us to study the kinetics of the hydroxylation of $Th^{+\cdot}$ in acetonitrile under a wide variety of conditions.[48,49] The order in H_2O was observed to be very complex ranging from 1 to 4.5 depending on the conditions. The reactions were studied in neutral acetonitrile and in the same solvent in the presence of acidic and basic buffers. The buffers $LH^{+-}OCOCF_3$ were prepared from 2,6-lutidine (L) and CF_3CO_2H in the presence of excess TFA (acidic) or L (basic). Both H_2O and D_2O were used as nucleophiles under all of the reaction conditions.

Even in the presence of very low concentrations of the base (L), the reaction order in H_2O changed from the high variable value observed under neutral or acidic conditions to 1. This suggested that the complexity in the water reaction order is simply a consequence of acid–base equilibria. In general terms, where the nature of the base B is not specified, the mechanism of the

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hydroxylation was formulated as in reactions 54–57.[49] The complexation mechanism versions of (54) and (55) are given in parentheses. When bonding takes place

$$\mathrm{Th}^{+}\cdot + \mathrm{H_2O} \overset{K_{54}}{\rightleftharpoons} \mathrm{Th\cdot{-}^{+}OH_2}$$

$$(\mathrm{Th}^{+}\cdot + \mathrm{H_2O} \overset{K_{54}}{\rightleftarrows} (\mathrm{Th/H_2O})^{+}\cdot) \tag{54}$$

$$\mathrm{Th\cdot{-}^{+}OH_2} + \mathrm{B} \overset{K_{55}}{\rightleftharpoons} \mathrm{Th\cdot{-}OH} + \mathrm{BH^+}$$

$$((\mathrm{Th/H_2O})^{+}\cdot + \mathrm{B} \overset{K_{55}}{\rightleftarrows} \mathrm{Th\cdot{-}OH} + \mathrm{BH^+}) \tag{55}$$

$$\mathrm{Th\cdot{-}OH} + \mathrm{Th}^{+}\cdot \underset{k_{-56}}{\overset{k_{56}}{\rightleftharpoons}} \mathrm{Th^{+}{-}OH} + \mathrm{Th} \tag{56}$$

$$\mathrm{Th^{+}{-}OH} + \mathrm{B} \xrightarrow{k_{57}} \mathrm{ThO} + \mathrm{BH^+} \tag{57}$$

at the cation radical stage, the complexation and half-regeneration mechanisms appear to be indistinguishable. In the opinion of the author, complexation is most likely. When B is H_2O, for every mole of ThO produced, 2 mol of H_3O^+ are formed, which can show their inhibiting influence via reaction 55. Under conditions where electron-transfer reaction 56 is rate determining,[38] a reaction order of 2 in water is predicted in the absence of other complications. The higher order in H_2O can be accounted for by equilibrium 58, assuming that H_3O^+ is a more effective participant in reaction 55 than is $H_3O^+(H_2O)_n$.

$$\mathrm{H_3O^+} + n\mathrm{H_2O} \overset{K_{58}}{\rightleftharpoons} \mathrm{H_2O^+(H_2O)}_n \tag{58}$$

Mechanism 54–57 accounts for the fact that the reaction order in H_2O is 1 in the presence of L. In this case, B/BH^+ is L/LH^+, and the only participation of H_2O is as the nucleophile in reaction 54. Equilibrium 58 is insignificant under these conditions due to the very low $[H_3O^+]$.

The deuterium kinetic isotope effects (k_H/k_D) for the reactions of $Th^{+}\cdot$ with H_2O and D_2O were correlated[48] with the composite reaction order in cation radical and substrate, $R_{A/B}$.[50] Three rate laws consistent with mechanism 54–57 can be of importance depending upon the relative magnitudes of k_{56}, k_{-56}, and k_{57}. The rate laws 59–61 must account for the kinetic isotope effects as well as the observed reaction orders. In neutral or

$$-\mathrm{d}[\mathrm{Th}^{+}\cdot]/\mathrm{d}t = 2k_{57}K_{54}K_{55}K_{56}[\mathrm{Th}^{+}\cdot]^2[\mathrm{H_2O}][\mathrm{B}]^2/[\mathrm{BH^+}][\mathrm{Th}] \tag{59}$$

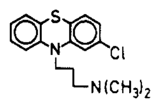
$$-\mathrm{d}[\mathrm{Th}^{+}\cdot]/\mathrm{d}t = 2k_{56}K_{54}K_{55}[\mathrm{Th}^{+}\cdot]^2[\mathrm{H_2O}][\mathrm{B}]/[\mathrm{BH^+}] \tag{60}$$

