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The Reaction of Anthracene with Nitrogen Dioxide Revisited

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The primary products of the reaction of anthracene (AN) with nitrogen dioxide are *cis*- and *trans*-9,10-dinitro-9,10-dihydroanthracene, identified by NMR and single-crystal X-ray analysis. The chemical literature contains conflicting product analyses for this reaction, and the discrepancies are rationalized in terms of the thermal and chemical lability of these primary products. These products are rationalized in terms of a radical reaction of AN with NO_2, rather than an electrophilic reaction mechanism. Analysis of the reaction kinetics reveal the formation of an intermediate, apparently of the charge-transfer type, between AN and one molecule of nitrogen dioxide. This intermediate precedes the formation of the 9-nitro-9,10-dihydroanthryl radical that readily couples with a molecule of nitrogen dioxide to yield *cis*- and *trans*-9,10-dinitro-9,10-dihydroanthracene in a 1:1 ratio.

The reaction of nitrogen dioxide with anthracene (AN) can be traced back to the year 1880, when Lieberman and Lindeman suggested that 9-nitro-10-nitrito-9,10-dihydroanthracene is the primary product when the reaction was carried in glacial acetic acid.[2] Almost simultaneously and under similar conditions, Leeds isolated only anthraquinone (AQ).[3] Twenty-one years later, Meisenheimer proposed that 9,10-dinitro-9,10-dihydroanthracene (DDA) is the primary product when the reaction is carried out in chloroform.[4] Meisenheimer also noticed the ease with which DDA gives 9-nitroanthracene (9NA) by elimination of the elements of nitrous acid. In 1924, Bass and Johnson[5] isolated only AQ under conditions similar to those of Meisenheimer. Barnett[6] recognized that DDA could exist in cis and trans forms, and Battegay,[7] Monti and coworkers,[8] and Sosnovsky[9] also studied its formation. In 1938, Topchiev and his collaborators[10] reported the formation of 9,10-dinitroanthracene in 80% yield when the reaction was performed in chloroform. In 1963, Dufraisse and co-workers,[11] using AN suspended in benzene or ether, were able to isolate two isomers that showed IR absorptions consistent with addition of NO_2 to the 9 and 10 positions. In chloroform, however, they obtained only 9-nitro-10-nitrato-9,10-dihydroanthracene, apparently due to participation of ambient oxygen in their reaction system. Dufraisse[11] also provided the first spectroscopic support for the identification of the isomers of DDA and clarified reports of conflicting melting points and structures.[2–4,10] Recently, 9NA and AQ were observed when the reaction was carried out in dichloromethane.[12–14] Quinones were not observed when other PAH were allowed to react with NO_2 under similar conditions, suggesting that the reaction of anthracene involves the formation of metastable primary products.[14]

We report herein a high-yield, one-pot method for the synthesis of the isomers of DDA. We also report the assignment of stereochemistry, ^1H and ^{13}C NMR resonances in solution, and the single-crystal X-ray analysis for *cis*- and *trans*-DDA. The reaction of AN with NO_2 in CCl_4, $CHCl_3$, and CH_2Cl_2 is discussed in terms of a radical reaction. Stopped-flow kinetics evidence for a first intermediate of the charge-transfer type has been obtained; a charge-transfer intermediate is consistent with the linear relationship previously found between the logarithm of relative rates of reaction of several PAH and their half-wave oxidation potentials.[14]

Experimental Section

Reagents and Materials. Anthracene (Baker, 99.9+%) was used without further purification. Nitrogen dioxide was purchased from Matheson, distilled, and dried over P_2O_5 until a white solid was obtained upon freezing the distillate, indicating that the distillate was freed of lower oxides of nitrogen. CCl_4 (Mallinckrodt Analytical Reagent) was dried over molecular sieves. CH_2Cl_2 (Mallinckrodt ChromAr HPLC) was dried over sodium sulfate, distilled, and stored over molecular sieves. $CHCl_3$ (Baker Analyzed Reagent) was repeatedly washed with water, dried over $CaCl_2$, distilled, and kept over $CaCl_2$. CD_2Cl_2 and $CDCl_3$ (Aldrich Chemical Company) were dried over sodium sulfate. Solvents were thoroughly purged with dry nitrogen or argon prior to use.

