that the *major* solvent effects on reactivity can be correlated with two solvent parameters, in our work *Y* and solvent nucleophilicity *N*; however we disagree on how the two solvent properties are extracted from the experimental data to give a physically significant empirical model of solvation effects on reactivity in protic media. The solvent polarity scales based on solvatochromism appear to be less suitable for probing heterolytic reactivity, possibly because of contributions from solvation effects which destabilize excited states.

Experimental Section

Chemicals. 1-Adamantyl iodide (I, X = I) was prepared and purified by literature procedures mp 75–77 °C (lit.[8,17] mp 75–76 °C). Trifluoroethanol, hexafluoroisopropyl alcohol, and ethanol were purified as described previously.[3d] Commercially available samples of acetone, dioxan and methanol (Fisons, dried and distilled), acetic acid (BDH, Aristar), and formic acid (BDH, AR) were used directly. Acetone, ethanol, and methanol samples were shown by Karl Fischer titration to contain <0.015% water. Distilled water was stored in glass bottles before use.

Kinetic Methods. The equipment and techniques described previously [3a,d] were adopted with the following additions and modifications. The microconductivity cell, constructed by A. M. Willis, had Pt/Pyrex seals (satisfactory close to 25 °C) with two 6 × 4 mm bright Pt electrodes 4 mm apart—cell volume, ca 0.4 mL, cell constant, 2.26 cm^{-1}. The ultrasonic bath was a Kerry type PUL55 (power, 50/100 W average/peak), and samples were sonicated for 2–15 min. Formolyses and acetolyses were studied in 0.005 M degassed solutions (initially with 0.015 M sodium acetate added) in 25-mL Wheaton bottles sealed with Teflon-faced butyl disks. Aliquots (1 mL) were withdrawn by using a Hamilton gas-tight syringe; formolyses were quenched in 4 mL of AR acetic acid,[34] and the excess of base was titrated with 0.01 M AR perchloric acid in acetic acid (derivative method, weak setting on Radiometer RTS822 autotitrator). Iodine solutions were freshly made in tetrahydrofuran before injection into methanol/water solvents. Iodine concentrations were obtained by adding solid KI (BDH, AR) equivalent to at least 0.1 M and monitoring the absorbance of I_3^- at 285 or 350 nm[35] (Pye Unicam SP1800 spectrophotometer); calibrations were made for a standard solvent (e.g., 60% methanol/water).

Acknowledgment. This work was supported by the Science and Engineering Research Council (Grants GR/A77105 and GR/C12739). Preliminary conductivity experiments with the microcell were carried out by I. Roberts and S. J. Morris. Helpful suggestions from D. N. Kevill and H. Maskill are gratefully acknowledged.

Registry No. 1-AdCl, 935-56-8; 1-AdBr, 768-90-1; 1-AdI, 768-93-4; *t*-BuBr, 507-19-7; iodide, 20461-54-5.

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Reaction of Polycyclic Aromatic Hydrocarbons (PAH) with Nitrogen Dioxide in Solution. Support for an Electron-Transfer Mechanism of Aromatic Nitration Based on Correlations Using Simple Molecular Orbital Theory

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Eight unsubstituted, polycyclic aromatic hydrocarbons (PAH) were allowed to react with nitrogen dioxide in dichloromethane at 25 °C, and relative rate constants were obtained by direct competition techniques. The rate constants depend markedly on substrate structure, with over a 10^4 difference in rate constants between the least reactive (benzene) and most reactive (perylene) compounds studied. The major products formed from most substrates are nitroaromatics. Anthracene, however, also reacts with nitrogen dioxide to form appreciable amounts of 9,10-anthraquinone. Linear free energy relationships were determined between rate data and molecular orbital parameters based on models involving rate-determining σ-complex formation or electron-transfer (ET) reactions. Based on the better correlations obtained using the latter model, it is suggested that the more easily ionized PAH undergo nitration by an ET mechanism. Values of absolute rate constants for the nitration of three of the PAH (as measured by stopped-flow) also are reported and correlate well with our relative rate constants. The formation of 9,10-anthraquinone is suggested to result from the trapping of the intermediate anthracene radical-cation by water.

