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Reaction of Dinitrogen Pentoxide with Fluoranthene

Barbara Zielinska,* Janet Arey, Roger Atkinson, Thomas Ramdahl, Arthur M. Winer, and James N. Pitts, Jr.

Contribution from the Statewide Air Pollution Research Center, University of California, Riverside, California 92521. *Received December 26, 1985*

Abstract: The products and mechanisms of the reactions of dinitrogen pentoxide (N_2O_5) with fluoranthene (FL) in aprotic solvents have been investigated. The influence of solvent polarity and temperature and the effects of addition of HNO_3 on the resulting nitrofluoranthene (NFL) isomer distributions have been studied. These data are compared with the NFL isomer distributions resulting from the reactions of FL with N_2O_5 and other nitrating agents in the gas and adsorbed phases. In the gas phase and in CCl_4 solution at ambient temperature, 2-NFL is the only mononitro isomer formed from the reaction of FL with N_2O_5. However, in more polar solvents (CH_3CN and CH_3NO_2) and in CCl_4 at subambient temperature (−15 °C), as well as with FL in the adsorbed state, reaction with N_2O_5 produces only the 3-, 8-, 7-, and 1-NFL isomers. A homolytic mechanism for the formation of the 2-NFL isomer is postulated.

Dinitrogen pentoxide (N_2O_5), a volatile white solid, is known to react violently with many organic compounds.[1] In its solid state N_2O_5 has the ionic structure $[NO_2^+NO_3^-]$,[2] while in the gas phase it exists as a covalent molecule consisting of two NO_2 groups joined to a fifth oxygen atom by noncollinear bonds.[3] N_2O_5 is completely ionized in nitric or sulfuric acid solution but exists in the covalent state in aprotic solvents such as CCl_4, $CHCl_3$, or CH_3NO_2.[4] Furthermore, it has been shown that in certain nitrating systems, such as benzoyl nitrate ($BzONO_2$) or concentrated nitric acid in acetic anhydride (with an excess of nitric acid over acetic anhydride), N_2O_5 is formed as a reactive intermediate.[4]

The nitration of halogen- and carboxyl-substituted benzenes by N_2O_5 in CCl_4 solution was first studied in detail by Ingold and co-workers.[5] They concluded that two reaction mechanisms occur: (a) an autocatalyzed reaction in which nitric acid produced during the nitration reaction by N_2O_5 causes heterolysis of N_2O_5 to nitronium (NO_2^+) and nitrate (NO_3^-) ions, and (b) a noncatalyzed reaction in which N_2O_5 in its covalent form is the reactive species.[5]

In the gas phase, covalent N_2O_5 exists in equilibrium with the gaseous NO_3 radical and NO_2 (eq 1). It has been shown that

$$N_2O_5 \rightleftarrows NO_3 + NO_2 \qquad (1)$$

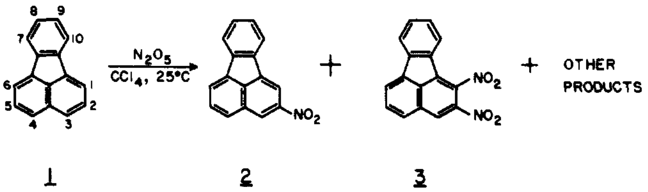
NO_3 radicals, and not N_2O_5, react at room temperature in the gas phase with many simple organic molecules such as alkenes,[6,7] monocyclic aromatic hydrocarbons,[7,8] and methoxy- and hydroxy-substituted aromatics.[8,9] However, we have recently observed that volatile polycyclic aromatic hydrocarbons (PAH) such as naphthalene[10] and fluoranthene[11,12] react in the gas phase with N_2O_5 (but not with NO_3 radicals[10-12]) to form products which include their nitro derivatives. We have also studied the nitration of pyrene, fluoranthene, benzo[a]pyrene, and benz[*a*]anthracene deposited on glass fiber (GF) and Teflon-impregnated glass fiber (TIGF) filters[13,14] by gaseous N_2O_5. Interestingly, different nitrofluoranthene isomers were formed in the reaction of gaseous N_2O_5 with the nonalternant hydrocarbon fluoranthene (FL) in its gaseous and adsorbed states.[11,12,14]

We present here the results of investigations of the reaction of FL with N_2O_5 in solution and compare the products (shown in Schemes I–IV) and nitro isomer distributions with our recent data obtained from reactions of fluoranthene in the gaseous and adsorbed states with gaseous N_2O_5.[11,12,14]

Results

Reactions of N_2O_5 with FL in CCl_4 Solution at 25 °C. Scheme I shows the mono- and dinitrofluoranthene (NFL) derivatives produced from the reaction of FL (1) with N_2O_5 in CCl_4 solution at ambient temperature (25 °C). In contrast to the electrophilic nitrations of FL by the NO_2^+ ion[15] or by NO_2/N_2O_4 in CH_2Cl_2 solution,[16] which have been shown to produce, in order of decreasing yield, the 3-, 8-, 7-, and 1-NFL isomers, the nitration by N_2O_5 in CCl_4 solution at 25 °C yields 2-NFL (**2**) as the sole mononitrofluoranthene isomer. This isomer has not been detected in the nitration reactions of FL mentioned above,[15,16] and its synthesis from 3-aminofluoranthene requires several steps.[17] Additionally, the reaction of FL with N_2O_5 in CCl_4 solution forms only a single dinitrofluoranthene (DNFL) isomer, identified[18] as 1,2-DNFL (**3**).

Scheme I



Other products identified from this reaction include traces of 2-hydroxyfluoranthene[19] (**12**, 2-HFL, Scheme IV), 10b-nitrato-

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[18] The structure of this isomer was deduced from ^1H NMR data, using double-resonance techniques. The positions of the nitro groups were established on the basis of an NOE experiment: irradiation of the singlet at 8.68 ppm caused nuclear Overhauser enhancement of the C_4H doublet, which demonstrates that the proton giving rise to the singlet was the C_3H.

[19] 2-HFL was identified in the reaction mixtures by utilizing GC/MS and comparing its retention time and mass spectrum with those of the five possible HFL isomers (1-, 2-, 3-, 7-, and 8-).

* Author to whom correspondence should be addressed.

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Table I. Yields of 2-NFL, 1,2-DNFL, and Unreacted FL in the Reaction of FL with N_2O_5 in CCl_4 Solution at 25 °C

[FL]/[N_2O_5] molar ratio	unreacted FL, %	2-NFL, %	1,2-DNFL, %	[2-NFL]/ [1,2-DNFL]	total quantified,[a] %
10	94	4	1	4	99
5	87	9	3	3	99
3.3	72	13	5	2.6	90
2	44	24	10	2.4	78
1.4	26	26	16	1.6	68
1	14	30	17	1.8	61

[a] Polar products were not quantified.