Instrumentation. NMR spectra were recorded on a Bruker AM 400 spectrometer operating at 400.13 MHz or on a Bruker 100 NR operating at 100.13 MHz. ^1H chemical shifts are referenced to residual $CHCl_3$ (7.26 ppm), and ^{13}C chemical shifts are referenced to $^{13}CDCl_3$ (77.00 ppm). GC/MS analysis was conducted on a Hewlett-Packard 5970 instrument equipped with mass-selective detector using a 50-m (0.18 mm i.d.) HP-1 Hewlett-Packard column. Stopped-flow experiments were conducted on a Hi-Tech spectrometer Model SF-3L interfaced to an On-Line Instrument Systems Model 3820 data system. Further details concerning the stopped-flow spectrometer and methodology are given elsewhere.[15] Kinetic experiments were conducted at 25.0 ± 0.1 °C.

Synthesis of *cis*- and *trans*-DDA. In a typical experiment, AN (170 mg, 0.955 mmol) was dissolved in CCl_4 (40 mL). An NO_2/N_2O_4 solution (2.8 mM NO_2 and 44.6 mM N_2O_4; 18 mL) was

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Table I. Crystal Data and Data Collection Parameters for *cis*- and *trans*-9,10-Dinitro-9,10-dihydroanthracene

	cis isomer	trans isomer
formula	$C_{14}H_{10}N_2O_4$	$C_{14}H_{10}N_2O_4$
FW	270.3	270.3
cryst. system	orthorhombic	monoclinic
space group	*Pnma*	$P2_1/c$
a, Å	7.368 (1)	7.733 (1)
b, Å	15.163 (1)	12.735 (2)
c, Å	10.853 (1)	6.383 (1)
β, deg		105.58 (1)
V, Å^3	1212.5(4)	605.5 (2)
Z	4	2
D, g cm^{-3}	1.480	1.482
T, °C	25	23
μ, cm^{-1}	8.9	8.9
cryst size, mm	0.20 × 0.36 × 0.40	0.14 × 0.19 × 0.43
min rel trans, %	89.2	94.5
θ limits, deg	2–75	2–75
scan rates, deg min^{-1}	0.33–3.30	0.69–3.30
unique data	1299	1240
obsd data	1101	1082
variables	129	112
extinction	5.5 (6) × 10^{-6}	8.4 (10) × 10^{-6}
R	0.060	0.040
R_w	0.090	0.055
GOF	5.62	3.05
max residual, e Å^{-3}	0.41	0.19
notes	one NO_2 disordered	

slowly added to the solution of AN at 25 °C with magnetic stirring under an argon or nitrogen atmosphere to rigorously exclude oxygen. A colorless crystalline material precipitated a few minutes after the addition was completed, consisting almost exclusively of *cis*-DDA. The trans isomer is much more soluble but can be quantitatively crystallized by cooling the reaction mixture down to −20 °C overnight. The total yield is typically about 90% with a cis/trans ratio of about 1.0. *cis*-DDA can be further purified by recrystallization from $CHCl_3$; *trans*-DDA can be purified by repeated recrystallization from hexane/CCl_4 (4:1). The reactions were scaled-down, carried out in the corresponding deuterated solvent, and analyzed by ^1H NMR in order to investigate the product distributions in chloroform and in dichloromethane.