The nitration of aromatic molecules in solution is among those reactions that are taught to students in their first exposure to organic chemistry. The subject has been extensively reviewed in basic textbooks, in the advanced literature,[2] and in monographs.[3,4] Most nitrations have been carried out in strongly acidic, polar media, and under these conditions the nitrating species is generally regarded as the nitronium ion.[5] Although less frequently discussed in textbooks, nitrations also can be carried out both in solution and in the gas phase by nitrogen dioxide (or its dimer, dinitrogen tetraoxide).[5–19] The high concentrations

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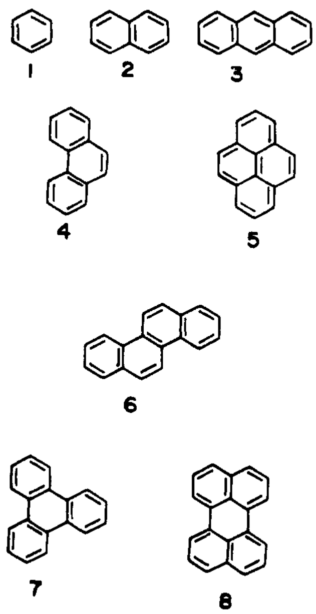

Figure 1. Structures of the PAH studied.

of nitrogen oxides in smog and the carcinogenic and mutagenic nature of the products of the reaction between nitrogen dioxide and aromatic hydrocarbons[10,16-21] give added importance to this type of nitration reaction.

We here report an investigation of the relative reactivity of the series of polycyclic aromatic hydrocarbons (PAH) shown in Figure 1 with nitrogen dioxide–dinitrogen tetraoxide in solutions of dichloromethane at 25 °C. The rate data have been correlated with the results of molecular orbital calculations carried out on likely models for the transition state. (We recently reported a similar study of the reaction of ozone with the same PAH.[22])

Experimental Section

Materials. The PAH were of the highest available commercial grade and were used without further purification. No contaminants could be detected by gas chromatography on a capillary column, and purities in excess of 98% are probable. The nitroaromatics, quinones, and anthrone used for product identification were obtained commercially or through standard laboratory syntheses. *p*-Diiodobenzene (MCB) was used without further purification and chlorobenzene (Eastman) was distilled prior to use. The purities of all these substances were comparable to those of the PAH. Nanograde dichloromethane (Mallinckrodt) was used. Solutions were freshly prepared for most runs by collecting gaseous dinitrogen tetraoxide (MCB) in a chilled vessel and diluting eightfold with dichloromethane. These solutions were maintained in screw-capped vials and used as rapidly as possible to prevent the uptake of moisture.

Analyses. Analyses of reaction mixtures were carried out on a Varian Model 3700 gas chromatograph and CDS 111 electronic integrator. An SE-30 capillary column (15 m, fused silica) was used in all runs.

Relative Rates by Internal Competition. Relative rates were obtained by direct competition between two PAH; solutions were 7.0×10^{-3} to 4.2×10^{-2} M in each PAH in the solvent dichloromethane. Reactions were initiated by the addition of about 0.5 equiv of dinitrogen tetraoxide in dichloromethane to samples of PAH solutions in screw-top vials. All reactions were run in at least five replicates. The temperature was 25 ± 1 °C; no attempt was made to exclude light or air from the reacting systems except during the "dark" or deaired runs discussed below. Although reaction was rapid, analyses of reaction mixtures were delayed until 4 to 12 h after mixing of reagents. (Because of the low reactivity of benzene, higher initial concentrations of PAH and nitrating agent as well as longer reaction times were used for this compound.) Any unreacted dinitrogen tetraoxide was removed prior to analysis by bubbling nitrogen through the well-chilled mixtures. Reaction mixtures were then analyzed directly; the final concentrations of PAH were determined by gas chromatography relative to an internal standard that was added just prior to analysis. Chlorobenzene, *p*-diiodobenzene, and phenanthrene were variously used as internal standards, the choice being based on maximum chromatographic separability. Addition of nitrating agent to hydrocarbons with reactivities equal to or greater than that of phenanthrene immediately produced brightly colored solutions. The majority of these were yellow; however, the anthracene solution was chartreuse while that for perylene (8) was crimson. Solutions containing the less reactive PAH turned yellow, but only upon standing.

