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Nevertheless, the present analysis clearly implicates the likely importance of rapid solvent dynamical components in activated ET processes and will hopefully encourage further experimental studies aimed at providing more detail comparisons along these lines in the near future. The application of ultrafast TDFS measurements to elucidate solvent friction effects in barrier-crossing dynamics is in its infancy and clearly constitutes a powerful if challenging means of unraveling the complexities of activated charge-transfer processes.

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Electrolysis at an Anthracene Crystal/Aqueous NO_3^- Solution Interface: The Role of Crystal Defects

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The electrolysis of a 1 M solution of $NaNO_3$ by means of an anthracene crystal electrode results in the production of many surface reaction products, including 9-nitroanthracene (9NA), bianthronyl (BA), and anthraquinone (AQ). The production of 9NA and BA have been shown to depend on the square of the current density. This dependence was rationalized by hypothesizing the need for the simultaneous discharge of two carriers at adjoining lattice defect sites. By annealing the crystals, it was found that the efficiency of producing 9NA was reduced by a factor of as much as 6; this supports the hypothesis.

In a previous publication[1] to be referred to as (I), it was shown that an anthracene crystal could be used as an electrode in the electrolysis of a 1 M aqueous solution of NO_3^- and of NO_2^- ions. The electrolytic reactions (oxidations) were carried out by the anthracene radical cation (positive hole). It was shown that in the course of the electrolysis, 9-nitroanthracene (9NA) was one of the products and that the amount of 9NA produced increased as the square of the current density, J^2. In (I) it was argued that the simultaneous participation of two holes (radical cations) on adjoining crystal sites was necessary to explain the observed results. The evidence consisted of the observation that the production of 9NA was strongly competitive with the production of the dimeric molecule bianthronyl (BA), (whose concentration also increased as J^2) but had little effect on the production of anthraquinone (AQ), which varied as J at current densities of 150 $\mu A/cm^2$. The rationale was that since bianthronyl (BA) had an absolute steric requirement for the participation of two adjoining sites in order to form the dimer, and since its production increased as J^2, the competitive production of 9NA depended on the participation of the same type of adjoining crystal sites as was used in the formation of bianthronyl. Furthermore, these special crystal sites were postulated to be defect sites created by emergent dislocation planes.

To check this hypothesis, a procedure was set up to determine the effect of crystal annealing on the efficiency of producing 9NA and of BA. The anthracene crystals were annealed at 170 °C for 18 h in an atmosphere of He at 0.5 atm.

Experimental Section

The experimental procedure for the electrolysis was the same as that used in (I). The injected holes were driven through the crystal bulk by an external field and were discharged at the crystal/water interface. Current densities (J) of from 40 to 500 $\mu A/cm^2$ were used under applied fields of from 13 to 85 kV/cm (300–2000 V). In a typical experiment, after a measured amount of charge was passed through a crystal, the hole-discharge side (anode) was washed with 25 μL of acetonitrile; this wash contained oxidized derivatives of anthracene and was immediately analyzed by HPLC. A Perkin-Elmer 3B pumping system with an LC-15 UV detector, Model 024 chart recorder, and a Model II integrator were used. A IBM ODS 25-cm octadecylsilane (reverse phase) column was used. The HPLC resolution was increased by more than 30% by adding a 10-cm Rainin Short-One (3-μm particle size) ODS column to the 25-cm IBM ODS column already described. All solvents used for the HPLC mobile phase were HPLC

TABLE I: Effect of Annealing on the Yield of Bianthronyl and 9-Nitroanthracene[a]

A

	anthraquinone in 1 M $NaNO_3$[b]	
I, μA	before annealing	after annealing
20	1	1.4
30	1.4	1.7
40	1.8	2.3

B

	before annealing 1 M $NaNO_3$	
I, μA	BA/AQ[c]	9NA/AQ[c]
20	0.3	0.05
30	0.2	0.05
40	0.2	0.03

C

	after annealing in 1 M $NaNO_3$	
I, μA	BA/AQ[c]	9NA/AQ[c]
20	0.1	0.02
30	0.1	0.01
40	0.1	0.01

D

	before and after annealing	
I, μA	BA(before)/BA(after)	9NA(before)/9NA(after)
20	2.7	3.1
30	1.8	4.6
40	2	6.6

[a] The crystal area in all experiments was 0.125 cm^2. [b] The absolute yield of AQ in the unannealed crystal at 160 $\mu A/cm^2$ for 30 min was 1.4×10^{-8} mol. Assuming 6 equiv/mol of AQ, the yield is 0.23 equiv of AQ per Faraday of charge, or 23%. This yield at this current density is consistent with the result in (I). [c] The AQ peaks in these measurements have already been normalized.

