

°C); 4,4'-dinitrodiphenylmethane, mp 181 °C (lit.<sup>50</sup> mp 181-182 °C); 4-nitrodiphenylmethane, mp 32 °C (lit.<sup>51,52</sup> mp 29-32 °C). Solvents were purified and solutions made up as described previously.<sup>3</sup> Buffers were purified commercial products.

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**Measurements.** Kinetic studies were made using a Durrum stopped-flow spectrophotometer, with a thermostatted cell compartment (25 ± 0.2 °C). Some slow kinetic measurements were made using a Shimadzu UV-160 spectrophotometer. pH determinations in water-DMSO mixtures containing 0.5 M NMe<sub>4</sub>Cl were carried out at 25 °C using the same procedure as that previously described.<sup>3</sup> A Tacussel Isis 20000 electronic pH meter was used for this purpose.

**Registry No.** 1a, 32255-27-9; 1b, 32255-28-0; C-1a, 126083-71-4; C-1b, 126083-72-5.

## A Dichotomy in the Nitration of Fluoranthene with NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub>: Mechanistic and Toxicological Implications

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The nitration of fluoranthene with nitrogen dioxide can occur by two distinctive reaction pathways. These paths can be distinguished by product analysis, since fluoranthene is a nonalternant hydrocarbon. Free-radical nitration and electrophilic nitration give different products. In solvents with dielectric constants lower than that of CH<sub>2</sub>Cl<sub>2</sub> and in the absence of acid catalysis, the exclusive reaction pathway is homolytic in nature. The products of the homolytic reaction pathway can be interpreted as arising via a multiple-step addition-elimination mechanism and are notable for the formation of 2-nitrofluoranthene (the major product in CCl<sub>4</sub> but absent under electrophilic nitration conditions) and the unusually large amounts of the expected 1,2-dinitrofluoranthene and 1,3-dinitrofluoranthene. The ionic reaction pathway is subject to both Lewis and Brønsted acid catalysis, particularly in CH<sub>2</sub>Cl<sub>2</sub>, and is inhibited by nonnucleophilic bases like 2,6-di-*tert*-butylpyridine. At temperatures lower than 25 °C, the ionic reaction pathway predominates, even in CCl<sub>4</sub>. 2-Nitrofluoranthene is a marker for the free-radical nitration of fluoranthene, and its presence in polluted tropospheric air suggests that free-radical nitration by NO<sub>2</sub> may occur under atmospheric conditions.

The reactions of polycyclic aromatic hydrocarbons (PAH) with nitrating agents have received much attention recently due to the potential for the formation of nitro-PAH in urban atmospheres<sup>2-5</sup> and the mutagenic and/or carcinogenic properties of many of these compounds.<sup>6,7</sup> Nitro-PAH are thought to arise from a variety of human activities including fossil fuel combustion and biomass burning. However, certain nitro-PAH that cannot be explained in terms of the conventional nitration mechanism have been identified in airborne particulate matter.<sup>4,8,9</sup> For example, 2-nitrofluoranthene (2NF), despite being the most abundant and ubiquitous nitro-PAH pollutant,<sup>4,8,9</sup> has not been observed in combustion emissions.<sup>3</sup> It also did not appear to be produced under various nitration

conditions;<sup>10,11</sup> however, recently 2NF has been identified as a product under homolytic nitration conditions,<sup>12-15</sup> and it was proposed that 2NF arises from radical reactions in polluted tropospheric ambient air.<sup>4,8,9,13,14</sup>

Despite the numerous works devoted to nitration of PAH, reports on the reaction of PAH with NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> are often controversial, and mechanisms involving electron-transfer, radical, or electrophilic substitution have been proposed.<sup>16</sup> We have recently reported on the radical nitration of fluoranthene, 1, with NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> in CCl<sub>4</sub>.<sup>14</sup> We proposed the use of 1 as a mechanistic probe for distinguishing between radical and electrophilic nitration because, being a nonalternant hydrocarbon, it gives a markedly different product distribution according to the type of reaction mechanism. Thus, the positional reactivity found with nitronium ion mediated nitration follows the order 3 > 8 > 7 > 1 > 2, in agreement with the theoretical calculations involving an intermediate  $\sigma$ -complex that