Absolute Rates by Stopped-Flow. Stopped-flow kinetics were carried out with a Hitech stopped-flow spectrophotometer (Model SF-3L) interfaced to an On-Line Instrument Systems Model 3820 data system. Reactions were run under pseudo-first-order conditions, typically using 5×10^{-4} M PAH and 5×10^{-3} to 5×10^{-2} M dinitrogen tetraoxide. Experiments were conducted in an ethanol/water constant-temperature bath in which the temperature was held constant at 20 °C within ±0.5 °C.

Results

Product studies had already been reported for several of our substrates, and our results are consistent with the literature. Benzene gave only nitrobenzene. The nitration of naphthalene by nitrogen dioxide led to both 1-nitro- and 2-nitronaphthalene in a ratio 1-nitro:2-nitro of 11.6 ± 0.5, with a material balance of 92 ± 2%. The ratio of these two products is in good agreement with values of 10.9 ± 1.0 and 9.2 ± 1.0 found by Perrin for the treatment of naphthalene with a mixture of nitric and sulfuric acid in acetonitrile and the electrochemically induced reaction between naphthalene and nitrogen dioxide, respectively.[23] Earlier, Dewar and co-workers found this ratio to be 9.3 for the acid-catalyzed nitration of naphthalene in acetic anhydride.[24a]

Pyrene (5) has been nitrated under both ionic conditions[25] and by nitrogen dioxide;[10,18,19] the only product in either case is 1-nitropyrene. Similar results are observed for the nitration of perylene (8) under the two sets of conditions, both of which yield 3-nitroperylene.[18,19,24a] We also observe the formation of the same unique nitration

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Table I. Relative Reactivities of PAH toward Nitrogen Dioxide at 25 °C and Parameters Used in Correlating Data

			σ-complex model			ET model		
system	k_{rel}[d]	avg devn	stat factor	HMO[e]	PMO[f]	SCF HOMO[g]	IP[h]	$Ox_{1/2}$[i] (vs. SCE)
benzene[b] (1)	0.021	0.005	6	2.54	2.31	0.0	9.25	2.30
naphthalene (2)	0.19	0.01	4	2.30	1.81	0.955	8.12	1.54
triphenylene (7)	0.37	0.05	6	2.38	2.00	0.966	8.08	1.55
phenanthrene (4)	1.00		2	2.30	1.80	1.061	7.85	1.50
chrysene[c] (6)	2.32	0.51	2	2.24	1.67	1.327	7.79	1.35
pyrene (5)	11.9	0.9	4	2.19	1.51	1.584	7.55	1.16
anthracene[c] (3)	20.9	2.8	2	2.01	1.26	1.562	7.40	1.09
perylene[c] (8)	215	35	4	2.14	1.33	1.841	7.22	0.85

[a] All electron-transfer terms given in electron volts. Those for SCF HOMO's are relative to benzene. [b] Run relative to naphthalene. [c] Run relative to pyrene. [d] Relative reactivity calculated from $k_{rel} = [\ln (A_t/A_0)/\ln (B_t/B_0)]$. [e] Reference 40. [f] Reference 41a. [g] Reference 42. [h] Reference 43. [i] Reference 44.