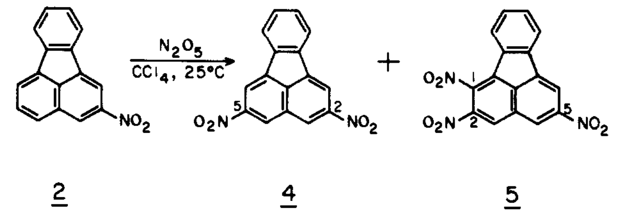
Table II. Yield of 2-NFL, 1,2-DNFL, and Unreacted FL from the Reaction of FL with N_2O_5 ([FL]/[N_2O_5] Molar Ratio = 2) in CCl_4 Solution at Different Temperatures

temp, °C	FL, unreacted, %	2-NFL, %	1,2-DNFL, %
25	52	20	10
0	66	~10	6
−15	82	traces	<1

Table III. Effect of HNO_3 Addition on the Yields of 2-NFL and 1,2-DNFL in the Reaction of FL with N_2O_5 in CCl_4 Solution at 25 °C

[HNO_3]/[N_2O_5] molar ratio	unreacted FL, %	2-NFL, %	1,2-DNFL, %	[2-NFL]/ [1,2-DNFL]
1	63	16	7	2.3
4	74	8	9	0.9
10	70	6	12	0.5

Scheme II



1-nitro-1,2,3,10b-tetrahydrofluoranthene 2,3-oxide[20] (**10**, Scheme IV) and 2-hydroxy-1-nitrofluoranthene[21] (**11**, 2,1-HNFL, Scheme IV). Three other unidentified HNFL isomers and fluoranthenequinone(s) were observed when relatively high amounts of N_2O_5 were employed ([FL]/[N_2O_5] < 2) or when the reaction mixture was allowed to stand for several hours before analysis. Traces of fluoranthene oxide[22] (presumably 2,3-oxide **9**, Scheme IV) were also identified by gas chromatographic/mass spectrometric (GC/MS) analyses in those reaction mixtures for which the molar ratio of [FL]/[N_2O_5] was >3.

The yields of these products varied with the molar ratio of FL to N_2O_5 used in the reaction mixture. The percentage yields of 2-NFL and 1,2-DNFL and the percentage of unreacted FL [as determined by high-performance liquid chromatography (HPLC) quantification] obtained from the reaction of FL with different amounts of N_2O_5 are presented in Table I. These reactions were carried out within a 12-h period using the same preparation of N_2O_5 dissolved in CCl_4 with HPLC quantification following each reaction. Slight variations (≤10%) were observed in the yields of nitration when the reactions with N_2O_5 were repeated at different times using different preparations of N_2O_5. This effect is attributed to differences in the N_2O_5 purity and to the slow decomposition of N_2O_5 in CCl_4 solution (these solutions slowly turn yellow with time).

From the experimental data presented in Table I it is apparent that the molar ratio of [2-NFL]/[1,2-DNFL] decreases when the N_2O_5 concentration is increased, suggesting that 1,2-DNFL is not formed in a direct reaction of FL with a single molecule of N_2O_5. In addition to 2-NFL and 1,2-DNFL, several di- and trinitrofluoranthene isomers, as well as dinitrohydroxyfluoranthene(s), were observed by GC/MS or MS (probe) in those reactions in which N_2O_5 was in excess of FL. Polar products including compound **10** and HNFL and fluoranthenequinone isomers were also formed in increasingly larger yields as the N_2O_5 concentrations increased, consistent with the percentage of unquantified products (Table I). With the exception of 2,1-HNFL, the remaining mono- and dinitrohydroxyfluoranthene isomers were not identified due to difficulties in isolating these products in pure form, and 10b-nitrato-1-nitro-1,2,3,10b-tetrahydrofluoranthene 2,3-oxide (**10**) was not quantified due to its instability.

Temperature Effects on the Reaction of FL with N_2O_5 in CCl_4 Solution. Figure 1 shows the GC/MS total ion chromatograms (TIC) of the products obtained from the reaction of FL with N_2O_5 in CCl_4 solution, at a molar ratio of [FL]/[N_2O_5] = 2, at three temperatures: 25 °C (Figure 1A), 0 °C (Figure 1B), and −15 °C (Figure 1C). The amounts of unreacted FL and the yields of 2-NFL and 1,2-DNFL formed are given in Table II. It can be seen from this table that the amounts of FL reacted decreased from 48% at 25 °C to 18% at −15 °C. As evident from the products identified in Figure 1, the distribution of mononitro isomers changed dramatically with temperature. Only 2-NFL was produced at 25 °C, all five possible NFL isomers were formed at 0 °C, and a mixture of 1-, 3-, 7-, and 8-NFL (with only traces of 2-NFL) was observed at −15 °C. This decrease in the 2-NFL isomer yield was also accompanied by a substantial decrease in the amount of 1,2-DNFL formed. Thus only traces of 1,2-DNFL and polar products were detected from the FL and N_2O_5 reaction mixture at −15 °C.

Solvent Effect. When CCl_4 was replaced with the more polar solvents acetonitrile or nitromethane, the major nitrofluoranthene isomers formed were 1-, 3-, 7-, and 8-NFL, together with traces of 2-NFL. The 1-, 3-, 7-, and 8-NFL isomer distributions were identical with those shown in Figure 1C (CCl_4 solution, −15 °C) for a similar [FL]/[N_2O_5] molar ratio of 2. The amount of reacted FL decreased to ~7–8% in contrast to the ~50% reaction observed in CCl_4 solution for the same [FL]/[N_2O_5] molar ratio. Furthermore, hydroxyfluoranthene and HNFL isomers were not observed as secondary products in these polar solvents.

Effect of HNO_3 Addition. Figure 2 shows the GC/MS TIC of the products resulting from the reaction of FL with N_2O_5 ([FL]/[N_2O_5] = 2) in CCl_4 solution at 25 °C with varying amounts of added HNO_3. The molar ratios of [HNO_3]/[N_2O_5] were equal to 1 (Figure 2A), 4 (Figure 2B), and 10 (Figure 2C). The percentages of unreacted FL, together with the yields of 2–NFL and 1,2-DNFL formed in these reactions, are tabulated in Table III. It can be seen from Figure 2 that the yields of 1-, 3-, 7-, and 8-NFL, relative to that of 2-NFL, increased as the

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(20) 10b-Nitrato-1-nitro-1,2,3,10b-tetrahydrofluoranthene 2,3-oxide (**10**) was identified by ^1H NMR using a double-resonance technique and by MS (probe). This compound is unstable; purification by open column chromatography or by crystallization leads to its partial decomposition. It also decomposes when stored in polar solvents (e.g., methanol or acetone), giving 2,1-HNFL as a major product.

(21) The structure of 2,1-HNFL was deduced from ^1H NMR data using a double-resonance technique. The positions of the HO and NO_2 groups were established by an NOE experiment: irradiation of the singlet at 7.48 ppm caused nuclear Overhauser enhancement of the C_4H doublet, which demonstrated that the proton giving rise to the singlet was C_3H.

(22) This compound has a shorter retention time than those of the five possible HFL isomers, and its mass spectrum shows an *m/z* 202 peak corresponding to an $[M - O]^+$ fragment ion.