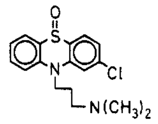
$$-\mathrm{d}[\mathrm{Th}^{+}\cdot]/\mathrm{d}t = 2k_{56}k_{57}K_{54}K_{55}[\mathrm{Th}^{+}\cdot]^2[\mathrm{H_2O}] \times [\mathrm{B}]^2/[\mathrm{BH^+}](k_{57}[\mathrm{B}] + k_{-56}[\mathrm{Th}]) \tag{61}$$

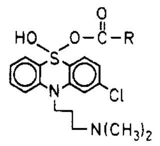
acidic acetonitrile, B is most likely H_2O. The large k_H/k_D observed (9–12) suggests that proton transfers 55 and 57 may both contribute to the rate, and rate law 61 provides for the nonintegral values of $R_{A/B}$ (1.3–1.6). In acidic buffer $R_{A/B}$ was observed to be equal to 1.83 and k_H/k_D was 1.08 ± 0.08. Under these conditions rate law 60 approximately holds, and the low k_H/k_D could be a consequence of the fact that proton transfer takes place in an equilibrium step (eq 55). In basic buffer $R_{A/B}$ was observed to be about 1.7 and k_H/k_D was about 2, which suggests that the rates of back-reaction 56 and reaction 57 are of comparable magnitude and that rate law 61 is approximated under these conditions.

The reaction of $Th^{+}\cdot$ with water in CH_2Cl_2/TFA/TFAn (97/2/1), where TFAn is trifluoroacetic acid anhydride, gives rise to kinetics consistent with the complexation mechanism.[47] In this case, a first-order dependence of the rate on $[H_2O]$ provides strong evidence that bond formation takes place at the dication stage. Water was certainly the strongest base in the system, and the alternative half-regeneration mechanism scheme predicts a second-order dependence on $[H_2O]$ by virtue of reactions 50 and 51. This suggests that the first step in the reaction, in either solvent, involves the formation of the π complex (eq 54). In acetonitrile, but not in acidic CH_2Cl_2, reaction 55 results in bond formation at the cation radical stage. In the less polar solvent, (55) is apparently not significant.

Reactions of Chlorpromazine Cation Radical with Anionic Nucleophiles. McCreery and coworkers[41–44] have carried out extensive kinetic studies on the reactions of chlorpromazine (**10**) cation radical in aqueous buffers. The product of the reaction, analogous to the hydroxylation product of $Th^{+}\cdot$, is the oxide **11**. The adduct **12** is a suspected intermediate


10


11


12

when the nucleophile is a carboxylate anion. The disproportionation mechanism was ruled out[41] by using the same analysis previously described[20] for the reaction of $Th^{+}\cdot$ with AnH.

In aqueous buffers the reaction of $\mathbf{10}^{+}\cdot$ with bifunctional nucleophiles (B^{2-}) such as HPO_4^{2-} has recently[44] been proposed to follow mechanism 62–65. The rationale for reaction 63 is that reactions of B^{2-} were observed to be very much faster than the corresponding reactions of HB^- as long as the anionic centers were spatially situated so that both centers could interact to give **10**=B, which is a tetravalent S derivative analogous to **12**, and a reaction order of 1 in HB^- was observed.

$$\mathbf{10}^{+}\cdot + \mathrm{B}^{2-} \overset{K_{62}}{\rightleftharpoons} \mathbf{10}\cdot\mathrm{B}^- \tag{62}$$

$$\mathbf{10}\cdot\mathrm{B}^- + \mathbf{10}^{+}\cdot \overset{K_{63}}{\rightleftharpoons} \mathbf{10}\cdot\mathrm{B}{-}\mathbf{10}\cdot \tag{63}$$

$$\mathbf{10}\cdot\mathrm{B}{-}\mathbf{10}\cdot \underset{k_{-64}}{\overset{k_{64}}{\rightleftharpoons}} \mathbf{10} + \mathbf{10}{=}\mathrm{B} \tag{64}$$

$$\mathbf{10}{=}\mathrm{B} + \mathrm{H_2O} \xrightarrow{k_{65}} \mathbf{11} + 2\mathrm{H^+} + \mathrm{B}^{2-} \tag{65}$$