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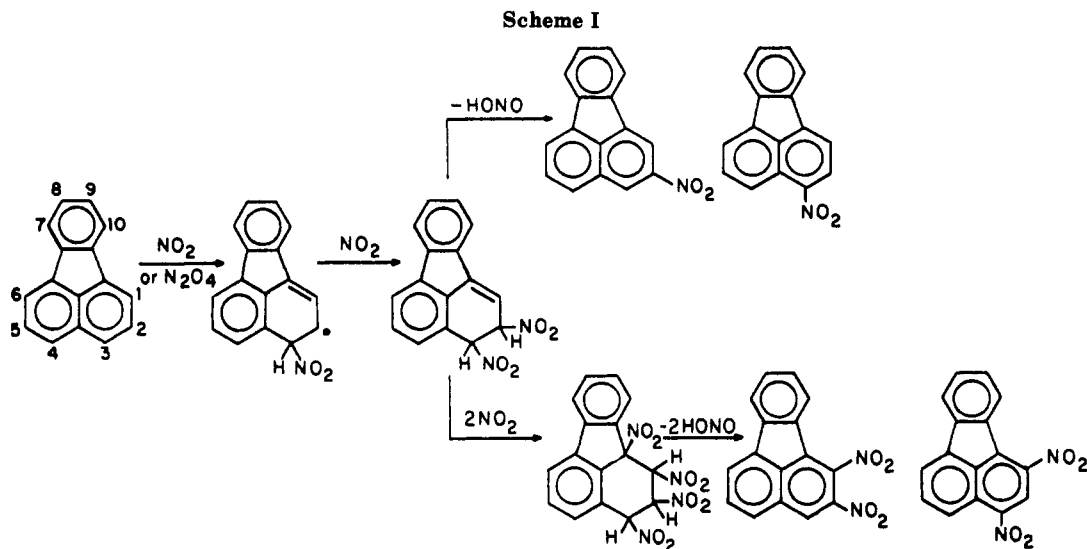
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dictates the regioselectivity of the process.<sup>17-19</sup> In contrast to the general behavior of cationic  $\sigma$ -complexes, which readily lose their highly acidic proton and rearomatize,<sup>20</sup> radical  $\sigma$ -complexes preferentially undergo radical coupling rather than aromatization via hydrogen atom abstraction.<sup>12-15</sup> Indeed, when the  $\sigma$ -complex theoretical model is applied to radical addition the order  $3 > 1 > 7 > 8 > 2$  is predicted.<sup>17-19</sup> The distribution of nitrofluoranthenes obtained experimentally, which favors 2NF, therefore is interpreted as a multiple addition-elimination pathway occurring after the formation of the radical  $\sigma$ -complex.<sup>14</sup> These observations led us to propose 2NF as a marker for radical nitration (Scheme I). In addition, the radical nitration of 1 leads to the facile formation of dinitrofluoranthenes of unusual substitution pattern, even at low conversions. The observed substitution patterns of these dinitrofluoranthenes can also be explained by the multiple addition-elimination mechanism.

In order to help unravel the mechanism of the nitration of PAH with  $\text{NO}_2/\text{N}_2\text{O}_4$ , we have studied the solvent effect, the effect of selected added species, and the temperature effect on the product distribution of 1.

### Experimental Section

**Materials.** Fluoranthene (Aldrich, 98% + GC-area %) was used without further purification. Anhydrous nitric acid was distilled prior to use from concentrated nitric acid (Mallinkrodt) and sulfuric acid (Baker). Methanesulfonic acid (Eastman Kodak) and nitrosonium tetrafluoroborate (Aldrich) were used as received. HPLC-grade carbon tetrachloride (Baker) was dried over potassium carbonate and/or distilled under dry nitrogen. Tetrahydrofuran (QO Chemicals) was distilled from sodium under nitrogen. Acetonitrile (Mallinkrodt) and nitromethane (Aldrich) were dried over sodium sulfate and distilled. Dinitrogen tetroxide (MCB) was distilled until a pure white solid was obtained, indicating that it was free of lower nitrogen oxides. The purified  $\text{N}_2\text{O}_4$  was stored over phosphorus pentoxide (Alfa).

Tetrabutylammonium nitrate and tetrabutylammonium nitrite were synthesized using modifications of the methods of Witschoke

and co-workers<sup>21</sup> and Pocker and co-workers,<sup>22</sup> respectively.

**Reaction Conditions.** The reactions were carried out in a thermostated bath at  $25.0 \pm 0.5$  °C unless specified otherwise. All solutions were thoroughly purged with dry nitrogen. The reactions were carried out under dim illumination. Typically, 27 mg of fluoranthene dissolved in 0.9 mL of  $\text{CCl}_4$  (15 mM) were allowed to react with 2.7 mL of a  $\text{CCl}_4$  solution 18.4 mM in  $\text{N}_2\text{O}_4$  (equal to 2.8 mM  $\text{NO}_2$  in equilibrium with 17 mM  $\text{N}_2\text{O}_4$  at this dilution) in a dark screw-capped vial with a minimum head space. Similar procedures were used with other solvents. When a third species was used, it was added to the solution containing the  $\text{N}_2\text{O}_4$ , preceding the mixing with the solution containing the fluoranthene. All reactions were carried out at least in duplicate and monitored by gas chromatography. The product distribution standard deviations, calculated by integration of the peak areas and correcting by their relative response factors to the flame ignition detector, were less than 10%.

Product distribution data represent 0-20% fluoranthene conversion, and no detectable change in product distribution was noticed as a function of the reaction progress.

**Instrumentation.** Quantitative analysis was done on a Varian 3700 gas chromatograph provided with a 55 m/0.25 mm i.d. DB-17 J&W capillary column and a flame ionization detector.

