to seven particle masses. An analogous spherical array of hexagonally packed closest neighbors around a central spherical particle involves a total of 13 particles in a sphere of diameter thrice that of the size of original particles (Figure 9). Hence we can design a cascade fracture process in which a large spherical aggregate breaks in each step in 13 subclusters participating in the next step fracture. The diameter of the resulting clusters will decrease by a factor 3 in every step. Alternatively we can introduce the probability that a certain number n = 1, 2, ..., 12 of subunits will not participate in the subsequent fracture process, remain unchanged, and give rise to the size distribution of clusters. In this way we can evaluate the power law both for the mass of clusters and for the size distribution. The fractal dimension will be

$$D = \log (13 - n) / \log 3$$

For n = 0, 1, 2, and 3 we get D = 2.33, 2.26, 2.18, and 2.10, respectively. Again, this model is equally applicable to an inverse process, the hexagonal aggregation, in which a new larger cluster is formed by accretion of (13 - n) smaller clusters and one *n*-mer. The dimers, trimers, or *n*-mers will have correspondingly lower diffusion coefficients than the simple subunits. Our experimental values D = 2.14-2.16 fall between 2.10 and 2.18 mentioned above. This can be considered as an indication that the species or clusters forming the larger self-similar structure are not equal in size, due to a certain probability of collision on their trajectories toward the larger cluster.

The fractal nature of objects is experienced over a broad range of scale measures. In view of this, our bizarre comparison of ice breaking and tris(2,2'-bipyridine)cobalt(II) perchlorate deposition may not be so remote if both processes are governed by the same hexagonal packing model. Further experiments are in progress with the aim of evaluating D for other electrochemical systems with different crystallographic structures.

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Electrochemistry at Anthracene Crystal/Aqueous NO₂⁻, NO₃⁻ Solution Interface

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Holes (radical cations) were injected into one face of an anthracene crystal slab and discharged at the other face, which was in contact with a neutral aqueous solution containing 1 M NO₃⁻ or NO₂⁻. Hole current densities (J) of up to 700 μ A cm⁻² generated a variety of surface oxidation products including anthraquinone, 9-nitroanthracene (9NA), oxanthrone, anthrone, bianthronyl (BA), and 9,10-dinitroanthracene with both NO_3^- and NO_2^- solutions. The amount of BA and 9NA increased as J^2 . With increasing NO₃⁻ concentration, the amount of 9NA produced increased, while that of BA decreased. It was concluded that 9NA is made by cooperation of two holes on adjoining molecules at defect sites.

Introduction

The existence of suitable hole-injecting electrodes¹ has made it possible to inject sizable electronic currents through an otherwise insulating crystal of anthracene. In some cases, aqueous solutions of oxidizing agents can act as hole injectors at one face of the crystal, and these holes can be driven across the crystal by the action of an applied electric field to the opposite face where they are discharged. The discharge electrode can be another electrolyte, in which case a series of chemical reactions can take place at the crystal/solution interface.² Chemically, the hole is a radical cation, and the reactions of this radical cation at the discharge surface are the subject of this paper. More specifically, in this study, we are concerned with the heterogeneous reactions of neutral solutions of NO_2^- , and of NO_3^- with the anthracene radical cation. Specific electrochemical reactions take place at the crystal/water interface even in the absence of any added ionic species;³ it is found, however, that both NO₂⁻ and NO₃⁻ induce additional reactions in which anthracene is nitrated to nitroanthracene. Most unusual is the apparent similarity of NO_2^- and NO_3^- ions in their nitrating behavior despite their differences (e.g., oxidation states), and an attempt is made herein to rationalize this result.

The nitration of organic substances has received extensive study for many years. Nitric acid in conjunction with a strong acid such as sulfuric acid is a well-known reagent for the nitration of aromatic compounds; the favored mechanism in this case involves the intermediate nitronium ion NO_2^+ , which is the active nitrating agent.⁴ From nitration studies of polycyclic aromatic hydrocarbons (PAH's), it is known that anthracene is extremely susceptible to addition at the 9- and 10-positions⁵ such that NO_2^+ attack results in an intermediate with a nitro group and a hydrogen atom on the same carbon atom; in fact, this anthracene intermediate has been directly observed.⁶ It is therefore surprising that information to date on the nitration of polycyclic aromatic hydrocarbons is sparse and was, in 1980, still considered to be of "no quantitative significance".⁷