products from each of these PAH. Our nitration of phenanthrene (**4**) led to a mixture of at least four mononitrated products that was not further characterized. (Under different conditions, involving reaction in the solid state, Tokiwa et al. report a single product.[10]) The ionic, acid-catalyzed nitration of phenanthrene is reported to yield all five of the possible mononitrated products.[24b] Our most interesting result involves the products of the nitration of anthracene (**3**). The exclusive mononitrated product was 9-nitroanthracene, consistent with the results of electrophilic nitrations.[26] However, in addition to this compound we find an appreciable amount of 9,10-anthraquinone. (No quinones could be detected by using our GLPC analysis among the products derived from benzene, naphthalene, or phenanthrene where authentic samples of quinones were available for comparison; Tokiwa et al. also report no quinone from phenanthrene.[10]) The ratio of 9-nitroanthracene to 9,10-anthraquinone was 1.64 ± 0.04 when approximately one-third of the initial anthracene present had reacted, with a material balance of 93 ± 2%. When reaction was allowed to progress to 70% completion based on consumption of anthracene, these values decreased to 1.42 ± 0.03 and 87 ± 2%, respectively. This change is probably due to the accumulation of water as the reaction progresses, as discussed below. 9,10-Dinitroanthracene was not detected under any of our reaction conditions.

The formation of 9,10-anthraquinone merits comment. Literature accounts of the products of the anthracene–nitrogen dioxide reaction are not in agreement. Over 100 years ago, Leeds reported that 9,10-anthraquinone is the sole product of the reaction between anthracene and nitrogen dioxide in glacial acetic acid.[27] Later workers obtained similar findings when the reaction is carried out in benzene or nitrobenzene.[28,29] Other early workers, however, observed the formation of nitrated products, even in some of the same solvents, when the reaction is carried out at low temperatures.[30] For example, Topchiev reports an 80% yield of 9,10-dinitroanthracene when anthracene is allowed to react with a large excess of dinitrogen tetraoxide in chloroform at 0 °C.[31] We have observed that carrying out this reaction in the dark or under a nitrogen atmosphere has no effect on our ratio of 9-nitroanthracene to 9,10-anthraquinone; the amount of water present, however, does markedly affect this ratio. When the solution of anthracene in dichloromethane is saturated with water before addition of nitrating agent, 9,10-anthraquinone becomes the favored product and the 9-nitroanthracene/9,10-anthraquinone ratio drops to 0.35 ± 0.03. Water is inevitably present in these reaction mixtures since it is produced from the dismutation of nitrous acid, eq 1.[32,33] Nitrous acid is formed when nitrogen dioxide reacts with PAH, eq 2. (Water has been shown to be formed when nitrogen dioxide reacts with alkenes.[34,35])

$$2HNO_2 \rightarrow NO + NO_2 + H_2O \quad (1)$$

$$2NO_2 + ArH \rightarrow HONO + ArNO_2 \quad (2)$$

Scheme I. Homolytic Substitution Mechanism for Aromatic Substitution by Nitrogen Dioxide That Involves σ-Complex Formation as the Rate-Determining Step. Conversion of the Initial Adduct to the Ultimate Nitroaromatic is Shown as Occurring by One of Three Possible Mechanisms: Electron Loss Followed by Proton Loss, Abstraction of a Hydrogen Atom by NO_2, or Formation of a Dinitrodihydro Compound That Loses HNO_2

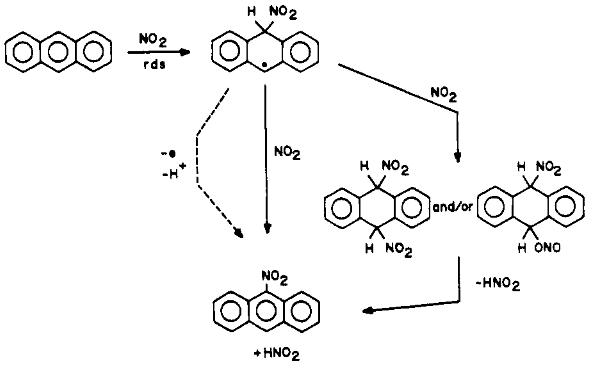

Table I lists the reactivities of PAH expressed relative to that of phenanthrene (**4**). The reactivities vary widely, with more than 4 powers of ten difference between the most and least reactive PAH. Although all results are presented relative to phenanthrene (**4**), the large difference in reactivities, as well as problems in gas chromatographic separation of PAH and reaction products, required that naphthalene (**2**) and pyrene (**5**) be utilized as secondary reference compounds. Table I also contains the parameters necessary for the correlations discussed below.