Samples for NMR studies were purified by HPLC using hexane-methylene chloride mixtures on a Varian 5000 liquid chromatograph equipped with a 25-cm silica gel column (IBM). The interpretation of the  $^1\text{H}$  NMR spectra of the nitrofluoranthenes has been published elsewhere.<sup>23</sup>

The GC/MS analysis was conducted on a Hewlett-Packard 5890 GC instrument equipped with an HP 5970 mass-selective detector using a 20 m/0.18 mm i.d. DB-17 J&W capillary column.

The photochemical experiment was conducted with a 200-W Hg lamp in a homemade quartz cell provided with a Teflon stopcock for a 1-h period.

**X-ray Crystallography.** Diffraction data were obtained from a yellow needle fragment of dimensions  $0.18 \times 0.24 \times 0.40$  mm on an Enraf-Nonius CAD4 diffractometer equipped with Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) and a graphite monochromator. Crystal data are  $\text{C}_{16}\text{H}_8\text{N}_2\text{O}_4$ , FW = 292.3, monoclinic space group  $P2_1/n$ ,  $a = 4.968$  (3) Å,  $b = 13.815$  (2) Å,  $c = 18.444$  (3) Å,  $\beta = 97.56$  (3)°,  $V = 1254.9$  (12) Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}} = 1.547$  g cm<sup>-3</sup>,  $T = 22$  °C,  $\mu(\text{Mo } K\alpha) = 1.07$  cm<sup>-1</sup>. One quadrant of data having  $1^\circ < \theta < 23^\circ$  was collected by  $\omega - 2\theta$  scans of variable rate 1.1-4.0 deg min<sup>-1</sup>. Data reduction included correction for background, Lorentz, and polarization effects; no significant intensity decay occurred during data collection. Of 1752 unique data, 1458 have positive net intensities and were used in the refinement.

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**Table I. Distribution of Nitro- and Dinitrofluoranthenes Formed in the Nitration of Fluoranthene with NO<sub>2</sub> in CCl<sub>4</sub> as a Function of Selected Added Species**

additive	% distribution of products						
	1NF	2NF	3NF	7NF	8NF	1,2DNF	1,3DNF
none	1	73	14	a	a	3	9
HNO <sub>3</sub> (6.6 mM)	1	53	30	a	3	5	9
HNO <sub>3</sub> <sup>b</sup>	3	1	67	4	24	a	a
NOBF <sub>4</sub> (10 mM)	5	9	60	5	19	1	1
CH <sub>3</sub> SO <sub>3</sub> H (4.3 mM)	2	34	43	2	10	3	7
oxygen <sup>c</sup>	2	59	19	1	7	8	4
TBANO <sub>2</sub> <sup>d</sup> (1.0 mM)	1	60	12	a	a	13	15
TBANO <sub>3</sub> <sup>e</sup> (1.3 mM)	1	58	12	a	a	13	17
DTBP <sup>f</sup> (1.3 mM)	1	58	14	a	a	13	14
H <sub>2</sub> O (30.9 mM)	1	67	18	a	a	5	10
CBrCl <sub>3</sub> (2.15 M)	2	72	10	2	1	4	12

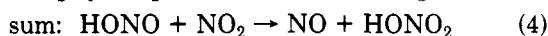
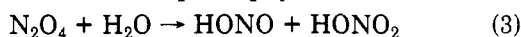
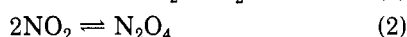
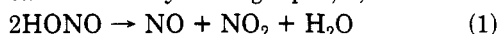
<sup>a</sup>Less than 0.5%. <sup>b</sup>HNO<sub>3</sub> 0.17 M. No NO<sub>2</sub> was added. <sup>c</sup>Reaction carried out in O<sub>2</sub>-saturated CCl<sub>4</sub>. <sup>d</sup>Tetrabutylammonium nitrite. <sup>e</sup>Tetrabutylammonium nitrate. <sup>f</sup>2,6-Di-*tert*-butylpyridine.

The structure was solved by direct methods using MULTAN<sup>24</sup> and refined by full-matrix least-squares based on  $F$  with weights  $w = \sigma^{-2}(F_o)$ , using the Enraf-Nonius SDP programs.<sup>25</sup> Non-hydrogen atoms were treated anisotropically while H atoms were located by difference maps and refined isotropically. A secondary extinction coefficient was refined to a value of  $4.3(6) \times 10^{-7}$ . Convergence was achieved with  $R = 0.053$  for 232 variables, maximum shift/esd  $< 0.01$ , and maximum residual density  $0.18 \text{ e } \text{Å}^{-3}$ . X-ray crystallographic data are listed in the supplementary material.

### Results and Discussion

**Product Identification.** The GC retention times of the nitrofluoranthenes (NF) follow the order 1NF  $<$  7NF  $\leq$  2NF  $<$  3NF  $<$  8NF  $<$  1,3-dinitrofluoranthene (1,3DNF)  $<$  1,2DNF under all conditions employed here. (2NF and 7NF have identical retention times on the 20 m/0.18 mm i.d. DB-17 J&W column, but are base-line resolved on the 55 m/0.25 mm i.d. column.) Mass spectra fragmentation patterns give characteristic M, M - 30, and M - 46 peaks, the last two corresponding to loss of NO and NO<sub>2</sub>, respectively.