Nitration in media other than strong mineral acid, and even in the absence of nitric acid, occurs with a variety of reported mechanisms and intermediates not necessarily involving a nitronium ion. Dinitrogen pentoxide has been found to participate in a direct nitrating attack on the aromatic molecule^{4,8a} and was recently used to demonstrate the possibility of gas-phase nitration with PAH's in the atmosphere.^{9,10} These same researchers⁹ also considered the disappearance of dinitrogen pentoxide in the

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TABLE I:	Major	Identified	Reaction	Products	with	HPLC	and	GC-M	S Retention	Times ^a
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peak	compound	rel abund, NO3 ⁻	$m/J(\mathrm{NO}_3^{-})$	rel abund, NO2 ⁻	$m/J(\mathrm{NO}_2^-)$	HPLC, s	GC-MS, min
A	oxanthrone	265	~0.05	109	~0.02	431	5.9* (m/e 210)
В	anthrone					799*	7.0* (m/e 194)
С	AQ	1623	~0.49	921	~ 0.28	902*	7.3* (m/e 208)
D	9,10-dihydro-9,10-dihydroxyanthracene						7.6 (m/e 212)
E	9-NA	343	~0.14	332	~0.14	1312*	$8.4*(m/e\ 223)$
F	9,10-DNA	29	~0.01	>20	~0	1473	., .
G	anthracene	na	na			1519*	6.1* (<i>m/e</i> 178)
Н	bianthronyl	168	~ 0.05 0.74^{b}	25	~0.01 0.45 ^b	1257	

^a Relative abundances given are for a typical experiment run for 30 min at 110 μ A for a charge density of 687 μ A/cm². Molecular ions are the highest abundant ion found in the mass spectrum for that peak. The mass number of the molecular ions is given in parentheses. * Indicates peak identified by comparison with spectrum of reference compound: otherwise peaks were by analysis of mass spectrum. The ratio m/J is the approximate number of equivalents of compound produced during the passage of 1 faraday. The assumed number of equivalents per mole are as follows: oxanthrone, 4; AQ, 6; 9NA, 2; 9,10-DNA, 4; bianthronyl, 6. na, not available. ^bTotal fraction of faradays used.

presence of organics strictly by its disproportionation to form the nitrate radical, the nitrate radical being the reactive intermediate in this case. Nitration with nitrogen tetroxide has been reported as a simple and selective route to mononitro derivatives.¹¹ It is probable that this occurs by direct attack since dissociation is very small in organic solvents.¹² Nitrous acid also acts as a nitrating agent through a process of nitrosation followed by oxidation.¹³

There has been relatively little study of nitration and nitration mechanisms by electrode reaction processes even though they have been known to occur for some time. For instance, when PAH's were electrolyzed in acetonitrile and nitromethane in the presence of nitrate ion¹⁴ and in molten tetrabutylammonium nitrate,¹⁵ the PAH compounds were nitrated. In both experiments the reactive species was postulated to be either a nitrate intermediate (e.g., NO₂⁺) or "reactive organic intermediates"; distinguishing evidence was not conclusive. However, it is of interest that NO₃⁻ dissolved in HNO₃ is reported to form N_2O_5 and NO_2^+ in the presence of an anode; both are known nitrating agents.¹⁶

The perylene cation radical, readily obtained by anodic oxidation, forms 3-nitroperylene when reacted with sodium nitrite in acetonitrile;¹⁷ pyrene similarly forms 1-nitropyrene. The two-step mechanism proposed was an initial nucleophilic addition of the nitrite ion to the cation radical. Subsequent reaction of the addition product with another cation radical deprotonated the addition intermediate, giving the nitro product and a neutral perylene molecule. No kinetic data were presented.

The nitration of PAH compounds is of particular interest because of the appearance of various pernicious nitro derivatives of organic species in the atmosphere.¹⁸ The nitrate radical has been definitely implicated, but the precise mechanism of nitration has not yet been postulated. Light can play an important role in these organic nitration reactions, especially in the creation of electronically excited molecular states, including charged species. Considering charged species, it is known that the surface of a crystal of anthracene acting as a anode can react with solution molecules in an efficient manner.^{2,3} In this paper we report the results of anodic reactions with crystalline anthracene in the presence of neutral solutions of nitrite and nitrate ions.