Discussion

In many ways nitrogen dioxide exhibits typical free-radical character in its reactions. It reacts with alkenes by both addition and allylic hydrogen atom abstraction pathways.[34,35] Hammett correlations of its reaction with

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Table II. Coefficients and Standard Deviations of Linear Correlations of Relative Rate Data

nature of correln	correln coeff	std dev
σ-complex model		
HMO	0.910	0.391
PMO	0.957	0.290
ET model		
SCF HOMO		
including benzene	0.948	0.325
excluding benzene	0.982	0.181
ionization potential		
including benzene	0.927	0.381
excluding benzene	0.990	0.114
oxidation potential		
including benzene	0.952	0.279
excluding benzene	0.988	0.100

substituted toluenes show it to be strongly electrophilic in nature.[36] If the nitration of PAH by nitrogen dioxide is analogous to aromatic substitution by other electrophilic radicals, the mechanism should involve a rate-determining σ-complex formation. This is illustrated in Scheme I using anthracene (**3**) as the the representative PAH. Ionic electrophilic nitration by N_2O_4 is unlikely in our system since dinitrogen tetraoxide produces nitrosonium and nitrate ions rather than nitronium and nitrite ions.[37] Another unlikely possibility is that the nitrosonium ion acts as an electrophile, forming a nitroso compound, which then is oxidized to the observed product. Nitrosation has been shown to occur in the reactions of dinitrogen tetraoxide with thiols[38] and secondary amines.[39] Electrophilic attack by the nitrosonium ion should also involve σ-complex formation as the rate-determining step.

A mechanism involving rate-determining σ-complex formation can be most easily treated by using a correlation with radical localization energies or equivalent parameters. Therefore, we examined correlations using HMO localization energies[40] and PMO "reactivity numbers".[41a] Although they are based on elementary level calculations, experience has shown that these parameters (particularly the latter) adequately correlate reactivities of PAH undergoing substitution.[41b] A linear plot of the logarithm of the statistically corrected relative rate against the localization energy or reactivity number of that position most susceptibile to attack yields correlations with coefficients of 0.910 and 0.957, respectively. (These and additional correlations are summarized in Table II.) Statistical correction is necessary to allow for different numbers of reactive positions among the PAH. For example, benzene has six identical positions, naphthalene has four reactive α positions, and anthracene has two reactive meso positions. The better correlation obtained with reactivity number was also observed in treating the relative reactivity data for ozonation of these same PAH.[22] The correlation of the present data with reactivity number is graphically presented in Figure 2.

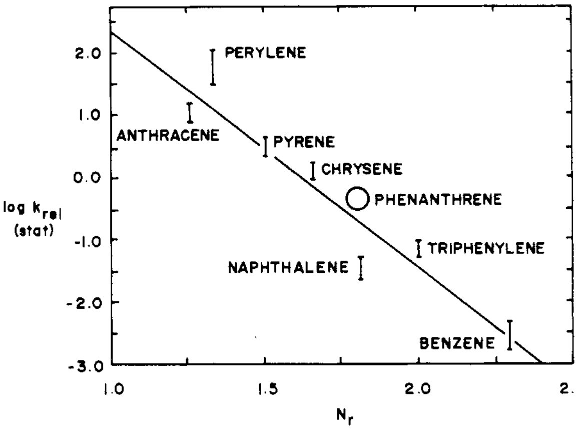


Figure 2. Logarithms of statistically corrected relative rate constants for reaction of PAH with nitrogen dioxide vs. PMO reactivity number.