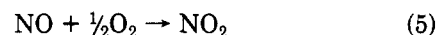
**Chemistry of Nitrogenous Species Present in the Nitration System.** Nitrogen dioxide is in rapid equilibrium with N<sub>2</sub>O<sub>4</sub>,<sup>26</sup> and the equilibrium lies toward the dimer<sup>27,28</sup> under the conditions studied here. Nitrous acid, a byproduct of the aromatization of the intermediates depicted in Scheme I, is unstable and rapidly decomposes at room temperature to NO, NO<sub>2</sub>, N<sub>2</sub>O<sub>3</sub>, and water. Water, in turn, hydrolyzes N<sub>2</sub>O<sub>4</sub> to HONO<sub>2</sub> and HONO. The result is a net accumulation of HONO<sub>2</sub> as the reaction proceeds, as can be seen by adding eqs 1, 2, and 3.



As the solvent polarity increases, heterolytic equilibria that produce NO<sup>+</sup> as a reactive species become increasingly dominant.<sup>29-31</sup> For example, the nitrosonium ion has been

found to play an important role in the electrochemical nitration of naphthalene by N<sub>2</sub>O<sub>4</sub> in the polar aprotic solvent sulfolane.<sup>29-31</sup>

In the presence of oxygen, NO is oxidized to NO<sub>2</sub>, eq 5.



It can be seen by adding eqs 4 and 5 that the presence of oxygen results in a net accumulation of HONO<sub>2</sub>, eq 6.



**The Effect of Selected Additives.** Table I shows the effect various additives have in the product distribution of the reaction of 1 with NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> in CCl<sub>4</sub>. A small amount of HONO<sub>2</sub> does not interfere with the radical nitration, probably because of the micelle-like characteristics of the dilute solutions of HONO<sub>2</sub><sup>32</sup> and the poor solvation of cationic intermediates in CCl<sub>4</sub>.<sup>14</sup> The inertness of HONO<sub>2</sub> is also evidenced by a product distribution independent of the extent of conversion (see the Experimental Section) in the nitration of 1 with NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> in CCl<sub>4</sub>, and, thus, independent of the HONO<sub>2</sub> build up as the reaction proceeds. Furthermore, when the reaction is run with 6.6 mM HONO<sub>2</sub> present initially, the ionic contribution seems to be minimal, as indicated by the formation of only 3% 8NF. Similarly, yields are virtually unchanged when the reaction is run with an initial concentration of water of 30.9 mM. The product distribution using only anhydrous HONO<sub>2</sub> (0.17 M) as nitrating reagent gave very small amounts of 2NF (1%) and much larger amounts of 3NF (67%), 8NF (24%), 7NF (4%), and 1NF (3%). Therefore, nitration by HONO<sub>2</sub> occurs only at higher concentrations and affords a very different product distribution than does NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub>.

The effect of acidity was also investigated. When the reaction was run in the presence of 4.3 mM CH<sub>3</sub>SO<sub>3</sub>H, the formation of substantial amounts of 8NF (10%) and greatly reduced amounts of 2NF (34%) was observed. An even more pronounced effect was observed when the reaction was carried out in the presence of ca. 10 mM NOBF<sub>4</sub>.

Tetrabutylammonium nitrite (TBANO<sub>2</sub>), tetrabutylammonium nitrate (TBANO<sub>3</sub>), and 2,6-di-*tert*-butylpyridine (DTBP) cause the formation of moderately larger amounts of dinitrofluoranthenes and lower the 2NF/3NF ratio. The higher yield of 3NF is, however, not paralleled

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**Table II. Distribution of Nitro- and Dinitrofluoranthenes Formed in the Nitration of Fluoranthene with NO<sub>2</sub> in CCl<sub>4</sub> as a Function of Temperature**

temp, °C	% distribution of products						
	1NF	2NF	3NF	7NF	8NF	1,2DNF	1,3DNF
40	2	65	13	a	1	10	10
25	1	73	14	a	a	3	9
10	4	54	22	3	5	7	6
-13	4	30	51	4	12	a	a

<sup>a</sup> Less than 0.5%.

**Table III. Distribution of Nitro- and Dinitrofluoranthenes Formed in the Nitration of Fluoranthene with NO<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> as a Function of Selected Added Species**

additive	% distribution of products						
	1NF	2NF	3NF	7NF	8NF	1,2DNF	1,3DNF
none	2	32	43	1	10	5	6
H <sub>2</sub> O (30.9 mM)	2	9	63	3	19	2	2
DTBP <sup>a</sup> (12.4 mM)	b	35	46	a	5	7	8
NOBF <sub>4</sub> (10 mM)	4	a	69	4	23	a	a

<sup>a</sup> 2,6-Di-*tert*-butylpyridine. <sup>b</sup> Less than 0.5%.

by a higher yield of 8NF as was observed with CH<sub>3</sub>SO<sub>3</sub>H and NOBF<sub>4</sub>.