Experimental Section

The electrolysis cell has been described previously.² Crystals of anthracene were cut along the *ab* face with a thread saw, polished with benzene-moistened filter paper, and used with this face exposed to the solution. The solutions forming the junction with the anodic anthracene surface, were 1 M NaNO₂ and NaNO₃, prepared from HPLC-grade H₂O and reagent-grade salts purchased from G. Frederick Smith Chemical Co. In the electrolysis experiments, a positive (hole) current was injected into the anthracene crystal by a Ce4+ electrolyte electrode (0.5 N Ce4+ in 6 N HClO₄). The hole current was discharged on the opposite face of the crystal which was in contact with a 1 M solution of either $NaNO_2$ or $NaNO_3$. The products of the reaction were analyzed by interrupting the experiment, demounting the crystal, and washing the reacted surface of the crystal with acetonitrile until the unreacted anthracene surface was exposed. The same crystal was then remounted to continue the experiment. In this procedure, the reproducibility of results is about 20%.

Extraction of the reacted anode surface with acetonitrile yielded a yellowish solution indicative of nitro derivatives and left an undissolved white residue on the surface tentatively identified previously² as consisting of high molecular weight anthracene polymers. Analysis of the extract was performed by high-performance liquid chromatography (HPLC) and gas chromatography-mass spectroscopy (GC-MS). The HPLC instrumentation included an IBM ODS 25-cm column on a Perkin-Elmer Series 3B liquid chromatograph, with peak detection by a Lambda 2B UV/vis spectrometer and a 6505 fluorescence detector connected in series. GC-MS instrumentation included a 12-m cross-linked methylsilane capillary column with 0.33-µm film in a Hewlett-Packard 5992 GC-MS modified by a capillary column inlet system. The HPLC resolution was increased by more than 30%by adding a 5-cm Rainin Short One (3- μ m particle size) ODS column to the 25-cm IBM ODS column already described.

Peroxynitrous acid was made with a mixture of H_2O_2 , NaNO₂, and H₂SO₄ as discussed by Papee and Riconi.¹⁹ Since peroxynitrous acid has a lifetime of only a few seconds, the solution containing nitrite was added dropwise to a mixture of the other components that also contained an excess of anthracene either as a fine powder or as a solution in dichloromethane.

Peroxynitric acid was prepared by cautiously mixing 70% HNO3 with 70% H_2O_2 .²⁰

Results

Typical HPLC spectra of the extract solution from the reactions with nitrate and nitrite ions are given in Figure 1. Similarly, GC-MS for the extracts from reactions with either anion gave spectra typified by Figure 2. Since the HPLC columns are "reverse phase" while the GC-MS column is "normal phase", retention of the various components appear in opposite order. Identification of the compounds (Table I) were determined by analysis of the mass spectra and by comparison of retention time, UV spectra, or mass spectra with reference compounds (Figure 3); these reference compounds were either purchased or synthesized, if the appropriate spectra were not available.

As was found in experiments with H_2O and NH_3 ,² the identified products indicate that both solute and solvent react with the substrate surface at the interface in a way consistent with the ease

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Figure 1. HPLC spectra of extracted products from anthracene electrolysis reactions with (a) nitrate ion solution and (b) nitrite ion solution. Column parameters are gradient elution starting at 70%/30% MeOH/ H_2O for 15 min; 12-min linear gradient to 100% MeOH followed by 5-min neat 100% MeOH. Flow rate was 1 mL/min. See Table I for identity and relative magnitude of labeled peaks.

in which the 9- and 10-positions of anthracene participate in addition reactions and subsequent elimination reactions. The oxidation and hydroxylation products have already been identified and discussed previously.^{3c} Refinements in product analysis in this laboratory led to the additional identification of 9,10-dihydro-9,10-dihydroxyanthracene, as a minor product in the reaction with water; this was not found previously.



Figure 2. GC-MS spectrum showing total ion abundance versus time for the electrolysis reaction with nitrite solution. See Table I for identity and magnitude of labeled peaks.



Figure 3. UV spectrum of HPLC fraction E (b) compared with reference compound 9-nitroanthracene (a). Ordinate in arbitrary units.

What is striking in the results is the similarity of nitration products, starting from either nitrate or nitrite ions. Parts a and b of Figure 1 can be observed to be the same qualitatively. Comparison of the yields for the major products given by the peak areas in Table I shows that despite the approximate equality of the 9-nitroanthracene (9NA) peak areas, the yields of all the other major components in the NO3⁻ reactant case are significantly larger than those in the NO_2^- reactant case. Since essentially the same number of coulombs of charge were used in both cases, it must be concluded that other, undetected water soluble products were formed in greater quantity in the NO_2^- system than in the NO_3^- system. One of these products is probably the NO_3^- ion, produced by the electrolytic oxidation of the NO_2^- ion. This point will be referred to again further on. The similarity of product formation in nitrate and nitrite reactions with other cation radicals has already been noted,²¹ but the mechanism is "entirely unknown". Comparison of the yields of the major products of nitration, 9-nitroanthracene (9NA), and of oxanthrone, 9,10anthraquinone (AQ), also reveal a surprisingly high relative yield for the nitration mechanism with the NA to AQ ratio as high as 0.5. Furthermore, data at different current densities (J) have indicated that the yields of NA for both nitrate and nitrite solutes

