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Note

Potential for artifact formation during Tenax sampling of polycyclic aromatic hydrocarbons

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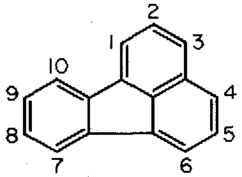
Tenax-GC solid adsorbent is widely used for sampling volatile organic compounds from the atmosphere[1–5]. Artifacts from the reactions of both the Tenax adsorbent and the adsorbed analytes with atmospherically important reactive gases, such as O_3 and NO_x, have been described[2,3]. Another reactive nitrogeneous species which has been calculated to be present at concentrations of up to *ca.* 15 parts per billion* (ppb) in nighttime atmospheres is N_2O_5 (ref. 6). We report here an artifact resulting from the reaction of the analyte fluoranthene with N_2O_5 during sampling on Tenax.



Fluoranthene

In recent studies of the gas-phase reaction of fluoranthene with N_2O_5 in a 6400-l environmental chamber[7,8], we have employed both Tenax-GC adsorbent cartridges and polyurethane foam (PUF) plugs for collection of the gas-phase reaction products. For sampling onto Tenax cartridges, flow-rate of *ca.* 1 l min^{-1} was used, while for sampling onto a PUF plug *ca.* 75% of a 6400-l chamber volume was sampled at the end of the exposure using a flow-rate of *ca.* $1.3 \cdot 10^3$ l min^{-1}. To serve as a control for any reaction between the collected fluoranthene adsorbed on the Tenax or PUF plug and N_2O_5 occurring during sampling, the Tenax cartridges and PUF plugs were doped with [$^2H_{10}$]fluoranthene.

Artifact formation, *i.e.* the reaction of [$^2H_{10}$]fluoranthene during sampling, was observed to be negligible on the PUF plugs. The only compounds observed from the PUF extracts were the doped [$^2H_{10}$]fluoranthene and fluoranthene and 2-nitrofluoranthene sampled from the chamber, demonstrating that 2-nitrofluoranthene is the gas-phase reaction product of fluoranthene with N_2O_5 (refs. 7, 8). In the extracts

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* Throughout this article, the American billion (10^9) is meant.

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from the Tenax cartridges, however, we observed all five isomers (1-, 2-, 3-, 7- and 8-) of nitrofluoranthene and nitro[$^2H_9$]fluoranthene, in addition to fluoranthene and [$^2H_{10}$]fluoranthene. Thus, all five nitrofluoranthene isomers were formed artifactually during sampling on Tenax. We have previously shown[7–9] that the 1-, 3-, 7- and 8-nitrofluoranthene isomers are the products of the reaction of fluoranthene adsorbed on filters and exposed to gaseous N_2O_5 (our expectation that these four isomers could be formed artifactually during sampling was the reason for doping the Tenax with [$^2H_{10}$]fluoranthene). The presence of 2-nitro[$^2H_9$]fluoranthene, however, was unexpected.

In our studies of the gas- and solution-phase reactions of N_2O_5 with fluoranthene under a variety of conditions[7,8] we have identified two distinct mechanisms of reaction which result in different nitrofluoranthene isomer distributions[8]. Both in carbon tetrachloride solution at ambient temperature and in the gas phase, N_2O_5 reacts with fluoranthene to produce 2-nitrofluoranthene as the sole mononitrofluoranthene isomer. We have postulated that this reaction occurs via a radical mechanism involving the molecule-assisted homolysis of covalent N_2O_5 (ref. 8). In contrast, the reaction of N_2O_5 with fluoranthene in the adsorbed state and in more polar solvents, or in carbon tetrachloride solution at subambient temperature (−15°C), produces the 1-, 3-, 7- and 8-nitrofluoranthene isomers by an ionic reaction mechanism involving the NO_2^+ ion[8]. The formation of 2-nitro[$^2H_9$]fluoranthene during sampling, therefore, indicates that the radical reaction mechanism involving covalent N_2O_5 with fluoranthene was occurring.

EXPERIMENTAL

During each experiment, the gases present in the chamber were sampled in parallel for 45 min through one Tenax cartridge held at ambient temperature (*ca.* 25°C) and a second cartridge cooled to *ca.* −15°C at a flow-rate through each cartridge of 1.2 l min^{-1}. The Tenax cartridges consisted of 6.3 mm O.D. Pyrex tubing packed with 0.1 g of Tenax-GC (60–80 mesh). The [$^2H_{10}$]fluoranthene (20 μg) was applied to the upstream end of the Tenax adsorbent in 200 μl of a diethyl ether solution, and pure nitrogen was flowed through the cartridges at *ca.* 1 l min^{-1} for 30 min to remove the solvent prior to sampling. For low temperature sampling, the U-tube Tenax cartridge was immersed in an ice–salt bath.