The presence of oxygen increases the 1,2DNF/1,3DNF and 3NF/2NF ratios and induces the formation of 8NF (7%), 1NF (2%), and 7NF (1%).

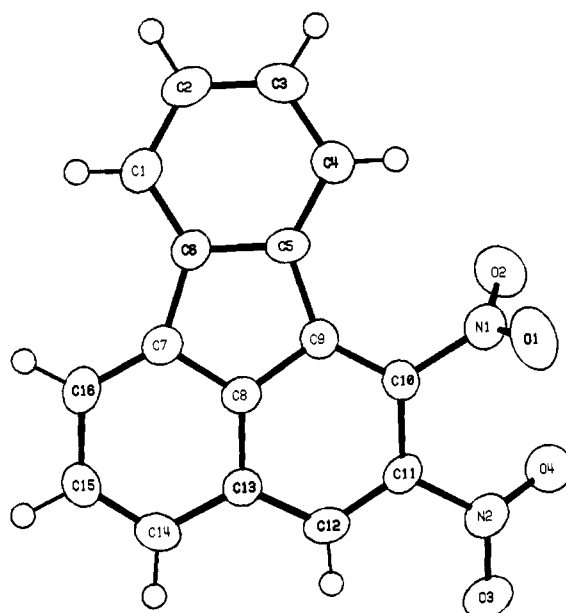
The effect of light was also investigated. Irradiation with a 200-W mercury lamp for 1 h afforded a complex mixture of chlorofluoranthenes and nitrochlorofluoranthene (data not shown).

**Temperature Effects.** Temperature effects on the reaction are shown in Table II. At lower temperatures, 1NF, 3NF, 7NF, and 8NF become increasingly predominant. In contrast, the dinitrofluoranthenes are reduced to trace levels.

**The Effect of Solvent Polarity.** Contrary to our results in CCl<sub>4</sub>, the reaction in CH<sub>2</sub>Cl<sub>2</sub> is strikingly sensitive to trace amounts of water, as shown in Table III. In dry CH<sub>2</sub>Cl<sub>2</sub>, and at low conversions, the reaction is predominantly radical, although there are substantial amounts of ionic products (e.g. 10% 8NF). When the reaction is run in the presence of 30 mM water, the ionic pathway predominates, producing larger amounts of 8NF (19%) and 3NF (63%). The addition of water reduces the yields of dinitrofluoranthenes. On the other hand, the ionic products are diminished when the reaction is run in the presence of 12.4 mM DTBP.

**Mechanistic Considerations.** In CCl<sub>4</sub>, the nitration of 1 by NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> is characterized by the formation of 2NF as the major product and by anomalously large amounts of unusual dinitration products even at low conversions. We have previously interpreted the formation of these products as arising via a free-radical mechanism involving multiple addition-elimination steps.<sup>14</sup> The formation of 2NF is favored over that of 3NF, apparently due to the interaction of the nitro group with the peri hydrogen in the latter case. Note that disubstitution occurs in the same ring of the naphthalene-like moiety, suggesting a radical mechanism. Thermodynamic control for the formation of the dinitrofluoranthenes is not achieved due to the instability of the tetrahydrotetra-nitrofluoranthene intermediates. The 1,3DNF/1,2DNF ratio is only 3, despite the strong steric repulsion present in 1,2DNF (as evidenced by its crystal structure shown in the ORTEP drawing in Figure 1).

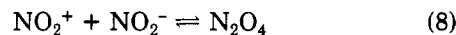
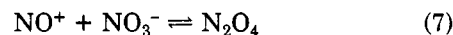
An ionic pathway, which is catalyzed by CH<sub>3</sub>SO<sub>3</sub>H and more efficiently by NOBF<sub>4</sub>, is characterized by a higher yield of 8NF and a product distribution in closer agreement with the cationic  $\sigma$ -complex theoretical prediction.

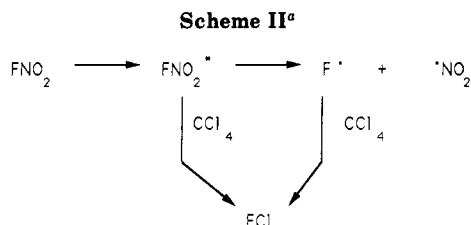


**Figure 1.** ORTEP drawing of the X-ray structure of 1,2-dinitrofluoranthene showing the spatial orientation of the nitro groups. Nitro group<sub>1</sub> and nitro group<sub>2</sub> form angles of 73.2° and 11.2° with the plane containing the carbon skeleton, respectively. The nitro groups are at an angle of 73.4° with respect to each other.

When HONO<sub>2</sub> is used as the only nitrating species, only a very small amount of 2NF (1%) is formed and the major products consist of those from an ionic electrophilic reaction pathway. Therefore, nitration by the byproduct HONO<sub>2</sub> is not an important reaction pathway in CCl<sub>4</sub> (in which less than 0.5% 8NF is formed).