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Figure 4. Comparison of the dependence of yield with charge density (J) for anthraquinone (AQ) (a) and 9-nitroanthracene (NA) (b). The straight line obtained for NA peak area/ J^2 versus J (b) indicates a squared dependency. The curved solid line in (a) for the plot of AQ area/ J^2 versus J and the straight dashed line of the plot of AQ peak area/ J^2 versus J (a) favor the linear dependence of AQ yield on J. While this plot is for reactions with nitrate ion, similar curves are obtained with nitrite ions.

are a function of J^2 and not J (Figure 4). The yield of AQ is shown to depend essentially linearly on J in agreement with previous data.^{3c} The relationship A (area under the HPLC curve for NA in Figure 4) $\propto J^n$ was subjected to a power curve fitting regression analysis, and it emerged that the best value for n was 2.00 with a correlation coefficient of 0.95. The data for AQ in Figure 4 fit a linear relationship (excluding the extreme value at $J = 315 \ \mu$ A) with a correlation coefficient of 0.94. At higher current densities, the amount of AQ produced became slightly sublinear with respect to J, due to competition from the increasing production of compounds whose yield varies as J^2 , such as bianthronyl, H_2O_2 , and 9NA.

The above experiments were carried out in air-saturated solutions. The yields of major known compounds, expressed as the fraction of the number of coulombs passing through the crystal, are shown in Table I. A few control experiments carried out in He-flushed systems showed the same qualitative results, but it was found that the yield of AQ and of NA decreased in the presence of atmospheric O₂. In arbitrary units, it was found that the yield of AQ in the eluate from the surface of the anthracene crystal after electrolysis in a He-purged system was 5.6 compared with 4.4 in the air-saturated system. This is a 20% reduction in yield. Under similar conditions, the yield of 9NA was 3.9 in the He-purged system as compared with 2.0 in the air-saturated system. This is approximately a 50% reduction in yield.

Discussion

The important experimental results are summarized as follows: (a) The production of 9NA is proportional to the square of the current density (J^2) , for both NO₂⁻ and NO₃⁻ in solution. (b) The production of 9NA is proportional to the NO₃⁻ concentration and not to $[NO_3^-]^2$. (The NO₂⁻ was not similarly tested.) (c) As the concentration of NO₃⁻ ion is increased, the efficiency of producing bianthronyl decreases; the efficiency of producing AQ is essentially unchanged. (d) The presence of atmospheric oxygen leads to a decrease in the amount of anthraquinone (AQ) and 9NA that is collected from the anthracene surface.

As has been mentioned, the reactive organic species is the radical cation. A case in which perylene radical cations react with

TABLE II: Effect of Increasing NO_3^- Concentration on Production of Anthraquinone (AQ), Bianthronyl (BA), and 9-Nitroanthracene (9NA) in Relative Units

[NO ₃ ⁻], M	[AQ]	[BA]	[9NA]	
8	2.9	0.3	3.5	-
6	2.8	0.6	1.5	
4	2.9	0.7	1.5	
2	2.6	1.1	0.6	
1	3.3	1.0	0.7	
0.5	2.5	1.3	0.3	

 NO_2^{-} in acetonitrile to produce nitroperylene in high yield has been reported by Shine.¹⁷ The perylene radical cations were created chemically by reaction of perylene (HP) with iodine in the solid phase. The proposed mechanism in this case was

$$HP^{+} + NO_2^{-} \rightarrow HPNO_2^{+}$$
(1)

$$HPNO_{2}^{\bullet} + HP^{\bullet+} \rightarrow HPNO_{2}^{+} + HP \qquad (2)$$

$$HPNO_2^+ \to H^+ + PNO_2 \tag{3}$$

In (1), the perylene radical cation (HP^{•+}), in which one of the perimeter hydrogens is indicated explicitly, reacts with NO_2^- to produce a hydronitroperylene radical (HPNO₂[•]) with the H and NO₂ on the same C site. In (2), the (HPNO₂[•]) radical reacts with another radical cation, resulting in the transfer of an electron from the HPNO₂[•] radical to the perylene radical cation, producing the cation HPNO₂⁺. In (3), the cation HPNO₂⁺ dissociates, liberating a proton from the NO₂-bonded carbon and producing the nitroperylene. The above reaction, as written, cannot explain our results, because the kinetics do not agree; this is shown below. Thus, ignoring all rate constants and assuming steady-state conditions, one has, from (3)

$$d[PNO_2]/dt \propto [HPNO_2^+]$$

from (3) and (2)