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grade. The column elution protocol was as follows: gradient elution starting at 70%/30% MeOH/H_2O for 8 min; 19-min linear gradient to 100% MeOH followed by 3 min of neat 100% MeOH. The flow rate was 1 mL/min.

All measurements of BA and 9NA represent the ratio of the peak heights for these compounds to the peak height of AQ in the same experiment. The peak areas of the AQ in the annealed and unannealed samples were calibrated by comparison with a series of solutions of AQ of known concentration. The assumption was made that the peak heights and peak areas were proportional to one another. This proportionality was confirmed during the calibration of the more dilute solutions of AQ.

Discussion

The first question to resolve is the effect of annealing on the yields of 9NA and of BA. According to the hypothesis given in (I), 9NA and BA are both formed preferentially at defect sites. There are various types of defects, such as point defects, line defects, and plane defects. By annealing a crystal, it is possible to greatly reduce the number of defects, particularly the line and plane defects, which are not in thermodynamic equilibrium with the lattice.[2] It would therefore follow that by annealing the crystal, there should be a significant reduction in the yield of BA and 9NA.

Since the analysis of the anthracene crystal surface was made many times, involving the use of varying amounts of the acetonitrile washing solution, it proved to be most convenient to refer all HPLC peak heights to that of anthraquinone (AQ) produced at a current density of 160 μA/cm^2, in the presence of 1 M $NaNO_3$, on an unannealed crystal. The absolute amounts of AQ produced were measured at each current density, both before and after annealing on the same crystals, and these results are also normalized to the AQ peak height at 160 μA/cm^2.

As can be seen in sections B–D of Table I the effect of the annealing is to reduce the yields of BA and 9NA. The effect of annealing was more pronounced on the 9NA and becomes increasingly more pronounced at higher current density, where there was a 6-fold reduction in yield of 9NA. Apparently, after annealing there was a greater effect on 9NA production than on BA production. This would indicate that 9NA is more dependent on defect formation than is BA.

As is shown in Table I, section A, the yield of AQ drops off with increasing current density. This is a consequence of the increasing efficiency of the bimolecular processes that produce such compounds as 9NA, bianthronyl, and bianthrone.[1]

Conclusion

The hypothesis put forth in (I) to explain the J^2 dependence of the amount of 9NA produced electrolytically at an anthracene crystal electrode postulated the crucial role of surface defects that bring anthracene molecules close enough to be bridged by a nitro group. A corollary of this hypothesis would be that any reduction in the number density of surface defects would bring about a decrease in the yield of 9NA. By annealing the crystal, the number of defects is diminished, and it has been found that there is a significant decrease in the efficiency of making 9NA electrolytically at an anthracene/NO_3^-(aq) interface. This decrease in some cases is a more than a factor of 6.

It thus appears that the production of 9NA on the crystal surface is best carried out at a crystal defect that permits two molecules to participate in the nitration process.

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Rotationally Resolved Electronic Spectra for the Ne–OH and Ne–OD van der Waals Complexes

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Laser-induced fluorescence spectra have been recorded for the $A^2\Sigma^+$–$X^2\Pi_{3/2}$ systems of Ne–OH and Ne–OD. All of the transitions observed originated from the ground-state zero-point level. Ground-state rotational constants of $\bar{B}''_0$ = 0.130 ± 0.003 and 0.127 ± 0.003 cm^{-1} were found for the H and D isotopes, respectively. Bands corresponding to excitation of the van der Waals stretch and bend–stretch combinations in the $A^2\Sigma^+$ state were seen. The energy ranges encompassed by these bands provided lower limits for the van der Waals dissociation energies of $D'_0 > 61.8$ cm^{-1} (Ne–OH(A)) and 68.5 cm^{-1} (Ne–OD(A)).

Introduction

van der Waals complexes consisting of a rare-gas atom bound to the OH radical provide interesting models for the study of weak bonding interactions in open-shell systems. Electronic spectra for OH–Ar and OD–Ar have been examined in the gas-phase[1–7] and in cryogenic rare-gas matrices.[8] Spectra taken in solid Ar were consistent with a linear OH–Ar geometry for both the ground ($X^2\Pi_{3/2}$) and electronically excited ($A^2\Sigma^+$) states.[8] More recently, ab initio calculations of the potential energy surfaces for OH–Ar have been made.[9] For the ground and excited states, these calculations predicted potential energy minima for both linear geometries (Ar–OH and OH–Ar), with the deeper minimum corresponding to the "hydrogen-bonded" configuration.[9] Bowman et al.[10] have shown that potentials of this form are capable of

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