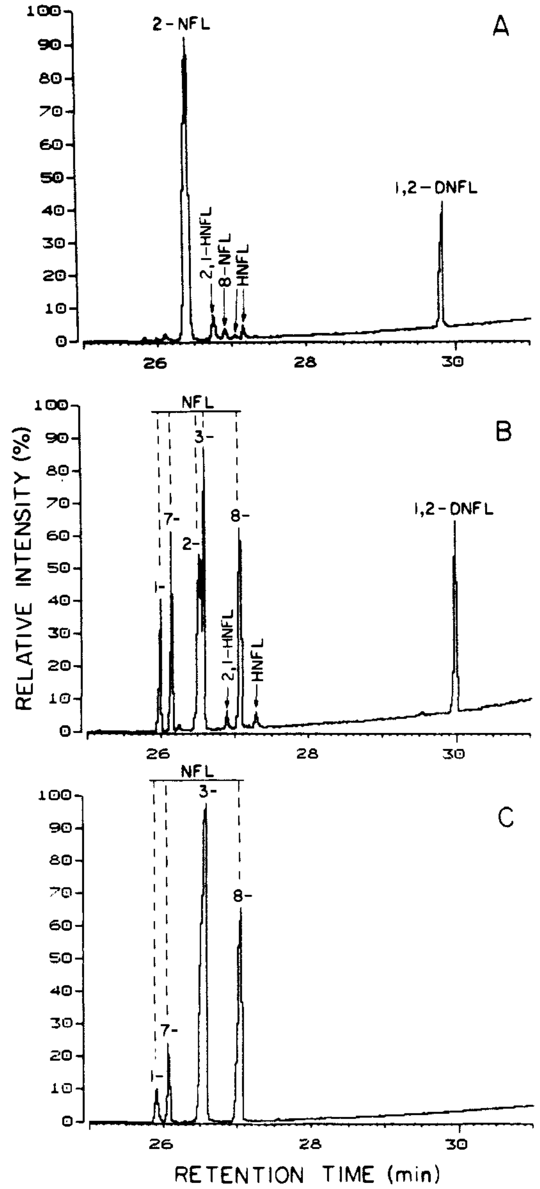
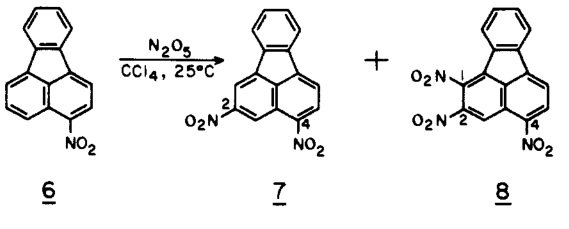


Figure 1. Effect of temperature on the product distributions resulting from the reaction of FL with N_2O_5 with $[FL]/[N_2O_5] = 2$ in CCl_4: (A) 25 °C, (B) 0 °C, (C) -15 °C. Shown are GC/MS total ion chromatograms. Column: 60-m DB-5, injection at 50 °C followed by temperature programming at 8 °C min^{-1} to 320 °C. See Table II for quantification of products.

Scheme III



HNO_3 concentration was increased. Simultaneously, the [2-NFL]/[1,2-DNFL] ratio decreased from 2.3 to 0.5 (Table III).

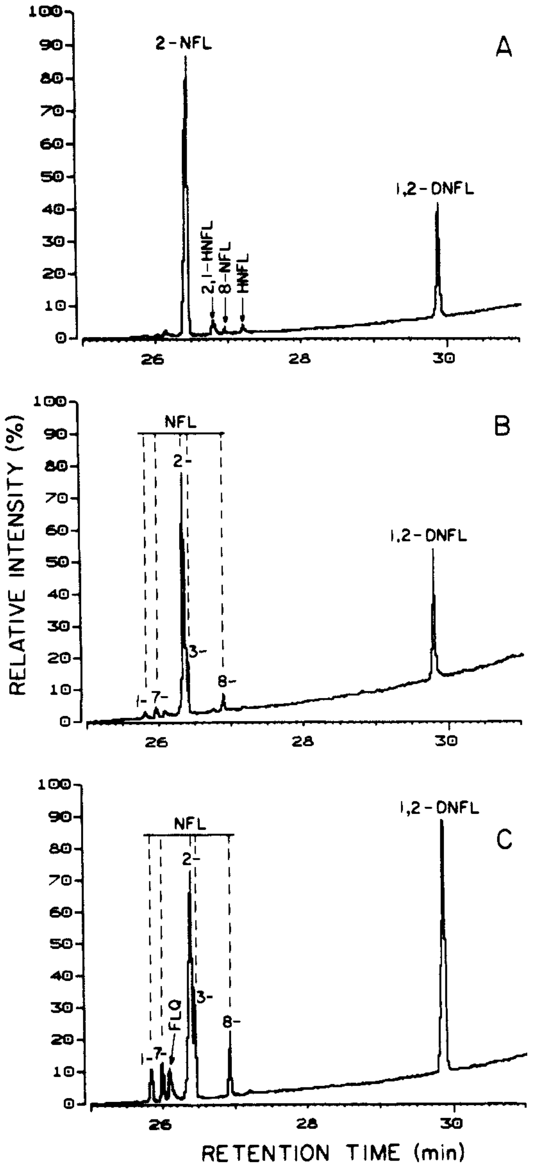


Figure 2. Effect of added HNO_3 on the product distributions resulting from the reaction of FL with N_2O_5 with $[FL]/[N_2O_5] = 2$ in CCl_4 at 25 °C: (A) $[HNO_3]/[N_2O_5] = 1$, (B) $[HNO_3]/[N_2O_5] = 4$, (C) $[HNO_3]/[N_2O_5] = 10$. Shown are GC/MS total ion chromatograms (FLQ, fluoranthenequinone). The column and conditions are as given in Figure 1. See Table III for quantification of products.

Reactions of 2-NFL and 3-NFL with N_2O_5 in CCl_4 Solution at Ambient Temperature. The nitration of 2-NFL (**2**) and 3-NFL (**6**) by N_2O_5 in CCl_4 solution at 25 °C each produced only a single DNFL and trinitrofluoranthene (TNFL) isomer, identified on the basis of their ^1H NMR spectra using double-resonance techniques. 2-Nitrofluoranthene produced 2,5-DNFL (**4**) and 1,2,5-TNFL (**5**) (Scheme II), while 3-NFL gave 2,4-DNFL (**7**) and 1,2,4-TNFL (**8**) (Scheme III). A nitrofluoranthene oxide (presumably 5-nitrofluoranthene 2,3-oxide)[23] was also tentatively identified as a product from the reaction of 2-NFL with N_2O_5.

Reactions of FL with Benzoyl Nitrate in CCl_4 and CH_3CN Solutions. Figure 3 shows a GC/MS mass chromatogram of the mononitro isomers resulting from the reaction of FL with $BzONO_2$ in CCl_4 solution at 0 °C. Analogous to the reaction of N_2O_5 with FL in CCl_4 solution at 0 °C, all five NFL isomers were produced in similar abundance. The NFL isomer distribution from the reaction of $BzONO_2$ in CH_3CN solution was similar to that obtained from the N_2O_5 reaction with FL in CH_3CN and with that from the N_2O_5 reaction with FL in CCl_4 at -15 °C (see Figure 1C); namely 3- > 8- ≫ 7- > 1-NFL. For reaction with $BzONO_2$, data could not be obtained at ambient temperature (25 °C) due to its decomposition.

Reactions of FL in a 6400-L All-Teflon Environmental Chamber. Figure 4 gives the GC/MS mass chromatograms of the *m/z* 247 molecular ion for NFL, showing the isomer distributions resulting from the exposure of FL adsorbed on filters and in the gas phase

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[23] This compound was tentatively identified on the basis of its mass spectrum, which shows a pronounced *m/z* 247 peak corresponding to an $[M - O]^+$ fragment ion. By analogy with the products formed in the reaction of FL with N_2O_5, the structure 5-nitrofluoranthene 2,3-oxide is proposed.