 $d[\text{HPNO}_2^+]/dt \propto [\text{HPNO}_2^\bullet][\text{HP}^{\bullet+}] - [\text{HPNO}_2^+] = 0$

$$[HPNO_2^+] \propto [HPNO_2^+][HP^{++}]$$

from (2) and (1)

$$d[HPNO_{2}^{\bullet}]/dt \propto [HP^{\bullet+}][NO_{2}^{-}] - [HPNO_{2}^{\bullet}][HP^{\bullet+}] = 0$$

 $[HPNO_{2}^{\bullet}] \propto [NO_{2}^{-}]$

from (1)-(3)

$$d[PNO_2]/dt \propto [HPNO_2^+] \propto [HPNO_2^+][HP^{++}]$$

 $\propto [\mathrm{HP}^{*+}][\mathrm{NO}_2^{-}] \propto J[\mathrm{NO}_2^{-}]$

Thus, according to the above, the formation of PNO_2 depends linearly on J.

Since $d[PNO_2]/dt$ depended on J^2 in our results, the Shine¹⁷ mechanism in its present form cannot be operative in our system.

To explain our results, we note the important fact that an increase in NO_3^- concentration increases the 9NA production linearly and leaves the AQ production essentially unchanged but *decreases* the production of bianthronyl [BA]. This is shown in Table II.

According to Slotnick,^{3c} the immediate precursor to the formation of bianthronyl is the species Q:



The species Q is also a precursor for the formation of AQ. Since the production of AQ is not affected by the increase in $NO_3^$ concentration, it appears to be the case that a specific precursor to the formation of bianthronyl must be eliminated by the NO_3^- .

The unique requirement for the production of bianthronyl is that the two precursors to its formation reside simultaneously on adjacent sites on the crystal surface. By the term "simultaneously" is meant a time interval long enough for the precursors to react with each other before disappearing into some other channel. The most probable site for the production of bianthronyl is a crystal defect.

Since the production of 9NA increases as the square of the current density, as does bianthronyl,^{3c} it appears that the same precursors are used to make 9NA as are used to make bianthronyl.

The proposed mechanism is thus the following, where NO_2^- is the dissolved species, and an asterisk is used to designate a singly dehydrogenated species:

$$h^+ + A_{(1)} \rightarrow {}^{\bullet}A_{(1)}^+$$
 (4)

In (4) the hole lands on anthracene in site 1.

$$^{\bullet}A_{(1)}^{+} + NO_2^{-} \rightarrow (^{\bullet}A_{(1)} \cdots NO_2)$$
(5)

Here the radical cation in site 1 forms a complex with NO_2^{-} .

$$(^{*}A_{(1)} \cdots NO_{2}) + H_{2}O \rightarrow ^{*}A^{*}_{(1)} + NO_{2}^{-} + H_{3}O^{+}$$
 (6)

Water, acting as a base, destroys the complex in (5), producing the dehydrogenated radical $*A^{\bullet}_{(1)}$. This competitive action of water is what is proposed to occur in the absence of any added ionic species to produce the intermediate (*A[•]) required for bianthronyl synthesis.

$$h^+ + A_{(2)} \rightarrow {}^{\bullet}A_{(2)}^+$$
 (7)

according to (7), the hole lands on anthracene in site 2 adjoining site 1.

$$A_{(2)}^{+} + ({}^{\bullet}A_{(1)} \cdots NO_{2}) \rightarrow [{}^{\bullet}A_{(2)}^{+} + ({}^{\bullet}A_{(1)} \cdots NO_{2})]$$
(8)

a cage is formed involving the reactants on sites 1 and 2.

$$[{}^{\bullet}A_{(2)}^{+} + ({}^{\bullet}A_{(1)} \cdots NO_2)] \rightarrow {}^{*}A_{(1)} NO_2 + A_{(2)} + H^+$$
(9)

9NA is formed with liberation of a proton and re-formation of $A_{(2)}$.

$$[{}^{\bullet}A_{(2)}{}^{+} + ({}^{\bullet}A_{(1)} \cdots NO_{2})] + H_{2}O \rightarrow \\ {}^{*}{}^{\bullet}A_{(2)} + NO_{2}{}^{-} + H_{3}O^{+} + {}^{\bullet}A_{(1)}$$
(10)

competitive reaction of H_2O with A_2^+ in the cage occurs in (10), causing dissociation of NO_2 complex with $A_{(1)}$. The action of water here is the same as in (6).