Thermolysis of *cis*-DDA. A capillary melting point tube (Kimax) was loaded under nitrogen with 5 mg of *cis*-DDA and the tube mouth was sealed with silicon grease. The tube was then placed in a Mel-Temp melting point apparatus set at 200 °C until a violent evolution of gas ceased and the sample turned from colorless crystalline to a bright yellow (about 45 s). The tube was then allowed to cool down and broken. The contents were dissolved in $CDCl_3$ and analyzed by ^1H NMR and GC/MS.

Table II. Coordinates for *cis*-9,10-Dinitro-9,10-dihydroanthracene

atom	*x*	*y*	*z*	*B* (Å^2)
O1	0.3459 (4)	0.2772 (4)	0.1071 (3)	9.0 (1)^a
O2	0.2164 (4)	0.2147 (3)	−0.0415 (3)	8.2 (1)^a
O3	−0.0839 (3)	0.3202 (1)	−0.2296 (2)	7.76 (5)
N1	0.2170 (3)	$^1/_4$	0.0608 (2)	4.68 (5)
N2	−0.1169 (4)	$^1/_4$	−0.1828 (2)	4.52 (5)
C1	0.0374 (4)	$^1/_4$	0.1346 (2)	4.35 (6)
C2	−0.0648 (2)	0.3328 (1)	0.1047 (2)	4.01 (4)
C3	−0.1920 (3)	0.3324 (1)	0.0098 (2)	3.78 (4)
C4	−0.2292 (4)	$^1/_4$	−0.0605 (2)	3.76 (5)
C5	−0.0343 (3)	0.4103 (2)	0.1711 (2)	5.42 (5)
C6	−0.1289 (3)	0.4864 (2)	0.1412 (2)	6.57 (5)
C7	−0.2518 (4)	0.4865 (2)	0.0485 (2)	6.09 (5)
C8	−0.2863 (3)	0.4101 (2)	−0.0175 (2)	4.91 (4)

^{a} Population = $^1/_2$.

Table III. Coordinates for *trans*-9,10-Dinitro-9,10-dihydroanthracene

atom	*x*	*y*	*z*	*B* (Å^2)
O1	0.4345 (1)	−0.1267 (1)	0.0211 (2)	5.30 (3)
O2	0.2632 (2)	−0.1559 (1)	0.2291 (2)	5.29 (3)
N	0.3054 (1)	−0.1064 (1)	0.0885 (2)	3.26 (3)
C1	0.1865 (2)	−0.0133 (1)	−0.0173 (2)	2.58 (3)
C2	0.1457 (2)	0.0508 (1)	0.1608 (2)	2.50 (3)
C3	−0.0279 (2)	0.0602 (1)	0.1828 (2)	2.46 (2)
C4	−0.0576 (2)	0.1161 (1)	0.3577 (2)	3.00 (3)
C5	0.0838 (2)	0.1635 (1)	0.5078 (2)	3.44 (3)
C6	0.2566 (2)	0.1556 (1)	0.4841 (2)	3.58 (3)
C7	0.2878 (2)	0.0994 (1)	0.3133 (2)	3.21 (3)