Tetrabutylammonium nitrite (TBANO<sub>2</sub>) and DTBP appear to exert their effects at the elimination steps in Scheme I that lead to aromatization. These nucleophiles increase the dinitrofluoranthene/mononitrofluoranthene ratio, slightly lower the 2NF/3NF ratio, and do not cause formation of 8NF. The fact that the same product mixtures are obtained in the presence and absence of these nucleophiles proves that NO<sup>+</sup> and NO<sub>2</sub><sup>+</sup> are not involved in CCl<sub>4</sub>; reactions involving NO<sup>+</sup> and NO<sub>2</sub><sup>+</sup> would be retarded by the mass action effects of TBANO<sub>2</sub> and TBA-NO<sub>3</sub> (as can be seen in eqs 7 and 8), but the product



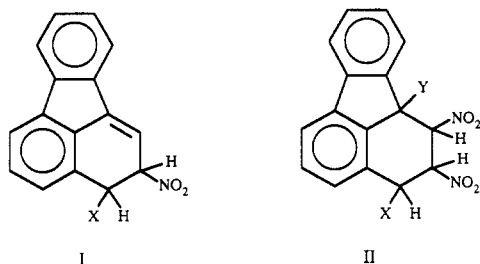


mixtures are not changed by TBANO<sub>2</sub> or TBANO<sub>3</sub>. The increase in the dinitrofluoranthene/mononitrofluoranthene ratio probably arises as a result of base catalysis of the elimination of nitrous acid from the tetranitrotetrahydrofluoranthene intermediate in Scheme I.

In the presence of BrCCl<sub>3</sub>, the intermediate radicals are trapped by NO<sub>2</sub> faster than they abstract bromine atoms from the solvent. Bromofluoranthenes are not detected nor is there a change in product distribution when the reaction is carried out in the presence of 2.15 M BrCCl<sub>3</sub> in CCl<sub>4</sub> (Table I).

The effect of light is complicated by the promotion of chlorine-atom abstraction from the solvent. Irradiation appears to induce homolytic dissociation of the mono- and dinitrofluoranthenes to the corresponding fluoranthenyl radicals, which can abstract a chlorine atom from the solvent leading to the chlorofluoranthenes (Scheme II). Alternatively, a radicaloid excited state may abstract a chlorine atom from the solvent, and, ultimately lead to the observed products.<sup>33</sup>

The effect of oxygen deserves special attention. Zielinska and collaborators<sup>12</sup> observed the formation of 1,2DNF (in addition to 2NF) when 1 was allowed to react with N<sub>2</sub>O<sub>5</sub> in CCl<sub>4</sub>. It is therefore possible that oxygen reacts with NO<sub>2</sub> to form small amounts of more highly oxygenated transient species, such as NO<sub>3</sub>, NO<sub>4</sub><sup>34</sup> and/or N<sub>2</sub>O<sub>6</sub>, that are more reactive than NO<sub>2</sub>. Elimination of the more highly oxygenated nitrogenous acids from adducts I and II (where X and Y are highly oxygenated nitrogenous



species) appears to be thermodynamically favorable, explaining the preference for the formation of 1,2DNF over 1,3DNF.<sup>35</sup> Thus, rearomatization of adduct II would lead exclusively to 1,2DNF. Following this reasoning, rearomatization of adduct I would lead to the formation of larger amounts of 2NF, in apparent contradiction with the experimental results. We suggest, therefore, that the larger amounts of 3NF observed in the presence of oxygen result

(33) Chow, Y. L. In Patai, S., Ed. *The Chemistry of Amino, Nitroso and Nitro Compounds and their Derivatives*; John Wiley & Sons: New York, 1982; Supplement F, Part I.

(34) Other authors also suggested the intervention of higher oxides of nitrogen based on different observations: (a) Titov, A. I. *Tetrahedron* 1963, 19, 557-580. (b) Dufraisse, C.; Perronnet, J., *C. R. Acad. Sci.* 1959, 249, 2687-2692. (c) Kha-Vang-Thang *Ibid.* 1961, 252, 3277-3279.

(35) The gas-phase heat of formation of nitric acid is 13.3 kcal/mol more exothermic than that of nitrous acid; *CRC Handbook of Chemistry and Physics*, 64th ed.; Weast, R. C., Ed.; CRC Press, Inc.: Boca Raton, FL, 1983.

**Table IV. Distribution of Nitro- and Dinitrofluoranthenes Formed in the Nitration of Fluoranthene with NO<sub>2</sub> as a Function of the Solvent**

solvent	% distribution of products <sup>a</sup>				
	1NF	2NF	3NF	7NF	8NF
THF	4	9	57	5	25
CH <sub>3</sub> CN	4	5	67	5	19
CH <sub>3</sub> NO <sub>2</sub>	4	1	72	4	22

<sup>a</sup>1,2DNF and 1,3DNF are present in less than 0.5%.

from a concomitant ionic reaction pathway, at least in part brought about by the oxidation of HONO to HONO<sub>2</sub>. The observation of larger amounts of other nitrofluoranthenes characteristic of ionic nitration (e.g. 8NF, 7NF, and 1NF) is consistent with this explanation.