A point that should be considered in assessing the probability of mechanism 62–65 is that both reactions 62 and 63 must be shifted to the left in order for the equilibrium approximation to hold. Thus, the thermodynamically favorable electron-transfer equilibrium 66 would be expected to compete and perhaps exclude (63) altogether. Reaction 67 would be expected to be rapid. Both mechanisms predict the same type of rate

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(50) The reaction order, $R_{A/B}$,[51] is 1 for a rate law such as $k_{obsd}[Th^{+}\cdot]^2/[Th]$ and 2 for $k_{obsd}[Th^{+}\cdot]^2$ and has a nonintegral value for rate law 23.

law and (66) and (67) would appear to be more likely than the mechanism proposed.[44]

$$10\cdot B^- + 10^{+}\cdot \overset{K_{66}}{\rightleftharpoons} 10^{+}\text{—}B^- + 10 \qquad (66)$$

$$10^{+}\text{—}B^- \xrightarrow{k_{67}} 10{=}B \qquad (67)$$

Our studies of the reaction of $10^{+}\cdot$ with acetate ion in aqueous acetonitrile show the feasibility of reactions such as (66) and (67).[52] We observed a reaction order in AcO^- of about 1.5 and proposed mechanism 68–70 and rate law 71 to account for our results. Although

$$10^{+}\cdot + AcO^- \overset{K_{68}}{\rightleftharpoons} 10\cdot\text{–}OAc \qquad (68)$$

$$10\cdot\text{–}OAc + 10^{+}\cdot \underset{k_{-72}}{\overset{k_{69}}{\rightleftharpoons}} 10^{+}\text{–}OAc + 10 \qquad (69)$$

$$10^{+}\cdot\text{–}OAc + AcO^- \xrightarrow{k_{70}} 11 + Ac_2O \qquad (70)$$

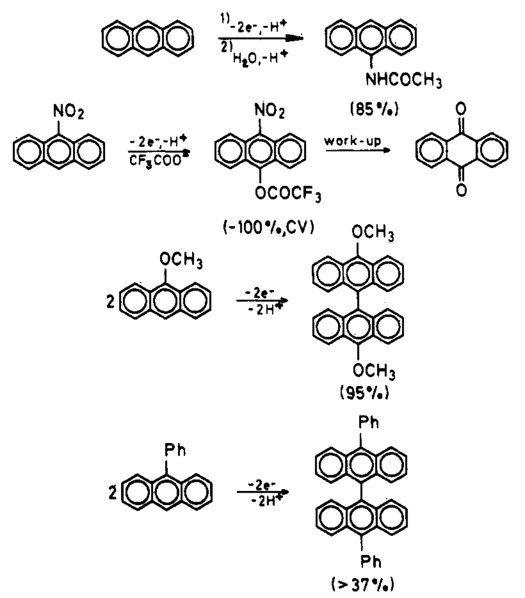
$$-d[10^{+}\cdot]/dt = 2k_{70}K_{68}K_{69}[10^{+}\cdot]^2[AcO^-]^2/([10] + k_{70}[AcO^-]/k_{-69}) \qquad (71)$$

(68) is written to imply a one-step reaction resulting in covalent bond formation, it most likely involves initial π-complex formation. The alternative to (70) involving the formation of the tetravalent S compound analogous to 12 cannot be ruled out but was deemed less likely.

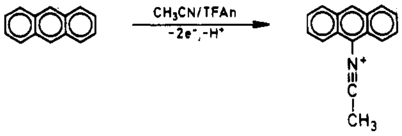
Multiplicity of Reaction Pathways of Cation Radicals of Anthracenes in Solvents of Low Nucleophilicity

Since the first kinetic studies dealing with the reactions of $DPA^{+}\cdot$ with nucleophiles were reported,[4,5] the reactions of the cation radicals of anthracene derivatives have been investigated intensively.[53-72] The reason for the selection of these models is that the charge and the odd electron are concentrated in the central rings of $1^{+}\cdot$ and the reactive 9,10-positions are sterically hindered by the two outside rings as well as by the substituents, R_1 and R_2. Consequently, $DPA^{+}\cdot$ is one of the least reactive aromatic hydrocarbon cation radicals. The cation radical of PA is somewhat more reactive and has been studied in a number of cases.[29,54,55,62,69]

Scheme II



When nucleophilic impurities are effectively removed from solvents such as acetonitrile or dichloromethane, either by deactivation with strong acids or by adsorption on neutral alumina, the solutions of the cation radicals of 9,10-diarylanthracenes are stable.[33] Under these conditions the reactions of the corresponding dications have been studied. On the other hand, oxidation of anthracene in nucleophile-free acetonitrile results in the formation of the corresponding nitrilium ion according to reaction 72.[70]



(72)

The reactions of a series of 9-substituted anthracene cation radicals in acetonitrile were studied with the objective of determining the effect of the substituents on the rate of reaction 72.[73] However, the preparative studies of the reactions showed that the products and the reaction mechanisms are strongly dependent upon the 9-substituent as shown in Scheme II.