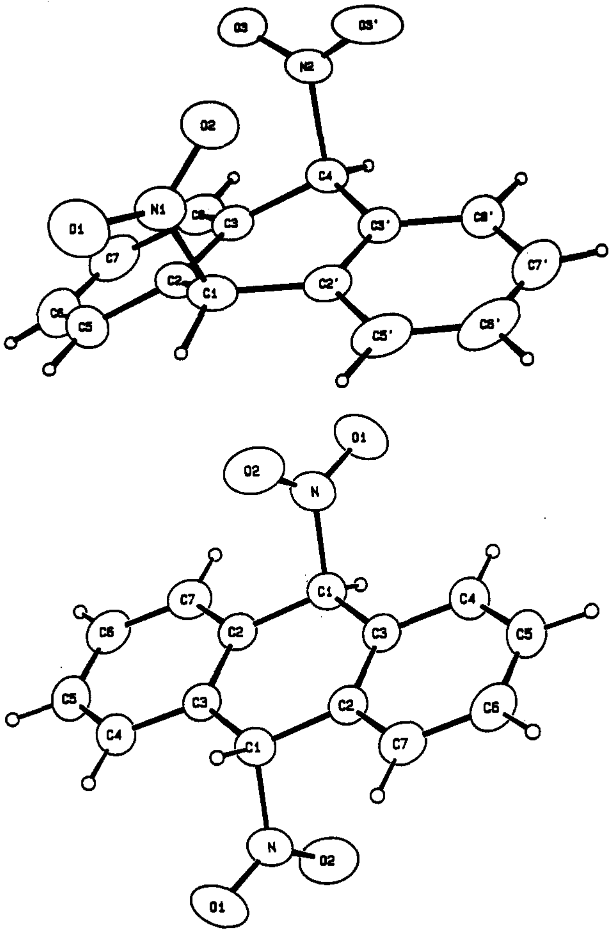


Figure 1. ORTEP drawings of *cis*- and *trans*-9,10-dinitro-9,10-dihydroanthracene.

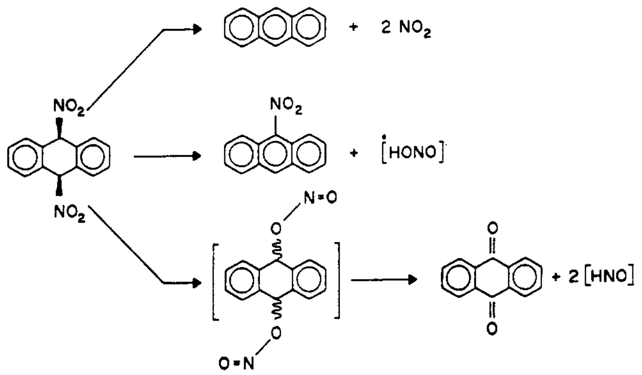
Crystallographic Measurements and Structure Solution. Crystals of *cis*-DDA were grown from $CHCl_3$ by slow evaporation. Crystals of *trans*-DDA were grown by the vapor diffusion method (benzene into $CHCl_3$). Intensity data were collected by ω–2θ scans of variable rate designed to yield measurements of equal relative precision for all significant reflections, using an Enraf-Nonius CAD4 diffractometer equipped with Cu K_α radiation (λ = 1.54184 Å) and a graphite monochromator. A maximum was placed on the scan time spent on any reflection. One quadrant of data was collected for *trans*-DDA and one octant for *cis*-DDA within the angular limits listed in Table I, which also gives crystal data and specifics for data collection. Data reduction included correction for background, Lorentz, polarization, and absorption, the latter based on Ψ scans. Data having $I > 3\sigma(I)$ were used in the refinements. Structures were solved by direct methods and refined by full-matrix least squares based on *F* with weights $w = \sigma^{-2}(F_o)$, using the Enraf-Nonius SDP programs. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were located in difference maps and refined isotropically. The *cis*-DDA molecule exhibits a rotational disorder of one of the nitro groups (N1, O1, O2) in which the oxygen atoms are tipped such that they occupy half-populated positions about 0.4 Å out of the mirror plane upon which N1 resides. Attempts to refine an ordered model in noncentrosymmetric space group $Pna2_1$ led to near-unit correlations and lack of convergence. The centrosymmetric group was thus chosen as most appropriate. Final *R* factors and residuals in final difference maps are given in Table I. Coordinates for the two structures are listed in Tables II and III, and the molecules are depicted in Figure 1.

Table IV. NMR Spectral Data for *cis*- and *trans*-9,10-Dinitro-9,10-dihydroanthracenes

	NOE results			chemical shifts, ppm						
isomer	irrad	obsd	enh (%)	H-1	H-2	H-9	C-1	C-2	C-9	C-11
cis[a]	H-9	H-1	8	7.75	7.60	6.59	131.17	130.75	86.70	130.16
cis	H-1	H-9	18							
trans	H-9	H-1	6	7.63	7.56	7.03	128.14	130.81	87.73	129.23
trans	H-1	H-9	10							

[a] A small positive NOE (1%) was noticed on H-2.