The kinetic scheme, disregarding rate constants and assuming steady-state conditions for reaction intermediates, is, from (9)

$$d[*ANO_2]/dt \propto [*A_{(2)}^+ + (*A_{(1)} \cdots NO_2)]$$
 (11)

and from (8)

$$d[{}^{*}A_{(2)}^{+} + ({}^{*}A_{(1)} \cdots NO_{2})]/dt \propto [{}^{*}A_{(2)}^{+}][{}^{*}A_{(1)} \cdots NO_{2}] - [{}^{*}A_{(2)}^{+} + ({}^{*}A_{(1)} \cdots NO_{2})][H_{2}O] = 0 (12)$$

Here, it is assumed that the destruction of the cage by water is the dominant reaction, although the same result is obtained if the nitration dominates. Therefore

$$[^{\bullet}A_{(2)}^{+} + (^{\bullet}A_{(1)} \cdots NO_{2})] \propto [^{\bullet}A_{(2)}^{+}][(^{\bullet}A_{(1)} \cdots NO_{2})]/[H_{2}O]$$

From (5) and (6)

$$\frac{d[({}^{*}A_{(1)} \cdots NO_{2})]/dt}{[({}^{*}A_{(1)}^{+}][NO_{2}^{-}] - [({}^{*}A_{(1)} \cdots NO_{2}][H_{2}O] = 0 (13)$$

Here, therefore

$$(^{A}_{(1)} \cdots NO_{2}) \propto [^{A}_{(1)}^{+}][NO_{2}^{-}]/[H_{2}O]$$

From (11)-(13), (4), and (7)

$$d[*ANO_2]/dt \propto [*A_{(1)}^+][*A_{(2)}^+][NO_2^-] \propto J^2[NO_2^-]$$
(14)

This satisfies the J^2 relationship found experimentally. The linear dependence on $[NO_2^-]$ was not explored, but it was found in the NO_3^- reaction system.

For the NO_3^- solution kinetics, step (4) would be the same:

$$\mathbf{h}^+ + \mathbf{A}_1 \to \mathbf{A}_{(1)}^+ \tag{15}$$

$$\mathbf{A}_{(1)}^{+} + \mathbf{NO}_{3}^{-} \rightarrow (\mathbf{A}_{(1)} \cdots \mathbf{NO}_{2} \cdots \mathbf{O})$$
(16)

gives the complex formed with NO_3^- , which destabilizes one oxygen atom.²²

$$(^{*}A_{(1)} \cdots NO_{2} \cdots O) \div H_{2}O \rightarrow ^{*}A^{*}_{(1)} + NO_{3}^{-} + H_{3}O^{+}$$
 (17)

Equation 17 shows the destruction of the complex in (16) by H_2O .

$$h^+ + A_{(2)} \rightarrow {}^{\bullet}A_{(2)}^+$$
 (18)

$$^{\bullet}A_{(2)}^{\bullet} + (^{\bullet}A_{(1)} \cdots NO_{2} \cdots O) \rightarrow [^{\bullet}A_{(2)}^{\bullet} + (^{\bullet}A_{(1)} \cdots NO_{2} \cdots O)]$$
(19)

$$[A^{+}_{(2)} + A_{(1)} - NO_{2} - O] + H_{2}O \rightarrow A_{(1)}NO_{2} + O + A_{(2)} + H_{3}O^{+}$$
 (20)

9NA forms with formation of atomic oxygen, liberation of proton, and re-formation of $A_{(2)}$.

$$[{}^{\bullet}A_{(2)}^{+} + ({}^{\bullet}A_{(1)} \cdots NO_{2} \cdots O)] + H_{2}O \rightarrow$$

 ${}^{\bullet}A_{(2)} + NO_{3}^{-} + H^{+} + {}^{\bullet}A_{1}^{+} (21)$

the competitive reaction of water with $^{+}A_{2}^{+}$ in the cage in (9) causes dissociation of the NO₃ complex with $A_{(1)}$.

