Formation of Mutagenic Nitrofluoranthenes in the Gas-Solid Heterogeneous Reaction of Particle-associated Fluoranthene in NO_2-O_3-O_2 System

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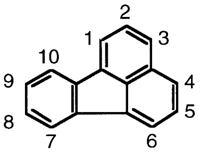
In the gas-solid heterogeneous reactions of particle-supported fluoranthene with ppm levels of nitrogen dioxide and ozone, dinitrofluoranthenes and 3-nitrofluoranthene (3-NF) were formed only in the dark and 2-NF was formed only under photoirradiation while 1-, 7-, and 8-NFs were formed under both conditions. Yield and distribution of the products varied depending on the kind of supports employed.

Nitrofluoranthenes (NFs) have been detected in large amounts among nitroarenes in airborne particles.[1] However, 3- and 8-NFs, which are the only NFs from combustion processes, have been found in relatively small amounts among these NFs. Thus, most part of NFs in airborne particles has been regarded to be formed through the atmospheric reaction.[2] Although the gas-solid heterogeneous nitration of particle-supported fluoranthene (FL) is supposed to be closely related to the atmospheric formation of NFs because of its presence on the surface of airborne particles,[3] most of investigations of the nitration of FL have been conducted using homogeneous systems.[4,5] Moreover, the support particles have been been reported to affect the reactivity of polycyclic aromatic hydrocarbons under heterogeneous conditions,[6] but no information is available yet on the variation of yield and distribution of NFs in the nitration of particle-supported FL. In this paper we report the heterogeneous reaction of FL supported on various kinds of inorganic particles under an atmosphere containing NO_2, which is the most probable pollutant associated with nitration, and O_3, which is the typical tropospheric pollutant to generate active species for nitration. The reaction has been conducted both in the dark and under photoirradiation to simulate the nighttime and daytime reactions, respectively, and it gave the first observation of the formation of strong mutagenic dinitrofluoranthenes (DNFs) and 2-NF as well as other NFs in heterogeneous reaction system. The variation of yield and distribution of NFs according to the type of support employed and by the presence of light is also reported.



FL

The simulated atmosphere was composed of 10 ppm NO_2, 5 ppm O_3, and O_2. The reactions were conducted under ambient pressure in the flow system equipped with a cylindrical reactor and a Pyrex-filtered Hg lamp at 298±2 K. The light shorter than 290 nm in wavelength was cut off and hence the photoexcitation of FL itself, which has a major absorption band at the shorter wavelength than 290 nm, can be neglected. FL-supporting particles (FL: 5μmol/g-particles) on a sheet of Polyflon filter were loaded into the reactor. As support particles, eight kinds of inorganic substances were employed; oxides of metals commonly found in airborne particles and graphite as a mimic soot. The reaction of FL deposited on a Teflon plate was also performed as a support-free reaction (blank test). FL-supporting particles were prepared by mixing a CH_2Cl_2 solution of FL and the support particles well, followed by removal of the solvent under N_2. After a given reaction time, FL and the products were extracted from the particles into CH_2Cl_2 by sonication. The combined extract was concentrated and analyzed by GC. The molecular formula of each product was determined by GC-MS.

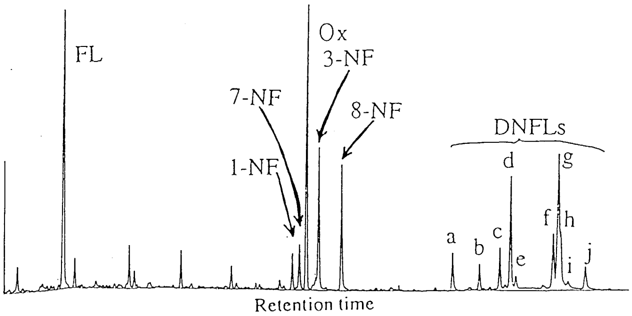


Figure 1. Typical GC-FID chromatogram of an extract from the sample supported on Fe_2O_3 after 4 h exposure to 10 ppm NO_2-5 ppm O_3-O_2 in the dark.

In the dark reaction, four NFs, 1-, 3-, 7- and 8-NFs, and more than seven DNFs, including 3,9-DNF as the only identified DNF, were formed (Figure 1) and the extensive degradation of FL was observed for all kinds of the support used. This is the first observation of DNF formation in the gas-solid heterogeneous reaction of FL, while up to seven DNFs, 1,2-, 1,3-, 2,4-, 2,5-, 3,4-, 3,7- and 3,9-DNFs, have previously been detected in the homogeneous nitration of FL.[4,5,7] The maximum percentage of degraded FL and maximum yields of NFs and DNFs, attained after 8 h, varied with the kind of support and ranged from 30.2% (on graphite) to 81.1% (on Fe_2O_3), from 8.0% (on MgO) to 12.4% (on Fe_2O_3), and from 2.1% (on graphite) to 8.9% (on Fe_2O_3), respectively (Table 1). Significant degradation was observed for Fe_2O_3, TiO_2, ZnO, and Al_2O_3 with the percentage of degraded FL more than 75%, while a smaller percentage of the degradation around 50% was observed for MgO, SiO_2, and CaO. The selectivity of nitration increased with the decrease of the degradation rate. This suggests the competition between nitration and another fast reaction, probably oxidation, in this system. Indeed, unidentified

Table 1. Yield of NFs on different supports in the dark reaction[a]