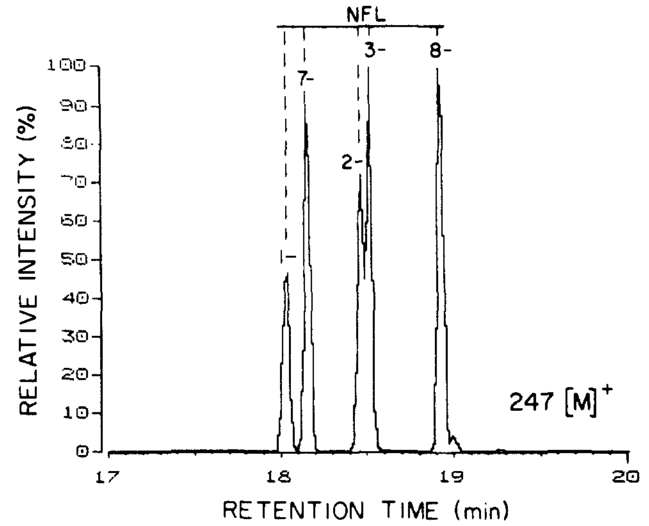

Figure 3. Nitrofluoranthene isomer distribution obtained from the reaction of FL with $BzONO_2$ in CCl_4 at 0 °C. The mass chromatogram of the *m/z* 247 molecular ion is presented. Column: 45-m DB-5, injection at 90 °C, programmed at 10 °C min^{-1} to 320 °C.

to 5 parts per million (ppm) N_2O_5 in air in a 6400-L all-Teflon environmental chamber.[11,12] Reaction of gaseous N_2O_5 with fluoranthene adsorbed on glass fiber filters yielded the 1-, 3-, 7-, and 8-NFL isomers (Figure 4A). However, the sole product of the gas-phase reaction between FL and N_2O_5 was 2-NFL (Figure 4B). Control exposures of gaseous FL to a mixture of NO_2 (10 ppm) + HNO_3 (1 ppm) and to N_2O_5 (5 ppm) with 10 ppm of added NO_2 showed that neither the NO_2/HNO_3 present in the N_2O_5 exposures nor the NO_3 radical present in equilibrium with N_2O_5 was the nitrating species.[11,12]

Discussion

Experimental data[15] and theoretical calculations[15,24,25] concerning the reactivity of FL all agree that the most reactive site for electrophilic substitution reactions of this nonalternant hydrocarbon is the 3-position, with the least reactive site being at the 2-position. However, there is some disagreement between the theoretical calculations and the experimental data concerning the order of the reactivity of the remaining positions, since the experimental data indicate a reactivity order of 3- > 8- > 7- > 1-isomer, whereas the MO calculations, using cation localization energy L^+ values,[15] yield a reactivity order of 3- > 7- > 8- > 1- > 2-isomer. Thus, the 2-NFL isomer has not been detected in nitration of FL by HNO_3 in CH_3COOH[15] or by NO_2/N_2O_4 in CH_2Cl_2.[16] It has recently been reported,[26] however, that small amounts of 2-NFL along with the 1-, 3-, 7-, and 8-isomers are produced in the nitration of FL by concentrated nitric acid in acetic anhydride.

Our data show that 2-NFL is the only mononitro isomer formed in the reactions of FL with N_2O_5 both in CCl_4 solution at 25 °C (Figure 1A) and in the gas phase (Figure 4B). In contrast, the 1-, 3-, 7-, and 8-NFL isomers are produced (a) in the reaction of gaseous N_2O_5 with FL adsorbed on filters[11,14] (Figure 4A), (b) in the solution-phase reactions of FL with N_2O_5 in CCl_4 when the temperature is lowered to −15 °C (Figure 1C), and (c) when a more polar solvent (for example, CH_3CN or CH_3NO_2) is substituted for CCl_4. However, in general the 1-, 3-, 7-, and 8-NFL isomer distributions from the adsorbed and solution state reactions were not identical.

Clearly, at least two different mechanisms of N_2O_5 reaction with FL must exist. This is consistent with the results of Ingold and co-workers who described two different mechanisms for nitration of aromatics by N_2O_5 in aprotic solvents:[5] (a) an "autocatalyzed" reaction in which the NO_2^+ ion arising from the ionizing action of HNO_3 produced during the reaction is the nitrating species, and (b) a "noncatalyzed" reaction mechanism in which the covalent N_2O_5 molecule acts as an electrophile. For a sufficiently low concentration of the reactant species, the noncatalyzed mechanism should be operative in CCl_4 solution at room temperature. However, the formation of the 2-NFL isomer in CCl_4 solution at room temperature and in the gas phase cannot be explained by electrophilic nitration of FL by the covalent N_2O_5 molecule since the available evidence suggests that the expected products would be the 3-, 8-, 7-, and 1-NFL isomers.[15,24,25]

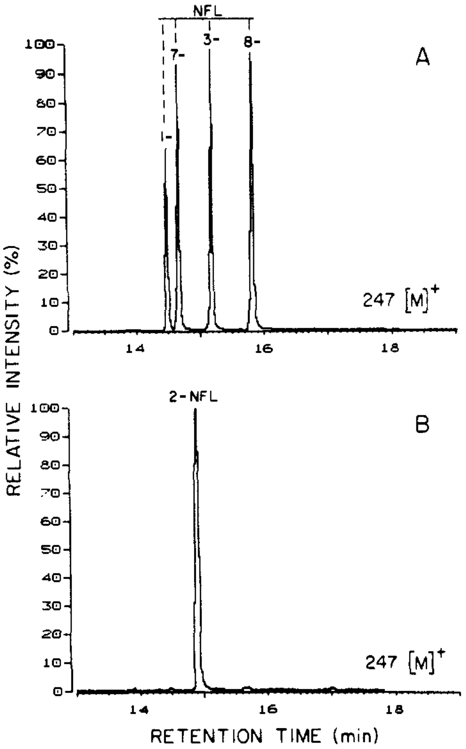

Figure 4. Nitrofluoranthene isomer distribution obtained from (A) the reaction of FL adsorbed on TIGF filters with 5 ppm N_2O_5 and (B) the reaction of gaseous FL with 5 ppm N_2O_5. The mass chromatogram of the *m/z* 247 molecular ion is presented. Column: 30-m DB-5, injection at 50 °C, programmed at 20 °C min^{-1} to 200 °C followed by 4 °C min^{-1}.

Another possibility for reaction of fluoranthene with covalent N_2O_5 involves the attack of the N_2O_5 molecule at the 2,3-bond, which has been shown to have the highest double bond character in the FL molecule.[24] Thus the production of nitro–nitrato derivatives from the reaction of N_2O_5 with alkenes in aprotic solution has been interpreted as an addition of molecular N_2O_5 to a double bond.[27] However, an analogous reaction of N_2O_5 with FL would be expected to yield 3-NFL (or at least a mixture of 2- and 3-NFL) since the attachment of the nitrate ester group (which would subsequently become a leaving group) would be expected to occur at the 2-position of FL which has the highest cation localization energy.[15]

There are a variety of products in addition to 2-NFL observed from the reaction of FL with N_2O_5 in CCl_4 solution at 25 °C, including 2-HFL (**12**), 2,1-HNFL (**11**), fluoranthene oxide (**9**), compound **10**, and 1,2-DNFL (**3**) (always the second most abundant product under our conditions). We believe that the formation of these products, as well as the formation of 2-NFL, can best be explained by the radical mechanism outlined in Scheme IV.