Scheme I



NMR Experiments. The compounds (4 mg) were dissolved in 0.5 mL of $CDCl_3$ using 5-mm tubes, and all experiments were done at 25 °C. Nuclear Overhauser effect (NOE) and ^{13}C–^{1}H correlation experiments were conducted by using Bruker standard software. The NOE were calculated by subtracting the corresponding on and off resonance FID's, Fourier-transforming the difference (with small line-broadening; 0.2 Hz) and relating the enhancement to the area of the same resonance in the control experiment. The ^{13}C–^{1}H correlations (see supplementary material) were recorded by using a 64 × 4096 data matrix size, 64 increments, and 128 transients for each t_1 value. Sine bell multiplication was performed in both dimensions prior to Fourier transformation and an absolute value calculation was done in the F1 dimension of the processed matrix. The recycle time was 2 s. Higher resolution ^{1}H and ^{13}C spectra have been used as projections.

Results and Discussion

Chemical and Thermal Lability of *cis*- and *trans*-DDA. Chromatographic analysis of a mixture of *cis*- and *trans*-DDA on silica gel yields 9NA, a product resulting from their decomposition on contact with the silica gel. Analysis by GC/FID or GC/MS yields 9NA and anthraquinone (AQ), together with a small amount of AN, with relative distributions depending on the injector temperature and the amount of sample injected. Finally, the 200 °C thermolysis of *cis*-DDA affords the same products detected by GC methods. Thus, *cis*- and *trans*-DDA are chemically and thermally labile, and techniques like GC, MS, HPLC, or a combination of them, commonly used for the analysis of mixtures of nitrated compounds,[12-14,16] cannot be employed. Scheme I describes the thermolytic routes leading to AN, 9NA, and AQ.

Structural Features of *cis*- and *trans*-DDA. Nuclear Overhauser effects resulting upon irradiation of H-9,10 or the peri protons are shown in Table IV. The observed ^{1}H–^{1}H NOE also provide the assignments of the ^{1}H spectrum. The effect observed on the cis isomer is the larger one, indicating an average shallow boat with pseudoaxial conformational preference for the nitro groups in solution. The ^{1}H–^{1}H NOE observed for *trans*-DDA are substantially greater than one-half of the corresponding NOE of the cis isomer. Making use of the internuclear distances obtained from the crystallographic study and the inverse sixth power relationship of the distance between the irradiated and the observed nuclei, the *trans*-DDA NOE are predicted to be 64% of those of the cis isomers. Thus, it appears that the trans isomer is forced toward an average near-planar conformation in solution. The average solution conformations agree with existing force-field calculations[17] and crystal structures of sterically demanding 9,10-disubstituted-9,10-dihydroanthracenes.[18-20] *trans*-9,10-Dipropyl-9,10-dihydroanthracene[18] and *trans*-bis(trimethylsilyl)-9,10-dihydroanthracene[19] were also found to be near-planar by X-ray analysis. Similarly, it was found that cis substituents tend to increase the angle between the planes of the aromatic rings in the butterfly-shaped dihydroanthracene series,[20] inducing planarity as well.