At lower temperatures, the ionic component of the reaction mechanism predominates at the reaction times studied here. This observation is consistent with one or more of the following rationalizations: (1) The NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> equilibrium could shift toward the less reactive dimer, N<sub>2</sub>O<sub>4</sub>, as the temperature is lowered, slowing the radical pathway down. (2) Ion pairs like NO<sup>+</sup>NO<sub>3</sub><sup>-</sup> and/or NO<sub>2</sub><sup>+</sup>NO<sub>2</sub><sup>-</sup> could be stabilized at lower temperatures. (3) The free-radical process could have a higher activation energy. Any of these possibilities would promote ionic nitration at lower temperatures, as we observe experimentally. A temperature-dependent product distribution also was observed by Zielinska and collaborators<sup>12</sup> for the reaction N<sub>2</sub>O<sub>5</sub> with 1.

A product distribution in closer agreement with the cationic  $\sigma$ -complex is obtained in solvents more polar than CCl<sub>4</sub>. The attacking electrophile does not appear to be the nitronium ion because the reaction rates depend on the PAH,<sup>36</sup> while the nitronium ion reacts at a diffusion-controlled rate with the PAH tested. In carefully dried CH<sub>2</sub>Cl<sub>2</sub> and at low conversions, it can be observed that there is substantial contribution of both the ionic and the radical reaction pathways (Table III). The addition of water promotes the ionic pathway by allowing the disproportionation of N<sub>2</sub>O<sub>4</sub> to HONO and HONO<sub>2</sub>. The addition of DTBP quenches the HONO and HONO<sub>2</sub> that are formed as the reaction proceeds and prevents the formation of NO<sup>+</sup>.<sup>28-31</sup> The nitrosonium ion is an efficient catalyst of the ionic reaction pathway as evidenced by the product distribution obtained in the presence of NOBF<sub>4</sub> (Table III).

In solvents of dielectric constant higher than CH<sub>2</sub>Cl<sub>2</sub>, only small amounts of 2NF are formed, as can be seen in Table IV. This is consistent with a better solvation of cationic intermediates relative to the radical intermediates as the solvent dielectric constant increases. It is also noticeable that emerald green charge-transfer complexes of these solvents with N<sub>2</sub>O<sub>4</sub> are formed.<sup>37,38</sup> These complexes may play a role in the formation of the ultimate electrophile by causing extensive polarization of N<sub>2</sub>O<sub>4</sub>.

The formation of charge-transfer complexes may give further insights to a more general mechanism. The relative rates of several PAH with NO<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> were found to correlate best with their half-wave oxidation potentials, which in turn, may parallel the energy of their charge-transfer complexes.<sup>36</sup> The possibility of the formation of charge-transfer complexes as rate-determining steps in the reaction of PAH with NO<sub>2</sub> is currently under investigation.<sup>39</sup>

(36) Pryor, W. A.; Gleicher, G. J.; Cosgrove, J. P.; Church, D. F. *J. Org. Chem.* 1984, 49, 5186-5194.

(37) Addison, C. C.; Sheldon, J. C. *J. Chem. Soc.* 1956, 1941-1949.

(38) Shechter, H. *Rec. Chem. Prog.* 1964, 25, 55-76.

Our proposed multiple-step addition-elimination mechanism for 1 also offers a plausible alternative explanation to certain anomalies noticed in the nitration of pyrene,<sup>40,41</sup> where unusually large amounts of dinitropyrenes, including the unexpected 1,3-dinitropyrene, are formed.

Although the synthetic applications of the nitration of PAH with NO<sub>2</sub> in organic solvents are attractive,<sup>10,36,42</sup> special attention should be given to the drying and choice of solvents, drying of the NO<sub>2</sub>, temperature, and catalysts. As we have demonstrated, the operative reaction mechanisms are highly dependent on the experimental conditions.

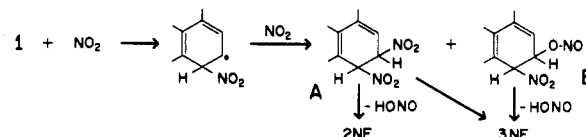
**Toxicological Implications.** Fluoranthene (1) is one of the most abundant PAH in environmental samples.<sup>43</sup> The reaction of 1 with NO<sub>2</sub> is slower than with N<sub>2</sub>O<sub>5</sub>,<sup>12,14</sup> nevertheless, the reaction with NO<sub>2</sub> might be the most important contributor to the formation of 2NF due to the relatively higher concentrations of NO<sub>2</sub> in urban atmosphere.<sup>44</sup> There currently is evidence for a substantial contribution from a nonionic reaction pathway in atmospheric reactions to the total nitro-PAH that are in the urban environment.<sup>4,8,9,13,14,45</sup> The distribution of nitro-PAH obtained upon nitration with NO<sub>2</sub> under free-radical conditions (in solvents of low dielectric constant) may model the atmospheric (gas phase) reaction. For example, 2-nitrofluoranthene is one of the most important nitro-PAH in ambient polluted air,<sup>46</sup> and, as we have found, is the major product of the homolytic nitration of 1 with NO<sub>2</sub>.<sup>47</sup> In contrast, 2-nitrofluoranthene is the only isomer