Nitration of saturated hydrocarbons by N_2O_5 in CCl_4 solution has been shown to occur via a homolytic process initiated by NO_3 radical attack.[28] In the gas phase N_2O_5 is in equilibrium with the NO_3 radical and NO_2[29] (eq 1). Kinetic studies have shown

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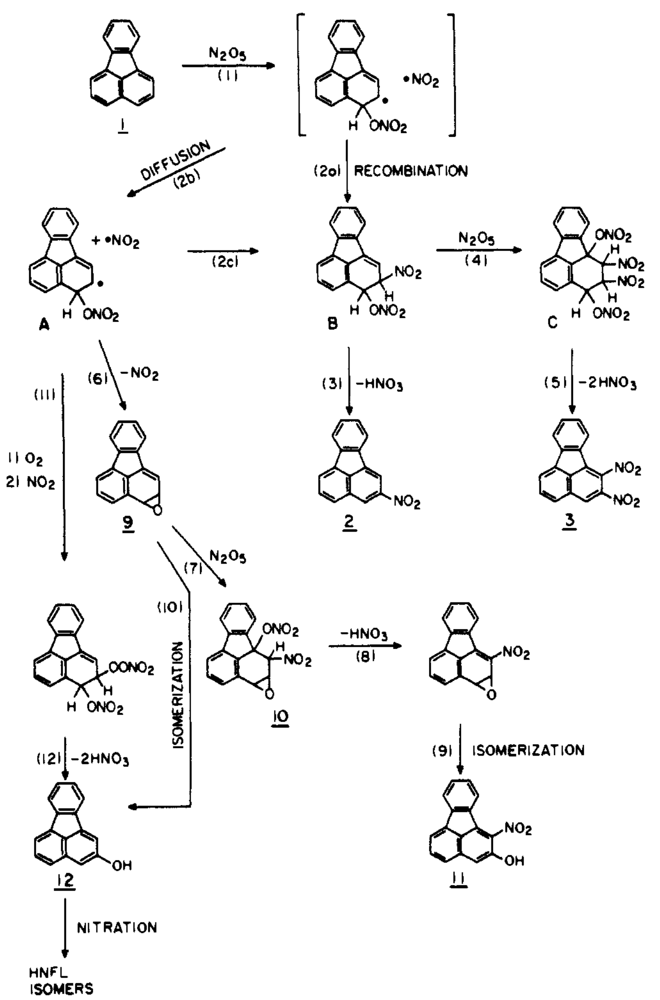
Scheme IV



that for naphthalene, N_2O_5, and not the NO_3 radical, is responsible for its gas-phase reaction.[10] Similarly, when gaseous FL was exposed to a mixture of 5 ppm N_2O_5 and 10 ppm NO_2 (to drive the equilibrium between N_2O_5, NO_2, and NO_3 radicals toward N_2O_5), the 2-NFL yield was higher than from the exposure of FL to 5 ppm N_2O_5 alone.[30] These data can be interpreted in terms of direct reaction of N_2O_5 with FL occurring by molecule-assisted homolysis[31,32] wherein the homolysis of N_2O_5 is assisted by bond formation with the FL molecule. The 2-NFL yield should thus be independent of the NO_3 radical concentration but may be enhanced by a higher NO_2 concentration, as observed.

It must be kept in mind, however, that in our gas-phase studies, as in ambient polluted atmospheres, the equilibrium (1) is shifted far to the left.[10] Therefore, if a rapid direct reaction of FL with N_2O_5 occurs in the gas phase, a competing reaction by the NO_3 radical followed by addition of NO_2 will not be distinguishable unless the NO_3 radical reaction is at least 10^3 times faster than the N_2O_5 reaction.

While no experimental data concerning the reactivity of FL toward homolytic substitution reactions are available, theoretical calculations predict[24] that the 3-position of FL (as assumed in Scheme IV) will be most reactive. The mechanism outlined in Scheme IV may be operative in both the gas phase and in CCl_4 solution at 25 °C, although the importance of pathways 2–12 will be different in the two phases. The only identified gas-phase reaction product of FL with N_2O_5 is 2-NFL,[11,12] but due to difficulties in sampling gas-phase reaction products, the presence of other products cannot be ruled out at this time.

In Scheme IV, the initially formed radical pair can undergo recombination within the solvent cage (solution phase, step 2a) or dissociation leading to the free radical A (gas phase and solution phase, step 2b). Cage recombination and addition of NO_2 to species A (step 2c) produces 3-nitrato-2-nitro-2,3-dihydrofluoranthene (B). Interestingly, it has been reported that the reaction of phenanthrene with N_2O_5 in benzene produces a nitro–nitrato product.[33] Compound B should be unstable and can either eliminate HNO_3 forming 2-NFL (path 3), or react further with a second molecule of N_2O_5 (covalent in the gas phase or possibly either covalent or ionized in the solution phase), forming 1,2-DNFL (pathways 4 and 5). In CCl_4 solution, the molar ratio of [2-NFL]/[1,2-DNFL] decreases with increasing N_2O_5 (see Table I) as expected if the 1,2-DNFL formation is second order with N_2O_5.

The radical species A may also eliminate NO_2, forming fluoranthene 2,3-oxide (**9**) (step 6), or may react further with O_2 followed by NO_2 (step 11), leading to 2-HFL (**12**). 2-Hydroxyfluoranthene (**12**) could also be produced from the isomerization of fluoranthene 2,3-oxide (step 10), although it is not clear if 3-HFL or 2-HFL would be preferentially formed from epoxide ring opening.[34,35] Fluoranthene 2,3-oxide (**9**) may also react with N_2O_5 (step 7), leading to 10b-nitrato-1-nitro-1,2,3,10b-tetrahydrofluoranthene 2,3-oxide (**10**). This compound has been isolated from the reaction mixture but is labile.[20] Compound **10** may eliminate HNO_3 (step 8), forming 1-nitrofluoranthene 2,3-oxide, which in turn could undergo isomerization (step 9) to 2,1-HNFL (**11**) (the formation of 3,1-HNFL would be rather unlikely due to the lower stability of the intermediate carbonium ion). The decomposition of compound **10** could occur either in the reaction mixture or during the work-up procedure or both.

Products **2**, **3**, **10**, **11**, and **12** were identified in this study; additional products formed in this reaction, including HNFL isomers other than **11** and fluoranthenequinone isomers, were observed when the amount of N_2O_5 was relatively high ([FL]/[N_2O_5] ratio <2) or when the reaction mixture was left for several hours before analysis. These compounds were possibly formed by further nitration of 2-HFL (**12**) by HNO_3 and subsequent decomposition of these unstable HNFL isomers to quinones.

In addition, the occurrence of a radical mechanism for the reaction of N_2O_5 with FL in CCl_4 solution at 25 °C is supported by the observation that nitro products analogous to those produced from FL are formed from the reaction of 2- and 3-NFL with N_2O_5 under similar conditions (Schemes II and III). This is consistent with the known relative insensitivity of radical reactions to the presence of substituent groups (in this case, 2- or 3-nitro substituents) in the aromatic molecule.[31] Additionally, the identification[23] of a nitrofluoranthene oxide (presumably 5-nitrofluoranthene 2,3-oxide) from the reaction of 2-NFL with N_2O_5 in CCl_4 solution supports the mechanism outlined in Scheme IV.

In contrast to the formation of 2-NFL, the 3-, 8-, 7-, and 1-NFL isomers are most likely produced by an ionic electrophilic nitration mechanism (by the NO_2^+ ion arising from the heterolysis of N_2O_5), which competes with the radical mechanism. Our results suggest that more polar solvents such as CH_3CN or CH_3NO_2 suppress the radical mechanism and/or promote this ionic mechanism. The addition of HNO_3 to the FL/N_2O_5 reaction mixture in CCl_4 increases the importance of the ionic mechanism, probably by promoting the ionization of N_2O_5. That the formation of 1,2-DNFL from intermediate product B can occur via reaction with the nitronium ion, as well as with N_2O_5, is suggested by the increased yield of 1,2-DNFL with the addition of HNO_3. Further, it has been shown[36] that an analogue of B, 2,3-dihydrofluoran-

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(30) We previously reported[11] similar yields of 2-NFL in exposures of FL to N_2O_5 and N_2O_5 + NO_2. From recent exposures designed to eliminate artifacts due to wall desorption processes, we observe that the yield of 2-NFL is greater in the N_2O_5 + NO_2 exposures than in the exposures to N_2O_5 alone.