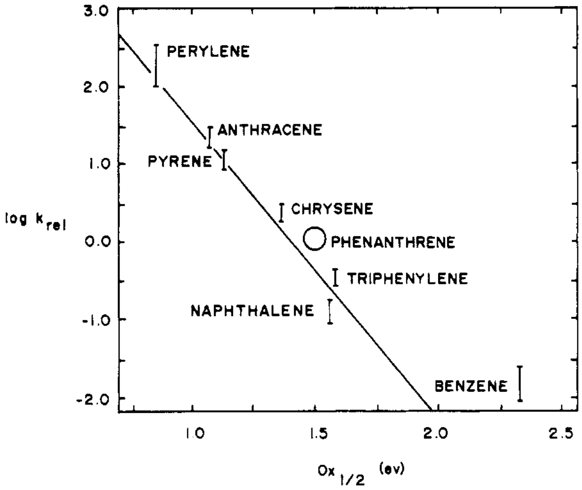
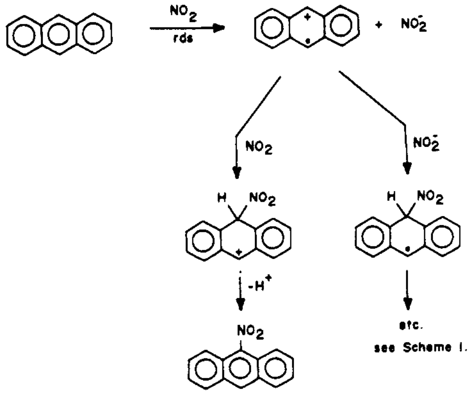


Figure 3. Logarithms of relative rate constants for reaction of PAH with nitrogen dioxide vs. half-wave oxidation potentials. The point for benzene is excluded for the correlations; see the discussion in the text.

Scheme II. Substitution Mechanism Involving an Initial Electron-Transfer Reaction That is the Rate-Determining Step (rds)



Unfortunately, this seemingly adequate approach is open to criticism. Equating the total PAH reactivity with attack solely at the most reactive site is justified in only about half the cases studied here. This treatment also provides no insight into the mechanism of production of quinones.

An Electron-Transfer Mechanism. An entirely different model can be developed[6,7] patterned after the electron-transfer mechanism for nitration by the nitronium ion proposed by Perrin.[23] Scheme II shows a mechanism, modified from that originally suggested by Perrin, utilizing nitrogen dioxide rather than the nitronium ion as the electron acceptor.

This electron-transfer (ET) mechanism obviates the difficulties encountered above since product formation occurs subsequent to the rate-determining step. Since

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electron transfer would be from the highest occupied molecular orbital (HOMO), several correlations utilizing either the HOMO energy or related physical properties have been performed. The average value of the coefficients for correlations obtained by plotting the logarithms of total relative reactivity against HOMO energies calculated by an SCF method,[42] gas-phase ionization potentials,[43] or half-wave oxidation potentials (obtained in acetonitrile)[44] is 0.987 ± 0.003 if the data for benzene are omitted. Details of the individual correlations may be found in Table II, and the last of these correlations is illustrated in Figure 3. The agreement among these three correlations is understandable in light of the interrelation that exists among the parameters measuring electron transfer. These correlations utilize nonstatistically corrected rate data since the PAH acts as a unit to generate radical-cations in the rate-determining step, and subsequent partitioning of the radical-cation among pathways leading to different products is not kinetically important.

The omission of the benzene data from the above correlations will be discussed in detail below. However, Perrin notes that the ionization potential of benzene is too high to allow the ready formation of the radical-cation; therefore, benzene probably reacts by rate-determining σ-complex formation. The average value for the correlation coefficients when the data for benzene are included drops to 0.942 ± 0.010.

Since electron transfer between PAH and the nitronium ion is regarded as a diffusion-controlled process, Perrin concludes that all aromatic systems more reactive than toluene should undergo nitration at the same rate. Clearly this is not the case for the results reported here. (Nor were identical rates observed for all PAH in earlier ionic nitrations.[45]) However, greater selectivity might well be expected for electron transfer from a PAH to the nitrogen dioxide radical rather than to the nitronium ion.

It is worth pointing out explicitly that the Perrin mechanism for nitration by the nitronium ion (eq 3) and ours for nitration by nitrogen dioxide (eq 4) both involve an electron transfer as the rate-determining step and the collapse of the intermediate species to give a σ complex as the product-determining step. Since the PAH is converted to a cation-radical in both cases, it is not surprising that the product distribution appears to be very similar (see Results section) for nitration by the nitronium ion and by nitrogen dioxide.