Thus, under essentially the same conditions, in acetonitrile containing TFA, 9-substituted anthracene cation radicals undergo three distinctly different reactions: dimerization, acetamidation, or trifluoroacetoxylation. Dimerization predominates when the 9-substituent is phenyl or methoxy. Both of these substituents strongly stabilize the charges in the 10,10′-positions of the initially formed dimer dications. Formation of the dimer dication is highly unfavorable with

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electron-withdrawing nitro groups in the 10,10′-positions, and trifluoroacetoxylation is the favored reaction in this case. Reaction with acetonitrile was only observed for the cation radicals of anthracene and 9-methylanthracene.

Concluding Remarks

The state of knowledge in the area of the mechanisms of the reactions of cation radicals with nucleophiles can be summarized in a few sentences. The reactions are invariably complex because the initial intermediates are in unstable oxidation states and further reactions must take place to afford stable products. Electron transfer and acid–base equilibria are most often coupled to the reaction between the nucleophile and the cation radical. Because of the multistep nature of the processes and the large number of intermediates involved, reactions taking place by the same pathway may exhibit widely different kinetic behavior, depending upon the reaction conditions. This is especially true of the concentration range of the reactants. In discussing mechanisms of these reactions, it is imperative to consider that a mechanism well-established under a particular set of reaction conditions may not hold with even rather subtle changes in the conditions. A disappointing feature brought about by the general complexity of these reactions is that it is seldom possible to isolate single steps for the purpose of determining the effect of structure on reactivity. A good example of a failure of this nature was pointed out for the manifold of reactions that take place involving 9-substituted anthracene cation radicals in acetonitrile.

Much of the work discussed in this account was carried out in stimulating collaboration with Dr. Ole Hammerich and Dr. Ulla Svanholm. I thank the staff at the Department of Chemistry, University of Nevada, Reno, for their gracious hospitality during my sabbatical leave and the Norwegian Council for Scientific and Industrial Research for support.

Two-Photon Spectra of Aromatic Molecules

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Received June 29, 1983 (Revised Manuscript Received December 23, 1983)

In her doctoral thesis of 1931, Maria Goeppert-Mayer[1] discussed the possibility that a molecule might simultaneously absorb two photons. However, it was 30 years later that Kaiser and Garrett[2] first observed fluorescence from Eu^{2+} induced by absorption of two photons. Development of the tunable dye laser served as the impetus behind much of the activity in two-photon (TP) spectroscopy over the last decade. An important step in this regard was made in 1973 by Cagnac et al.[3] who showed that TP excitations can be induced by relatively low power but narrow line lasers. Ingenious technological developments for the detection of TP transitions have allowed this spectroscopy to become widespread. An Account by Johnson[4] discusses one such method, multiphoton ionization, while other common methods, such as direct absorption or fluorescence excitation, and thermal lensing are reviewed in Accounts by McClain[5] and Kliger,[6] respectively.

In the past few years much of the attention has been paid to the TP spectroscopy of aromatic molecules. Many remarkable similarities and regularities in the aromatic molecule TP spectra have become apparent. These spectra show that the chemical principles that have been successful in interpreting traditional one-photon (OP) spectra are equally successful in interpreting TP absorption, but that the two spectra are frequently opposite in their response to the same perturbation. Here we give an Account of the insight that has been gained concerning the mechanisms controlling TP absorption into the lowest excited states of aromatic molecules.

This complementary behavior begins with the gerade[7] ↔ gerade (g ↔ g) parity selection rule for a TP transition in a centrosymmetric molecule, contrasted to the well-known gerade ↔ ungerade (g ↔ u) OP rule.[5] This difference between TP and OP excitation is analogous to the difference between Raman and infrared spectroscopies. In the pioneering period, 1968–1977, when the basic photophysics of molecular TP absorption were being established, this rule led to the expectation that TP spectroscopy would be especially valuable in investigating the excited g states, largely unobservable by OP absorption. There have been important observations of g-parity states by this approach.[8] Some ex-

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