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(32) Pryor, W. A. *Organic Free Radicals*: American Chemical Society: Washington, DC, 1978; p 33.

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(34) Keller, J. W.; Heidelelberger, C. *J. Am. Chem. Soc.* **1976**, *98*, 2328–2336.

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thene, reacts readily with electrophiles, giving 1-substituted derivatives.

As seen from Figure 1, temperature has a pronounced effect on the mechanism of this reaction, with low temperature favoring the ionic reaction mechanism. Thus at 0 °C, all five possible NFL isomers are formed in similar amounts, while at −15 °C only the four (3- > 8- > 7- > 1-) NFL isomers are formed.

The formation of 1-, 3-, 7-, and 8-NFL isomers from the reaction of FL adsorbed on filters with gaseous N_2O_5[11,12,14] also indicates that the mechanism of this reaction is ionic. It is interesting to note that the abundance of the four NFL isomers in this reaction with N_2O_5 (Figure 4A) is more nearly equal than those obtained in most electrophilic nitration reactions of FL (e.g., with NO_2^+ ions). A similar distribution of these four isomers was obtained from the reaction of N_2O_5 with FL in CCl_4 at 0 °C (overlooking for the moment the presence of 2-NFL). We may speculate that N_2O_5 becomes ionized on the filter surface prior to the reaction with FL but that the resulting NO_2^+ ion is not the "free" nitronium ion. Similarly, in CCl_4 solution at 0 °C, the N_2O_5 may be partially ionized but not completely dissociated.

Finally, in the reaction of $BzONO_2$ with FL the same nitro products were formed as in the reaction of N_2O_5 with FL carried out under the same conditions, providing strong evidence that N_2O_5 is indeed the nitrating species in the $BzONO_2$ system.[4]

The mechanisms proposed for the reaction of N_2O_5 with FL explain the formation of the observed NFL isomers under the different conditions examined. Detailed proof of these mechanisms requires additional experimental data, particularly kinetic data, and further work is in progress in this laboratory to furnish some of these data.

Finally, it should be noted that the reaction of N_2O_5 with FL may be of environmental significance. Thus 2-nitrofluoranthene, which has not been identified as being emitted from combustion sources,[37,38] is the major NFL isomer found in ambient air and its concentration is relatively high in comparison with those reported for other nitrated polycyclic aromatic hydrocarbons.[11,37]

Experimental Section

Reagents and Reaction Conditions. Fluoranthene standard grade, Aldrich Chemical Co. (98% purity level), was used as received. CCl_4 (Spectra AR, Mallincrodt) was stored over a 5-Å molecular sieve prior to use. N_2O_5 was prepared from the reaction of NO_2 with O_3, with collection of the product at −77 °C.[7] 3-Nitrofluoranthene was synthesized by nitration of FL with concentrated nitric acid in glacial acetic acid, as described in the literature.[17] Hydroxynitrofluoranthene isomers were obtained from Dr. Joseph E. Rice of Naylor Dana Institute for Disease Prevention (Valhalla, NY). All experiments were carried out in a drybox under an atmosphere of N_2 and in yellow light to prevent photodecomposition of N_2O_5. The solutions of N_2O_5 in CCl_4 were prepared by differential weighing and stored in liquid N_2 prior to use. Typically, the N_2O_5 concentration ranged from 5 to 10 mg mL^{-1}.

Instrumentation. The ^1H NMR spectra were recorded with a Nicolet 300 pulsed Fourier transform NMR spectrometer. Mass spectra were recorded by using a Finnigan 3200 gas chromatograph/mass spectrometer (GC/MS). The mass spectrometer was operated in the electron impact mode and fitted with a cool on-column injector. Several DB-5 capillary columns of different lengths were used, each directly eluting into the ion source. A Spectra-Physics Model 8100 high-performance liquid chromatograph (HPLC) equipped with a Model 8400 UV detector Model 4100 computing integrator and a 250- x 10-mm Ultrasphere Si column (Altex) was employed for product quantification (90% *n*-hexane, 10% CH_2Cl_2 for 5 min, and then a linear gradient to 60% *n*-hexane, 40% CH_2Cl_2 over 10 min). UV spectra were recorded on a Cary 219 UV/vis spectrophotometer. All melting points are uncorrected.

Reactions of Fluoranthene with N_2O_5 in CCl_4 at 25 °C. Six sets of experiments were performed with molar ratios of $[FL]/[N_2O_5]$ ranging from 10 to 1 (Table I). The general procedure was as outlined below: To a solution of FL in CCl_4 (1 mg mL^{-1}), a suitable amount of N_2O_5 solution in CCl_4 (5.4 mg mL^{-1}) was added during ~30 s with stirring at room temperature. Stirring was continued for an additional ~5 min, and the reaction mixture was analyzed by GC/MS (for product identification) and HPLC (for quantification).

The HPLC quantifications of FL, 2-NFL, and 1,2-DNFL were carried out immediately after reaction as follows: to 1 mL of reaction mixture, a suitable amount of internal standard (triphenylbenzene) in CCl_4 solution was added. FL and its nitro derivatives were quantified on the basis of their UV absorption at 254 nm, using calibration curves relating their concentration to the (compound/internal standard) ratios previously constructed for each compound. The resulting data are given in Table I.

For preparative scale work, a 1:1 FL-to-N_2O_5 molar ratio was employed, and the reactions were carried out as described above. Mono- and dinitrofluoranthene derivatives were isolated from the reaction mixture by chromatography on silica gel 60 (Merck) by using CCl_4/CH_2Cl_2 (9:1 v/v) elution. For separation of the more polar products of this reaction, elution with benzene/acetone (15:1 v/v) was used. The following compounds were isolated and identified on the basis of their spectral data.

2-Nitrofluoranthene (2), recrystallized from ethanol, mp 154–155 °C [lit.[38] 156–157 °C); ^1H NMR ($CDCl_3$) δ 8.85 (d, 1, $J_{(1,3)}$ = 2 Hz, C_1H), 8.68 (d, 1, C_3H), 8.08 (d, 1, $J_{(5,6)}$ = 7 Hz, C_6H), 8.02–7.91 (m, 3, C_4H, C_7H, and $C_{10}H$), 7.79–7.73 (m, 1, C_5H), 7.51–7.42 (m, 2, C_8H and C_9H); MS, *m/z* (relative intensity) 247 (M^+, 67%), 217 ($[M - NO]^+$, 2%), 201 ($[M - NO_2]^+$, 100%), 200 ($[M - HNO_2]^+$, 70%), 189 ($[M - NO - CO]^+$, 36%); UV λ_{max} (EtOH) 258 nm (ϵ 39 000).