Indeed, the single-crystal X-ray diffraction analysis of the isomers of DDA afforded results consistent with the expected average solution conformational preferences as inferred by NMR. Both isomers of DDA lie on symmetry elements in the solid state, and both exhibit significant flattening of the central ring. The cis isomer has C_s symmetry in the crystal; thus C2, C3, and their mirror equivalents lie in a common plane with NO_2-substituted carbon atoms C1 and C4 lying 0.338 (3) Å and 0.311 (2) Å, respectively, out of this plane in a boat deformation. The trans isomer has crystallographic C_i symmetry, thus the deformation of the central ring is slightly chair-like. Nitro-substituted atom C1 and its inversion equivalent lie ±0.055 (1) Å from the plane defined by C2, C3, and their inversion equivalents. Maximum deviation from planarity of the aromatic ring is 0.005 (2) Å for the cis isomer and 0.007 (2) Å for the trans isomer. The two aromatic rings of the cis isomer form a dihedral angle of 150.6 (1)°, while those of the trans isomer are constrained by symmetry to be parallel. The nitro groups of the trans isomer form dihedral angles of 97.9 (1)° with the best plane of the central ring, and the O1–N–C1–C3 torsion angle is 98.8 (2)°. In the case of the cis isomer, one nitro group (N2, O3, O3′) lies orthogonal to the crystallographic mirror, while the other (N1, O1, O2) is tipped slightly out of the mirror plane, forming a dihedral angle of 26.9 (2)° with it, and resulting in the disorder.

The ^{13}C chemical shifts and assignments are listed in Table IV and were obtained by using ^{13}C–^{1}H 2D correlations (see supplementary material).

Implications for Nitration Mechanism. Previous studies on the nitration of fluoranthene with NO_2 revealed that the mechanism can be dramatically solvent[21,22] and temperature[22] dependent. The reaction mechanism for the

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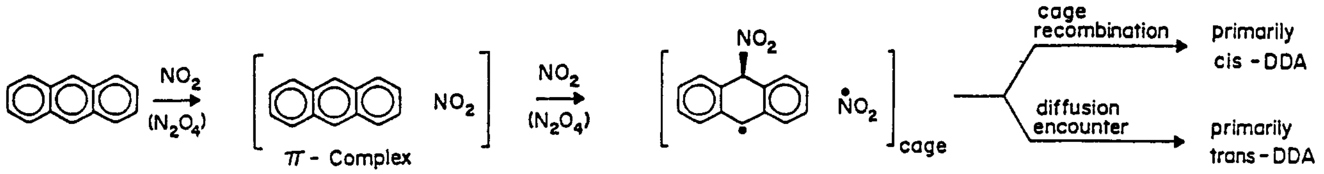
Scheme II



nitration of fluoranthene[21,22] and naphthalene[23] with NO_2 in CCl_4, at 25 °C and in the absence of acid catalysis, is best formulated as a homolytic process.

The nitration of AN with NO_2 in several solvents has often been found to afford substantial amounts of AQ,[2,5,12–14] while other PAH yield none or only traces of quinonoid products.[12–14,21] Eberson and Radner noticed that the nitration of AN with NO_2 in CH_2Cl_2 afforded a much lower yield of mononitroproduct when compared to other PAH under the same conditions.[12] We partially accounted for the formation of AQ by trapping of the incipient radical-cation of AN by water and further oxidation under the reaction conditions,[14] since the ratio AQ/9NA increased when the reaction was carried out in water-saturated CH_2Cl_2.[24] More recently, Kochi and Masnovi utilized the same argument to explain the formation of related compounds.[25] Our present studies reveal that *cis*- and *trans*-DDA are the primary products in CH_2Cl_2, $CHCl_3$, and CCl_4, as indicated by the ^1H NMR spectra of the corresponding reaction mixtures. Under conditions of incomplete conversion, *cis*- and *trans*-DDA typically account for about 90% of the material balance of fresh reaction mixtures, with no detectable amounts of AQ or 9NA by ^1H NMR.