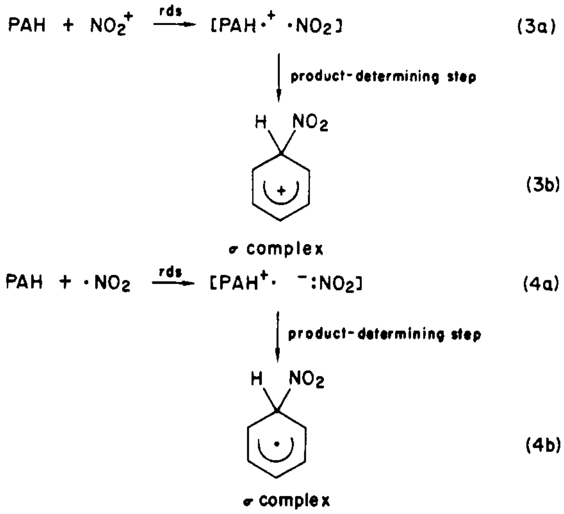

Table III. Comparison of Our Relative Rate Constants with Absolute Values Obtained by the Stopped-Flow Method

compd	competn values[a]	stopped-flow values[b,c]	
	k_{rel}	k (M^{-1} s^{-1})	k_{rel}
perylene	215	16 500 (2000)	147
anthracene	21	2180 (75)	19
pyrene	12	1350 (100)	12

[a] See text for discussion. At 25 °C. [b] Pryor, W. A.; Cosgrove, J. P.; Church, D. F., unpublished results. [c] k is the calculated second-order rate constant in L mol^{-1} s^{-1}. Parentheses give the standard deviation. Rates were determined at 20 °C.

A Rapid Exchange Reaction. Szwarc and Jagur-Grodzinski[46a] have shown that radical-cations derived from PAH are sufficiently long-lived to equilibrate with other PAH (eq 5). The rate of such equilibration is reported

$$PAH_1^{+}\cdot + PAH_2 \rightleftharpoons PAH_1 + PAH_2^{+}\cdot \quad (5)$$

to be close to the diffusion-controlled limit.[46b] When such an equilibrium occurs, it usually is not possible to obtain reliable kinetic data by using a competitive technique, since the first-formed PAH cation-radical can exchange via eq 5 and the rates of disappearence of PAH_1 and PAH_2 reflect the equilibrium concentrations rather than the relative rates of the ET reaction of the two PAH with nitrogen dioxide. In the present case, however, it is unlikely that the exchange shown in eq 5 perturbs our results for the more easily ionized PAH's. It seems likely that the electron-transfer reactions of nitrogen dioxide with PAH have transition states that are "late" and have stabilities that are similar to those of the first intermediate, which we presume to be the cation-radical. Therefore, the rates of reaction of the PAH with nitrogen dioxide would be expected to parallel the stabilities of the intermediate cation-radicals, and, if this is true, the equilibrium shown in eq 5 will not alter the order of reactivity.

We have preliminary data[47] which demonstrate that our relative rate constants are not affected by the exchange reaction, eq 5, at least for the faster reacting PAH that can undergo an electron-transfer reaction with nitrogen dioxide. We have studied the reaction of nitrogen dioxide with the three PAH shown in Table III, using the same stopped-flow technique that we used for the study of the reaction of ozone with olefins.[59] These reactions were run in dichloromethane, the solvent used for the relative rate study, under pseudo-first-order conditions with nitrogen dioxide in large excess relative to the PAH. As the data in Table III show, the absolute and relative rate constants for these three compounds agree very closely. It should be noted, however, that the slower reacting compounds appear to react more slowly by the relative rate method than by the absolute stopped-flow method, the discrepancy being a factor of from 2- to 10-fold. This fact, like the lack of correlation of the point for benzene in Figure 3, indicates