Support for the caged reactions shown in (10) and (20) comes from the work of Daniels et al.,²² where it is proposed that the atomic oxygen released in (20) is disposed of by reaction with NO_3^- , namely, $NO_3^- + O \rightarrow NO_2^- + O_2$. The possible reaction of O with H₂O to form H₂O₂ was not considered likely. It is also possible for the oxygen atom to react with the crystal surface. At present, the fate of the oxygen atom is not known.

An alternate mechanism to that of (15)-(21) could involve the coincident formation at the crystal/water interface of NO₃ radicals (from NO_3^- , or NO_2 radicals from NO_2^-) and OH radicals (from OH-) on adjacent sites, following the discharge of the corresponding ions. These radicals, when present side by side, resemble respectively peroxynitric and peroxynitrous acids. It was of interest therefore to determine whether these acids could produce the observed products in these experiments since they have been shown to be capable of nitrating aromatic compounds.²³ These acids were synthesized and reacted with the anthracene crystals. The peroxynitrous acid did not react with the anthracene solid unless the anthracene was dissolved in dichloromethane; in this solution, 9NA was produced quickly. The peroxynitric acid reacted with crystalline anthracene to produce 9NA, but the fuming nitric acid used to make the peroxynitric acid also produced 9NA. The experiments with the peroxy acid were thus inconclusive. An additional difficulty with this alternate mechanism is that the solution adjacent to the crystal is presumed to be acidic due to the formation of H^+ ions during the hole-discharge process. Thus, the concentration of [OH⁻] ions is of course very low. No experiments have yet been carried out to determine the [OH⁻] dependence of the 9NA production. In our work with a 14 M aqueous NH₃ solution electrolyte,² where the concentration of OH⁻ ions is at least 10⁴ times greater than that adjacent to the crystal in the NO_3^- , NO_2^- studies, there is evidence that the OH⁻ ion is participating in a series of solution and crystal reactions. In fact, the mechanism for the production of H_2O_2 also involves a J^2 dependence, and if $H_2 O_2$ is produced (or, for that matter, if HONO or HO₂NO is produced) at the bianthronyl precursor sites, then one might have an explanation for the lower yield of surface products and of bianthronyl in the NO2⁻ system as compared with

⁽²²⁾ Daniels, M.; Meyers, R. V.; Belardo, E. V. J. Phys. Chem. 1968, 72, 389.

⁽²³⁾ Halfpenny, E.; Robinson, P. J. Chem. Soc. 1952, 928; J. Chem. Soc. 1951, 939.

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the NO₃⁻ system. since the H_2O_2 (and HONO or HO₂NO) are water soluble, they would not be detected in our procedure, thus providing an avenue for the undetected consumption of coulombs of charge. Then, if for a reason not yet known, there was a greater production of H_2O_2 (or HONO) in the NO₂⁻ system, there would be observed a simultaneous drop in the relative yield of surface products and a drop in the competitive bianthronyl production in the NO₂⁻ system, relative to that in the NO₃⁻ system. It is thus not possible at this time to discriminate between the mechanism described in (15)-(21), and that involving the peroxy acids.

As for the energetics of the cation radical discharge reaction, some data are available:²⁴

 $NO_2^{-}(aq) \rightarrow NO_2(aq) + e^{-}(vac); \quad E = 7.5 \text{ eV}$ (22)

$$NO_3^{-}(aq) \rightarrow NO_3(aq) + e^{-}(vac); \quad E = 8.5 \text{ eV}$$
 (23)

$$OH^{-}(aq) \rightarrow OH(aq) + e^{-}(vac); E = 8.5 eV$$
 (24)

 $A(s) \rightarrow A^+(s) + e^-(vac); \quad E = 5.8 \text{ eV} (\text{see ref } 1) (25)$

Thus, for the discharge of a $NO_3^-(aq)$ or a NO_2^- on an anthracene surface, the energy balance is

$$NO_3^{-}(aq) + {}^{\bullet}A^{+}(s) \rightarrow A(s) + {}^{\bullet}NO_3(aq); \quad E = 2.7 \text{ eV}$$
 (26)

$$NO_2^{-}(aq) + {}^{\bullet}A^{+}(s) \rightarrow A(s) + {}^{\bullet}NO_2(aq); E = 1.7 \text{ eV}$$
 (27)

As may be seen in (26) and (27), it is energetically impossible for one anthracene radical cation to oxidize a NO₃-(aq) ion to a free 'NO₃(aq) radical or a NO₂⁻(aq) ion to a free 'NO₂(aq) radical in a single step. If free radicals as such are to be involved as reactive species, they must be produced by the cooperation of two radical cations or by a considerable overvoltage at the crystal/water interface. This overvoltage cannot be sustained in water, particularly in the presence of $\bar{N}O_2^-$ ions, since both the water and NO_2^{-1} ions will be oxidized first. It is already known that the water is oxidized.³ In addition, an examination of Table I shows that only about half of the current flowing through the crystal in the presence of NO_2^- ions is converted to surface products, as compared with a 75% conversion when the NO_3^- ion is present. This is consistent with an interpretation that the NO_2^{-1} ion in solution is being oxidized to NO_3^- by the radical cation with no subsequent chemical reaction with the surface.