The low yield of 9NA observed by Eberson and Radner[12] is probably due to the combined effects of a nonquantitative thermolysis of DDA to form 9NA, to a reaction stoichiometry different than the one they expected (A/NO_2 ratio of 1:2 instead of their expected 1:1.5 ratio), and, at least in part, to trapping of an incipient anthracene radical-cation by adventitious water.[14,24,25] Previous reports of various yields of AQ can be explained in a similar manner. Also, special care has to be given to drying the solvents and the NO_2 in order to observe the radical reaction pathway because small amounts of Lewis or protic acids catalyze an ionic electrophilic reaction pathway.[12,26–28]

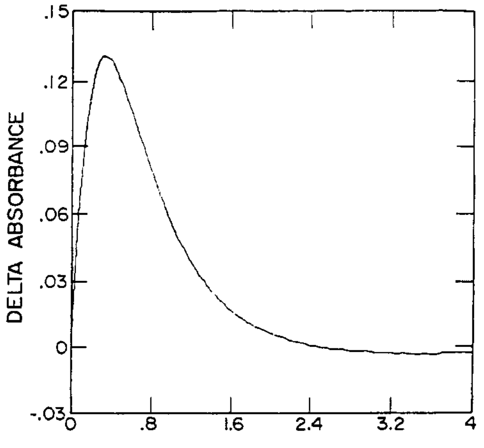


Figure 2. Typical rise and fall stopped-flow trace (λ = 278 nm) obtained for the reaction of anthracene with NO_2 in CH_2Cl_2 at 25 °C.

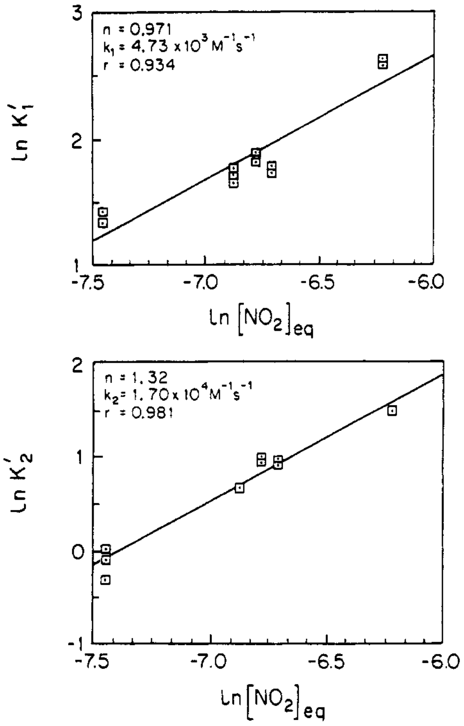


Figure 3. Double natural logarithmic plot of the pseudo-first-order rate constants and the concentrations of NO_2 (in equilibrium with N_2O_4) for the apparent early phase (top trace) and the apparent late phase (bottom trace).

Stopped-flow spectroscopy of the reaction of AN with NO_2 in CH_2Cl_2 shows the formation of a transient intermediate. This intermediate is likely to precede the formation of the 9-nitro-9,10-dihydroanthryl radical because the coupling of even more bulky dihydroanthryl radicals with NO_2 approaches diffusion control.[29] Under pseudo-first-order conditions in NO_2, at 278 nm,[30] the raw data of absorbance (D) versus time can be analyzed as two exponentials (formation and decay) in the following manner. Figure 2 shows a typical run from which a single

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(30) At 278 nm, only A, the first intermediate, and the 9-nitro-9,10-dihydroanthryl radical are the absorbing species.[26] However, because of its high reactivity, the 9-nitro-9,10-dihydroanthryl radical contribution to the total optical absorbance is expected to be negligible at all times.

exponential was generated from the end of the apparent decay phase;[31] this exponential, when subtracted from the raw data, generates a second exponential (apparent formation). The kinetic profile fits well with a series reaction,[32] according to eq 1. A double logarithmic plot of k_{obs}

$$A + xNO_2 \rightarrow B + yNO_2 \rightarrow \text{products} \qquad (1)$$

vs NO_2 (in rapid equilibrium with N_2O_4[15]) gives reasonably straight lines for both reaction phases, as can be seen in Figure 3, and as expected for the first case, the pseudo-first-order series reactions kinetic model. The order in NO_2 of the apparent first phase is 0.971 ($r = 0.932$; [AN] = 0.04–0.50 mM) and that of the apparent second phase is 1.32 ($r = 0.981$; [AN] = 0.04–0.50 mM), suggesting the possibility of some contribution of N_2O_4, to the apparent later reaction phase.[33] The rate expression is shown in eq 2, where ϵ_A and ϵ_B are the extinction coefficients of AN