1,2-Dinitrofluoranthene (3), recrystallized from ethanol, mp 196–198 °C; ^1H NMR ($CDCl_3$) δ 8.68 (s, 1, C_3H), 8.1 (d, 1, $J_{(5,6)}$ = 7 Hz, C_6H), 7.96 (d, 1, $J_{(4,5)}$ = 8 Hz, C_4H), 7.91 (d, 1, $J_{(9,10)}$ = 7.5 Hz, $C_{10}H$), 7.87–7.81 (m, 2, C_5H and C_7H), 7.53 (t, 1, C_9H), 7.43 (t, 1, C_8H); MS, *m/z* (relative intensity) 292 (M^+, 100%), 262 ($[M - NO]^+$, 6%), 200 ($[M - 2NO_2]^+$, 86%), 188 ($[M - NO_2 - NO - CO]^+$, 63%); UV λ_{max} (EtOH) 250 nm (ϵ 33 000).

2-Hydroxy-1-nitrofluoranthene (11), purified by semipreparative HPLC on an Ultrasphere ODS column (Altex, 1- × 25-cm, 80% CH_3-OH, 20% H_2O); ^1H NMR (CD_3OD) δ 8.7 (br s, OH), 8.1 (d, 1, $J_{(9,10)}$ = 7.5 Hz, $C_{10}H$), 8.05 (d, 1, $J_{(5,6)}$ = 6.8 Hz, C_6H), 7.86 (d, 1, $J_{(4,5)}$ = 7.6 Hz, C_4H), 7.84–7.75 (m, 2, C_5H and C_7H), 7.64–7.57 (t, 1, C_9H), 7.54–7.46 (t, C_8H), 7.48 (s, C_3H); MS, *m/z* (relative intensity) 263 (M^+, 100%), 218 ($[M - HO - CO]^+$, 9%) 217 ($[M - NO_2]^+$, 6%), 205 ($[M - NO - CO]^+$, 10%), 189 ($[M - NO_2 - CO]^+$ 40%), 188 ($[M - NO_2 - HCO]^+$, 25%), 187 ($[M - NO_2 - H_2CO]^+$, 28%).

10b-Nitrato-1-nitro-1,2,3,10b-tetrahydrofluoranthene 2,3-oxide (10), purified by semipreparative HPLC on an Ultrasphere Si column (Altex, 1- × 25-cm, 40% *n*-hexane, 60% CH_2Cl_2 for 5 min and then a linear gradient to 100% CH_2Cl_2 over 5 min, 100% CH_2Cl_2 for 15 min); ^1H NMR ($CDCl_3$) δ 8.47 (d, 1, $J_{(9,10)}$ = 8 Hz, $C_{10}H$), 7.7–7.63 (m, 2, C_7H and C_6H or C_4H), 7.56–7.48 (m, 2, C_8H and C_5H), 7.43–7.35 (m, 2, C_9H and C_4H or C_6H), 6.3 (d, 1, $J_{(1,2)}$ = 2.3 Hz, C_1H), 5.4 (quartet, 1, C_2H), 3.3 (d, 1, $J_{(2,3)}$ = 4.6 Hz, C_3H), MS, *m/z* (relative intensity) 326 (M^+, 6%), 263 ($[M - HNO_3]^+$, 100%), 247 ($[M - HNO_3 - O]^+$, 4%), 234 ($[M - 2NO_2]^+$, 15%), 233 ($[M - HNO_3 - NO]^+$, 18%), 218 $[M - 2NO_2 - O]^+$, 20%), 217 ($[M - HNO_3 - NO_2]^+$, 18%), 209 ($[C_{14}H_9O_2]^+$, 40%), 205 ($[M - HNO_3 - NO - CO]^+$, 65%), 189 ($[M - HNO_3 - NO_2 - CO]^+$, 96%), 188 ($[M - HNO_3 - NO_2 - HCO]^+$, 63%), 187 ($[M - HNO_3 - NO_2 - H_2CO]^+$, 79%), 176 ($[M - HNO_3 - NO - CO - HCO]^+$, 83%).

The remaining products from the reaction of FL with N_2O_5 were identified on the basis of GC/MS and MS (probe) data as follows: *m/z* (relative intensity) for **2-hydroxyfluoranthene (12)**, 218 (M^+, 100%), 189 ($[M - HCO]^+$, 45%); for **fluoranthene oxide** (presumably 2,3-, **9**), 218 (M^+, 100%), 202 ($[M - O]^+$, 6%), 189 ($[M - HCO]^+$, 65%); for **hydroxynitrofluoranthene** (three isomers), 263 (M^+), 189 ($[M - NO_2 - CO]^+$); for **fluoranthenequinone**, 232 (M^+, 25%), 204 ($[M - CO]^+$, 81%), 176 ($[M - 2CO]^+$, 100%).

Reactions of FL with N_2O_5 in CCl_4 at 0 and −15 °C. These reactions were carried out as described above with a $[FL]/[N_2O_5]$ molar ratio of 2. The solutions of FL in CCl_4 (20 mL, 1 mg mL^{-1}) were cooled to 0 °C (ice bath) or −15 °C (ice/NaCl bath), and 0.5 mL of N_2O_5 solution in CCl_4 (10.6 mg mL^{-1}) was added.

Reactions of FL with N_2O_5 in CH_3CN and CH_3NO_2 Solutions. These reactions were carried out at ambient temperature with a $[FL]/[N_2O_5]$ molar ratio of 2. FL was dissolved in 20 mL of CH_3CN or CH_3NO_2 (1 mg mL^{-1}), and 0.5 mL of N_2O_5 in CCl_4 (10.6 mg mL^{-1}) was added.

Effect of HNO_3 Addition. Concentrated HNO_3 (70%) was added to three solutions of FL in CCl_4 (20 mL, 1 mg mL^{-1}) prior to N_2O_5 addition (0.5 mL, 10.6 mg mL^{-1}). The amounts of HNO_3 used were 3, 12.5, and 30 μL, respectively. In the control experiment, when 30 mL of HNO_3 was added to the FL solution in CCl_4 (20 mL, 1 mg mL^{-1}), no FL reaction was observed.

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Reaction of 2-NFL and 3-NFL with N_2O_5 in CCl_4. These reactions were carried out at 25 °C as described above with the following amounts of reagents used: 2-NFL, 5 mg (0.02 mmol) in 10 mL of CCl_4 and 2.2 mg of N_2O_5 (0.02 mmol) in 1 mL of CCl_4; 3-NFL, 10 mg (0.04 mmol) in 20 mL of CCl_4 and 4.4 mg of N_2O_5 (0.04 mmol) in 2 mL of CCl_4. Products from both reactions were separated by chromatgraphy on silica gel 60 with CCl_4/CH_2Cl_2 (9:1 v/v) elution. From the reaction of 2-NFL with N_2O_5 the following products were isolated (unreacted 2-NFL, 20%).

2,5-Dinitrofluoranthene (**4**, 1.5 mg, 25% yield); ^{1}H NMR ($CDCl_3$) δ 8.99 (d, 2, $J_{(4,6)}$ = 1.7 Hz, C_1H and C_6H), 8.81 (d, 2, $J_{(1,3)}$ = 1.7 Hz, C_3H and C_4H), 8.04–7.99 (m, 2, C_7H and $C_{10}H$), 7.58–7.53 (m, 2, C_8H and C_9H); MS, m/z (relative intensity) 292 (M^+, 100%), 246 ($[M - NO_2]^+$, 40%), 200 ($[M - 2NO_2]^+$, 88%).

1,2,5-Trinitrofluoranthene (**5**, 1 mg, 15% yield); ^{1}H NMR ($CDCl_3$) δ 8.88 (d, 1 , $J_{(4,6)}$ = 2 Hz, C_6H), 8.79 (d, 1, C_4H), 8.52 (s, 1, C_3H), 8.05–7.97 (m, 2, C_7H and $C_{10}H$), 7.66–7.52 (m, 2, C_8H and C_9H); MS, m/z (relative intensity) 337 (M^+, 100%), 307 ($[M - NO]^+$, 7%), 245 ($[M - 2NO_2]^+$, 17%), 199 ($[M - 3NO_2]^+$, 43%), 187 ($[M - 2NO_2 - NO - CO]^+$, 61%).