Support	Degraded FL /%	Yield /%					Sel.[c] /%
		ΣDNF[b]	1-NF	3-NF	7-NF	8-NF	
Fe_2O_3	81.1	8.9	1.4	4.5	2.3	4.2	26.3
TiO_2	76.0	5.9	2.0	3.7	2.4	3.5	23.0
ZnO	75.8	5.6	1.6	3.6	2.2	2.3	20.2
Al_2O_3	75.4	8.1	2.0	4.5	3.1	4.7	29.7
MgO	54.1	5.1	1.0	2.6	1.1	3.3	24.2
SiO_2	52.1	4.0	2.1	2.6	1.9	3.5	27.1
CaO	50.4	7.4	1.2	2.8	1.4	3.1	31.5
graphite	30.2	2.1	1.9	3.5	1.5	3.4	41.1
Teflon[d]	37.3	2.7	1.0	2.8	0.8	2.5	26.3

[a]After 8 h under 10 ppm NO_2 - 5 ppm O_3 - O_2. [b]Based on the assumption that all isomers exhibit the same molar sensitivity for GC-NPD analysis. [c]Selectivity of nitration: (ΣDNF + ΣNF) / degraded FL. [d]Employed for blank.

Table 2. Yield of NFs on different supports under photoirradiation[a]

Support	Degraded FL /%	Yield /%				Sel.[b] /%
		1-NF	2-NF	7-NF	8-NF	
Fe_2O_3	50.4	1.7	5.6	1.4	1.2	19.6
TiO_2	88.8	2.5	5.6	1.8	0.2	11.4
ZnO	87.1	2.1	6.1	2.0	0.4	12.2
Al_2O_3	79.2	5.4	7.0	2.0	1.0	19.4
MgO	54.7	2.1	6.3	1.1	1.2	19.6
SiO_2	62.3	3.8	6.0	0.8	1.1	18.5
CaO	51.5	2.0	5.4	2.8	0.9	21.6
graphite	41.0	1.9	4.9	1.9	0.7	22.9
Teflon[c]	43.8	1.0	3.6	1.0	0.6	14.2

[a]After 4 h under 10 ppm NO_2 - 5 ppm O_3 - O_2. [b]Selectivity of nitration: ΣNF / degraded FL. [c]Employed for blank.

phthalate as an oxidation product was also formed. The ease of these two reactions, which depends on the kind of support used should cause the variation of the degradation rate and product yield as observed. The isomeric distribution of NFs also varied with the support used.

In the photoreaction, the maximum percentage of degraded FL and the maximum yield of NFs and DNFs were reached after 4 h, and interestingly the distribution of NFs changed greatly (Table 2). Outstanding are the emergence of 2-NF as the major product and the disappearance of DNFs and 3-NF on all kinds of the support used. Insoluble tarry compound was formed as an oxidation product in addition to phthalate. It may be formed by the oxidative photopolymerization. The lower selectivity of the nitration showed that under photoirradiation, the contribution of oxidative degradation of FL was larger than that in the dark. The orders of the supports in degradation percentage and yield of the total nitro derivatives were similar to those observed in the dark reaction, except for Fe_2O_3. The largest yield of the total NFs was obtained for Al_2O_3 both in the photoreaction and in the dark reaction.

We assume that the nitration proceed as follows; for the dark reaction, electrophilic (ionic) nitration by N_2O_5, formed via eqs. 1 and 2, is the major process as has been observed in the nitration of arene in polar solvent since 3- and 8-NFs were the major products accompanied by some amount of 1- and 7-NFs.[4]

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (1)$$

$$NO_3 + NO_2 \rightarrow N_2O_5 \quad (2)$$

The nitrating species in this process has been proposed to be NO_2 from N_2O_5.[4] The electrophilic nitration by NO_2 observed in polar solvent[5] would be a minor process because it should have given only trace amount of 1- and 7-NFs accompanied by large amount of 3- and 8-NFs. Although the reaction of arenes with NO_3 radical also leads to nitroarenes,[8] FL is not reactive enough to undergo this type of reaction and NO_3 radical is rapidly consumed for the formation of N_2O_5 in the dark (eq.2). DNFs may be mainly formed by the reaction of NF with N_2O_5 since they disappeared in the photoreaction. Under photoirradiation, the photolysis of N_2O_5 and NO_2 results in the decrease of N_2O_5 and NO_2, and increase of NO_2 radical. Hence the nitration taking place in the dark can not arise and the formation of 3- and 8-NFs by this reaction is virtually suppressed. The increase of the concentration of NO_3 radical is responsible for the formation of 2-NF via the reactions proposed in gas-phase and in nonpolar solvents.[4,5] It involves the following three steps; first step involves the addition of NO_3 or NO_4 radical to position 3 of FL to form a transient adduct. Position 3 of FL is the most reactive site for radical addition and the NO_4 may be formed by the reaction of NO_2 with O_2.[5] Second step is the addition of NO_2 to the adjacent position 2, and the final step is the elimination of nitrogenous acid from the adduct.[4,5] Also 1-, 7-, and 8-NFs can be formed by the radical reaction since the order of positional reactivity for radical addition has been predicted to be 3 > 1 > 7 > 8 > 2.[9]

The heterogeneous reactions studied herein should be regarded as an important process for the atmospheric formation of mutagenic nitroarenes both during daytime and nighttime, since some DNFs which are formed in the dark have about twenty times as strong direct-mutagenic as 3-NF,[7] and 2-NF which is the major product under photoirradiation has been reported to be the most abundant atmospheric nitroarene.[1] Moreover, for graphite as a support the total yield of NFs was comparable to that for metal oxide supports both in the photoreaction and in the dark reaction, suggesting that oxidative degradation of FL should be retarded by carbonaceous particles of which source is vehicle exhaust abundant in urban area with heavy traffic. We are going to further our investigation about this heterogeneous nitration of FL under various conditions aiming to elucidate the effect of support particles on the reactivity of FL.

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