$$U = A_0[\epsilon_A - k_1'\epsilon_B/(k_1' - k_2')] \text{ and } V = A_0k_1'\epsilon_B/(k_1' - k_2')$$

$$D = U \exp(-k_1't) + V \exp(-k_2't) \qquad (2)$$

and the transient intermediate and k_1' and k_2' are the observed rate constants of the apparent formation and decay phases, respectively.

A mechanism for this reaction is depicted in Scheme II. The lack of stereoselectivity of the reaction is consistent with the stepwise addition of two molecules of NO_2. Cage recombination is likely to yield a slight excess of the cis isomer, whereas the less stable trans isomer can be rationalized as being formed in slight excess by the kinetically controlled coupling of the free radicals, as is shown in Scheme II. The cis isomer is the more stable product in which steric interactions of the nitro groups with the peri hydrogens are minimized. Attack from the less hindered side yielding *trans*-DDA can be rationalized as kinetically controlled diffusive encounters of the 9-nitro-9,10-dihydroanthryl radical and NO_2.[34]

The high regioselectivity of the addition of NO_2 to the middle ring of AN is noteworthy. Nitrogen dioxide is known to react with organic radicals to form nitro and nitrite products in the gas phase,[35] in the gas–liquid interface,[36] and in solution.[37] Coupling at the nitrogen atom of NO_2 has been regarded as a thermodynamically controlled process in the reaction of NO_2 with aliphatic radicals in the gas phase.[35]

Recently, we proposed multiple-addition intermediates for the radical reactions of fluoranthene[21,22] and naphthalene[23] with NO_2 on the basis of changes in product distributions as function of solvent, temperature, and selected added species. The intermediates in these reactions are unstable and rapidly lose nitrous acid to aromatize. With AN, however, a minimal aromatization energy for the central ring warrants a higher thermal stability of its addition products (*cis*- and *trans*-DDA) and supports the viability of the fluoranthene adducts. A common pattern for the reaction of these polycyclic aromatic hydrocarbons with NO_2, in the absence of acid catalysis, is now apparent.

Toxicological Implications. *cis*- and *trans*-DDA are expected to be formed as the result of the gas-phase reaction of AN with NO_2 in polluted tropospheric air. The presence of *cis*- and *trans*-DDA in polluted air samples has not been demonstrated, but their concentrations must be low because of their thermal lability and their lability to bases and nucleophiles. Interestingly, 9NA and AQ, the expected decomposition products of DDA, are important atmospheric pollutants.[38]

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Supplementary Material Available: Tables of bond distances, bond angles, coordinates for hydrogen atoms, anisotropic thermal parameters, and $^{13}C-^{1}H$ 2D NMR correlations for *cis*- and *trans*-DDA (12 pages); structure factor amplitudes for *cis*- and *trans*-DDA (14 pages). Ordering information is given on any current masthead page.

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(31) Whether the reaction consists of a "true" fast formation followed by a slow decay, or vice versa, depends on the magnitude of the absorption coefficient of the intermediate. In fact, the rates of the two kinetic phases of the reaction can be interchanged, providing a second mathematical solution to the problem. Thus, we are at this point unable to tell which phase has some contribution from the undissociated NO_2 (N_2O_4). For further details, see: Alcock, N. W.; Benton, D. J.; Moore, P. *Trans. Faraday Soc.* **1970**, *66*, 2210–2213.

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(34) One of the reviewers offered an alternative explanation to the lack of stereoselectivity on the nitration of anthracene with NO_2, suggesting that the nitro group may be sufficiently small for the diffusion encounter to be rather nonselective.

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