not detected under nitrations mediated by the nitronium ion or a carrier thereof. The nitration of 1 with NO<sub>2</sub> under free-radical conditions also leads to the facile formation of highly mutagenic dinitrofluoranthenes.<sup>15,48</sup> Dinitrofluoranthenes have been detected as atmospheric pollutants; they display GC retention times similar to the more studied dinitropyrenes<sup>41,49,50</sup> and also have the same molecular weight and similar MS fragmentation patterns. Thus, what has previously been identified as dinitropyrenes by lower resolution gas chromatography may actually reflect the sum of dinitropyrenes and dinitrofluoranthenes.

**Acknowledgment.** This work was supported by a grant from the National Institutes of Health (HL-16029) and by a contract from the National Foundation for Cancer Research. We also thank Dr. David Giamalva for his continuous interest and helpful suggestions throughout this study.

**Supplementary Material Available:** X-ray crystallographic data for 1,2-dinitrofluoranthene: complete tables of coordinates, bond distances and angles, coordinates for hydrogen atoms, and anisotropic thermal parameters (6 pages); listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

(47) A referee has suggested that the 2NF/3NF ratio could be controlled by trapping the 3-nitrofluoranthenyl radical either on nitrogen or oxygen by NO<sub>2</sub>, as shown below.



However, nitro-nitrite addition intermediates lead to the formation of oxidation products (usually quinones or ketones), presumably via hydrolytic and/or thermolytic cleavages (for a review see, for example: Titov, A. I. *Tetrahedron* 1963, 19, 557-580). We have detected only traces of a fluoranthenequinone and of hydroxynitrofluoranthenes in a few experiments, suggesting that radical coupling of the 3-nitrofluoranthenyl radical with NO<sub>2</sub> at one of the oxygen atoms is not an important reaction pathway.

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(50) Tokiwa, H.; Otofujii, T.; Nakagawa, R.; Horikawa, K.; Maeda, T.; Sano, N.; Izumi, K.; Otsuka, H. In *Carcinogenic and Mutagenic Effects of Diesel Engine Exhaust*; Ishinishi, N., Koizumi, A., McClellan, R. O., Stöber, W., Eds.; Elsevier: Amsterdam, 1986; pp 253-270.

(39) Squadrito, G. L.; Fronczek, F. R.; Watkins, S.; Church, D. F.; Pryor, W. A., manuscript in preparation.

(40) Ross, D. S.; Hum, G. P.; Schmitt, R. J., paper presented at the 192nd American Chemical Society National Meeting, Anaheim, CA, Sept 1986.

(41) A study on the nitration of pyrene with NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> in nonparticipating solvents is currently in progress in our laboratories, Squadrito, G. L.; Wu, M.-D.; Church, D. F.; Pryor, W. A., unpublished results.

(42) Ebersson, L.; Radner, F. *Acc. Chem. Res.* 1987, 20, 53-59.

(43) Vogt, N. B.; Brakstad, F.; Thrane, K.; Nordenson, S.; Krane, J.; Aamot, E.; Kolset, K.; Esbensen, K.; Steinnes, E., *Environ. Sci. Technol.* 1987, 21, 35-44.

(44) Atkinson, R.; Winer, A. M.; Pitts, J. N., Jr. *Atm. Environ.* 1986, 20, 331-339.

(45) Another possible route to 2NF in polluted air is attack by the hydroxyl radical at C3, trapping of the resulting 2-hydroxy-2-hydroxy-3-fluoranthenyl radical by NO<sub>2</sub>, and elimination of water.

(46) Greenberg, A.; Darack, F.; Wang, Y.; Harkov, R.; Louis, J.; Atherholt, T. Proc.-APCA (Air Pollution Control Association), 80<sup>th</sup> Annual Meeting, Vol. 6, pp 1-33.

## Acyl Hypofluorites. A New Class of Organic Compounds

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Acyl hypofluorites, RCOOF, with hydrogen containing alkyl residues have been prepared from the corresponding carboxylic acid salts and F<sub>2</sub>. For these compounds to have a reasonable stability, at least one electron-withdrawing group has to be attached to the  $\alpha$ -position and lengthy chains should be avoided. All hypofluorites have an electrophilic fluorine which can readily react with an electron-rich double bond, as in tetralone enol acetate to give  $\alpha$ -fluorotetralone.

There is considerable interest in compounds possessing the O-F bond since they are found to be strong electrophilic fluorinating agents. This bond is found mainly in

two groups of compounds: fluoroxyperfluoro alkanes and perfluoroacyl hypofluorites. The first member of the fluoroxy family, CF<sub>3</sub>OF, was initially prepared by Cady<sup>1</sup>