As for the observation that the presence of an excess of O_2 reduces the yield of AQ and NA, this can be explained by the results of Jarnagin et al.,^{3a} who also carried out experiments involving the use of an anthracene crystal as an electrode. They found that, in the presence of atmospheric O_2 , the oxidation of AQ proceeded to the point of cleavage of the AQ into water-soluble fragments. This reaction would remove AQ (and also NA) from the surface and thus diminish the observed yield of these compounds in our procedures. The enhanced effect of the atmospheric oxygen on the NA production may be due to the weakening of the anthracene ring system brought about by the presence of the electron-withdrawing nitro group.

A question that may be asked is why two neighboring molecules must be involved in the production of 9NA, as opposed to the sequential attack on the NO_2^- (or NO_3^-) by two holes on the same molecule:

$$h^+ + A \rightarrow {}^{\bullet}A^+ \tag{28}$$

$$^{*}A^{+} + NO_{2}^{-} \rightarrow ^{*}A \cdots NO_{2}$$
 (29)

(24) Delahay, P.; Dziedic, A. J. Chem. Phys. 1984, 80, 5381.

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$$^{\bullet}A \cdots NO_{2} + h^{+} \rightarrow A^{+} \cdots NO_{2} \rightarrow ^{*}ANO_{2} + H^{+}$$
(30)

To begin with, there are steric considerations. The fact that the production of 9NA competes with the production of bianthronyl implies that 9NA benefits from the same steric configuration that facilitates the production of bianthronyl. The concept of caging employed in the proposed mechanism for nitration would require a close positioning of the two reactive molecules, in conformance with this conclusion. It should also be noted that even in the alternate mechanism that involves the OH radical precursor as a neighbor to the NO₃ (or NO₂) radical precursor, the necessity for nearest-neighbor participation is obvious.

In addition, a hole approaching an 'A···NO₂ complex from the inside of the crystal would be faced with the choice of overcoming the Coulomb repulsion of the partially positively charged end of the complex or choosing a surface site adjoining the complex (of which there probably are more than one), where the greater dielectric screening of the aqueous solution should minimize the coulomb repulsion. According to Willig,²⁵ the movement of the hole at the crystal/water interface is subject to a significant attractive image force, implying greater dielectric screening of the availability of more than one favorable site for the second hole, together with the increased screening provided by the water, would favor the surface pairing of the precursors to the formation of 9-nitroanthracene. This would add an energetic to the entropic justification for the second hole to choose a surface site adjoining the complex.

In passing, it may be noted that the experimental current densities are equal to or greater than $100 \,\mu A/cm^2$. With a molecular surface density of about 10^{14} molecules cm⁻², each molecule would on the average be visited by a hole at least 6 times a second. The complex 'A--NO₂ is thus required to have a relatively long lifetime.

Conclusion

We have studied the heterogeneous electrolytic reaction of surface cation radicals of anthracene with aqueous solutions of NO_3^- and NO_2^- ions. Cation radicals of polycyclic aromatic hydrocarbons can also be produced photochemically, so the reactions described herein are presumably relevant in the atmosphere, where light plays an important role. We have shown that the presence of NO_3^- and NO_2^- leads identically to the formation of 9-nitroanthracene (9NA) in good yield, with an efficiency of about 0.1 equiv of 9NA/faraday of charge. The yield of 9NA varies as the square of the current density and is competetive with the production of the dimeric molecule, bianthronyl. We conclude that the 9NA is created at the same sites as bianthronyl, most probably at defect sites.

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Registry No. 9NA, 602-60-8; BA, 434-84-4; NO_2^- , 14797-65-0; NO_3^- , 14797-55-8; anthracene, 120-12-7; anthraquinone, 84-65-1; oxanthrone, 549-99-5; anthrone, 90-44-8; 9,10-dinitroanthracene, 33685-60-8.

⁽²⁵⁾ Willig, F. Adv. Electrochem. Electrochem. Eng. 1981, 12, 65.