5-Nitrofluoranthene oxide (presumably 2,3-oxide) was isolated from the reaction mixture by semipreparative HPLC on an Ultrasphere Si column (55% *n*-hexane, 45% CH_2Cl_2): MS, m/z (relative intensity) 263 (M^+, 62%), 247 ($[M - O]^+$, 98%), 217 ($[M - NO_2]^+$, 33%), 201 $[M - O - NO_2]^+$, 100%), 200 ($[M - O - HNO_2]^+$, 70%), 189 ($[M - NO_2 - CO]^+$, 20%).

From the reaction of 3-NFL with N_2O_5 the following compounds were isolated (unreacted 3-NFL, 20%).

2,4-Dinitrofluoranthene (**7**, 3 mg, 30% yield); ^{1}H NMR ($CDCl_3$) δ 9.68 (d, 1, $J_{(1,3)}$ = 2 Hz, C_3H), 8.72 (d, 1, $J_{(5,6)}$ = 8.5 Hz, C_5H), 8.69 (d, 1, C_1H), 8.09 (d, 1, C_6H), 7.99–7.91 (m, 2, C_7H and $C_{10}H$), 7.58–7.48 (m, 2, C_8H and C_9H); MS, m/z (relative intensity) 292 (M^+, 100%), 262 ($[M - NO]^+$, 30%), 246 ($[M - NO_2]^+$, 15%), 200 ($[M - 2NO_2]$, 60%), 188 ($[M - NO_2 - NO - CO]^+$, 40%).

1,2,4-Trinitrofluoranthene (**8**, 2 mg, 15% yield); ^{1}H NMR ($CDCl_3$) δ 9.58 (s, 1, C_3H), 8.81 (d, 1, $J_{(5,6)}$ = 8 Hz, C_5H), 8.15 (d, 1, C_6H), 7.98 (d, 1, $J_{(9,10)}$ = 7 Hz, $C_{10}H$), 7.82 (d, 1, $J_{(7,8)}$ = 7 Hz, C_7H), 7.62–7.51 (m, 2, C_8H and C_9H); MS, m/z (relative intensity) 337 (M^+, 100%), 307 ($[M - NO]^+$, 14%), 245 ($[M - 2NO_2]^+$, 5%), 199 ($[M - 3NO_2]^+$, 36%), 198 ($[M - 3NO_2 - H]^+$, 42%), 187 ($[M - 2NO_2 - NO - CO]^+$, 86%).

Reactions of FL with Benzoyl Nitrate ($BzONO_2$) in CH_3CN and CCl_4 Solutions. The reactions were carried out according to methods described in the literature.[39] For the reaction in CH_3CN, 2 g of FL (0.01 mol), 1.9 g of $AgNO_3$ (0.01 mol), and 1.5 g of benzoyl chloride (BzOCl, 0.01 mol) were used. BzOCl, dissolved in 10 mL of CH_3CN, was added dropwise to a stirred solution of FL and $AgNO_3$ in 80 mL of CH_3CN at 0 °C.

For the reaction in CCl_4 solution, $BzONO_2$ was generated from 4.8 g of BzOCl (0.034 mol), in 10 mL of CCl_4 and 7.3 g of $AgNO_3$ (0.043 mol) at −15 °C. Immediately after filtration, 50% of the reaction product was added to a solution of FL (2 g, 0.01 mol) in 40 mL of CCl_4 at 0 °C. The $BzONO_2$ was assumed to be in excess of FL, but the $BzONO_2$ solution was not analyzed.

After 2.5 h of stirring at 0 °C, the reaction mixtures were poured onto crushed ice, and diluted sodium hydroxide was added. Thirty milliliters of benzene was also added to the CH_3CN solution. The organic layers were separated and the solvents distilled under reduced pressure. The remaining material was dissolved in CH_2Cl_2 and analyzed by GC/MS.

It was also checked in a separate reaction that the NFL isomer distribution from the reaction of FL with $BzONO_2$ in CCl_4 solution was identical when the reaction mixture was analyzed by GC/MS after 1.5 and 2.5 h of reaction, without $BzONO_2$ hydrolysis. It was concluded from HPLC quantification, which was carried out after every 30 min of reaction, that the maximum yield of FL conversion (~10%) was reached after 1.5 h and did not change after an additional 1 h of stirring.

Reaction of Gaseous N_2O_5 with FL in Gaseous and Adsorbed States. Teflon-impregnated glass fiber (TIGF) filters coated with FL were exposed in the dark for 45 min in a collapsible 6400-L all-Teflon chamber, as described elsewhere.[11-13] Three 45-min exposures were conducted with initial concentrations of 5 ppm N_2O_5, 5 ppm N_2O_5 + 10 ppm NO_2, and 10 ppm NO_2 + 1 ppm HNO_3 (control exposure). At the end of each exposure, approximately 75% of the chamber volume was sampled through a polyurethane foam (PUF) plug to collect the gas-phase products of FL reactions, and the FL-coated filters were removed. The exposed filters were Soxhlet extracted with CH_2Cl_2, and the NFL isomers were quantified by HPLC[11,14] and identified by GC/MS analysis with multiple ion detection (MID). The PUF plugs were Soxhlet extracted with CCl_4 and, after semipreparative HPLC purification,[11,12] were analyzed by GC/MS.

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Registry No. 1, 206-44-0; **2**, 13177-29-2; **3**, 33611-88-0; **4**, 102493-21-0; **5**, 102493-22-1; **7**, 102493-19-6; **8**, 102493-20-9; **9**, 102493-17-4; **10**, 102493-16-3; **11**, 102493-15-2; **12**, 85923-82-6; HNFL, 32516-82-8; N_2O_5, 10102-03-1; fluoranthenequinone, 39407-42-6; 5-nitrofluoranthene 2,3-oxide, 102493-18-5.

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N-Hydroxypyridine-2-thione Esters as Radical Precursors in Kinetic Studies. Measurements of Rate Constants for Hydrogen Atom Abstraction Reactions

Martin Newcomb* and Seung Un Park

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received February 3, 1986*

Abstract: *N*-Hydroxypyridine-2-thione esters were employed as radical precursors in kinetic studies. Radical chain reactions of the precursor esters gave 2,2-dimethyl-3-butenyl and 5-hexenyl. These radicals either were trapped by H-atom donors or rearranged, and the rate constants for trapping were determined from the known rate constants for rearrangement and measured product yields. For hydrogen atom donors that reacted too slowly to trap radicals before rearrangement, an estimate of the rate constants for hydrogen atom transfer was made from the yields of rearranged hydrocarbon and alkyl pyridyl sulfide (formed by scavenging of the alkyl radical by the precursor ester). The methods work for a variety of H-atom donors, including thiols, stannanes, phosphines, silanes, and reactive hydrocarbons. The rate constants determined for reduction of alkyl radicals by dicyclohexylphosphine, 1,4-cyclohexadiene, and THF are important for mechanistic studies of potential electron-transfer processes in reactions of nucleophiles with alkyl halides.

The rate constants for reactions of radicals can be measured directly by the use of a spectrophotometric or spectroscopic technique or indirectly by the use of competition reactions which are often based on a radical clock reaction. The limitations of

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