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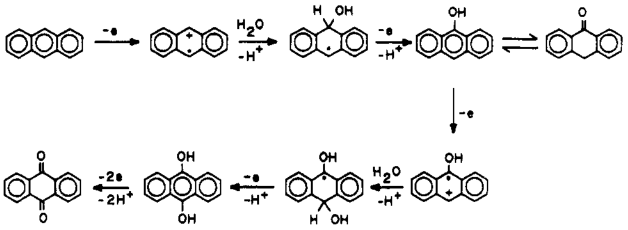
[47] Pryor, W. A.; Cosgrove, J. P.; Church, D. F., to be submitted. Our preliminary data indicate that the kinetics for the reaction of NO_2/N_2O_4 with PAH are quite complex. While we are not prepared to describe these data in detail, our tentative conclusions are as follows: These reactions appear to occur in two steps with the rapid formation of an intermediate followed by the slow decay to products. Both the disappearance of PAH and the appearance of the intermediate appear to be second order in NO_2 (or first order in N_2O_4) and occur at the same rate. Surprisingly, the overall course of the reaction *appears* to be fourth order in NO_2 (or second order in N_2O_4).

Scheme III. Production of Oxygen-Containing Compounds from the One-Electron Oxidation of Anthracene Followed by Trapping of the Cation Radical by Water[50,51]



that while the ET mechanism can satisfactorily rationalize the data for the faster reacting PAH, the slower reacting PAH may not react by an electron-transfer mechanism, as expected from previous discussion of this point by Eberson.[7b]

Radical-Cations as Intermediates and the Formation of Quinone Products. PAH radical-cations react with nucleophiles and/or radicals to ultimately yield substituted PAH. For example, combination of nitrite ion with the electrochemically produced pyrene (**5**) and perylene (**8**) radical-cations is a synthetically useful reaction yielding a single nitroaromatic in each case.[48] The anodic oxidation of anthracene (**3**) to 9,10-anthraquinone, shown in Scheme III, is believed to involve the reaction of radical-cations with water followed by one-electron transfers and deprotonations.[49–51] Since water is a poor nucleophile, it might be anticipated that only those radical-cations with relatively large amounts of localized positive charge density would be converted to phenols by this mechanism. Among the radical-cations in this study, the highest positive charge density is found at the meso positions of anthracene (**3**), the compound for which we find quinone formation.[52]

Effect of Light. During the course of this investigation, an interesting article describing the photoinduced nitration of phenolate anion by tetranitromethane was published.[53] This technique could not be used to nitrate all of the PAH we studied; e.g., anthracene (**3**) reacts under these conditions, but pyrene (**5**) does not. Although no attempt had been made to exclude light in our original studies, we have investigated the selectivity of nitration by nitrogen dioxide for a few of our PAH in the dark. For the pairs of PAH examined, naphthalene–phenanthrene and anthracene–pyrene, the relative reactivities were the same in the light and in the dark, within the experimental uncertainty.

Conclusion. We suggest that the reaction of the more reactive (and more easily ionized) PAH with nitrogen dioxide in solution is best accommodated by an electron-transfer (ET) mechanism. Firstly, the correlations with calculated parameters are slightly better when the ET mechanism is modeled. More significantly, this approach readily explains the formation of quinone products as resulting from a competing reaction of the intermediate radical-cation with water.

It is important to stress that the present results need not be directly comparable to those obtained for reactions of PAH and nitrogen dioxide in physically different environments. For example, a large body of data exists for the reaction of PAH in the combustion of diesel fuels to form nitrated products.[54–57] Under these conditions, much more complex mixtures of nitrated products are found than in the present study, and a higher percentage of oxygenated materials are produced. (It has been noted, however, that the yield of oxygenated products is very dependent upon the manner in which samples are collected.[58])

Finally, it is interesting to note that the order of PAH reactivity toward nitrogen dioxide does not completely parallel the order of reactivity of these same compounds toward ozone.[22] This reflects fundamental mechanistic differences between the two processes. We continue to view the ozone reaction as involving rate-determining, reversible σ-complex formation in contrast to the electron-transfer process suggested for the mechanism of nitration.

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Registry No. **1**, 71-43-2; **2**, 91-20-3; **3**, 120-12-7; **4**, 85-01-8; **5**, 129-00-0; **6**, 218-01-9; **7**, 217-59-4; **8**, 198-55-0.

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