For the first two runs, 5 ppm of N_2O_5 were added to the 6400-l all-PTFE environmental chamber filled with dry purified air. For the third chamber run, 10 ppm of NO_2 was also added to drive the equilibrium between N_2O_5, NO_2 and the NO_3 radical towards N_2O_5:

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

After sampling, the Tenax cartridges were each eluted with 3 ml of diethyl ether. The ether was evaporated just to dryness and the solvent changed to acetonitrile for injection onto a high-performance liquid chromatography (HPLC) column. Polar Tenax degradation products were removed by fractionation on an Altex semi-preparative Ultrasphere ODS column (25 cm × 1 cm I.D.) with isocratic elution (acetonitrile–water, 70:30). The fraction containing the [$^2H_{10}$]fluoranthene and nitro[$^2H_9$]fluoranthene products was analyzed by gas chromatography–mass spectrometry (GC–MS) with multiple ion detection (MID) using a Finnigan 3200 GC–MS instrument, operating in the electron-impact mode and fitted with a cool on-column injector and a DB-5 capillary column eluting directly into the ion source.

For nitro[$^2H_9$]fluoranthene quantification, triphenylbenzene was added to an aliquot of the sample as an internal standard. [$^2H_{10}$]fluoranthene and its nitro derivatives were quantified by HPLC on the basis of their UV absorptions at 254 nm according to calibration curves determined for [$^2H_{10}$]fluoranthene and 2-nitro[$^2H_9$]fluoranthene.

RESULTS AND DISCUSSION

Fig. 1 shows the typical nitro[$^2H_9$]fluoranthene, isomer distribution resulting from sampling either an N_2O_5 (runs 1 and 2) or N_2O_5 + NO_2 (run 3) reaction mixture through Tenax cartridges doped with [$^2H_{10}$]fluoranthene and held at *ca.* 25°C (Fig. 1A) and *ca.* −15°C (Fig. 1B). The figure gives the *m/z* 256 molecular ion for the nitro[$^2H_9$]fluoranthene isomers together with the *m/z* 226 $[M - NO]^+$ characteristic fragment ion. While the 2- and 3-nitrofluoranthene isomers (or their deuterated analogues) were not baseline separated on the DB-5 capillary column used[10,11], the low abundance of the $[M - NO]^+$ fragment ion of the 2-nitrofluor-

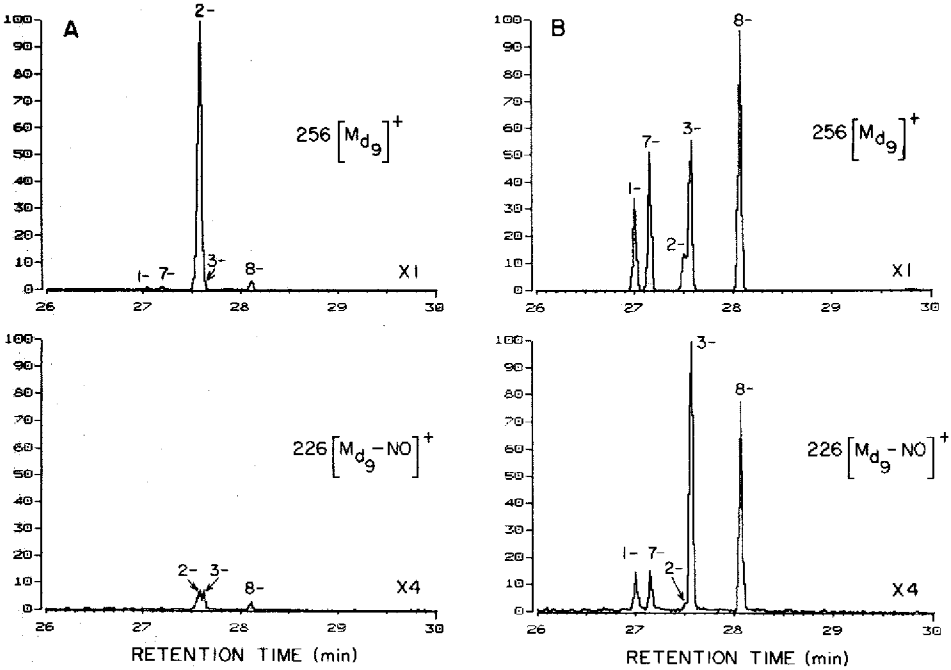

Fig. 1. MID traces showing the nitro[$^2H_9$]fluoranthene isomer distributions resulting from sampling a 5 ppm N_2O_5 + 10 ppm NO_2 reaction mixture from a 6400-l PTFE chamber for 45 min at *ca.* 1.2 l min^{-1} through Tenax-GC cartridges doped with [$^2H_{10}$]fluoranthene. (A) Tenax cartridge maintained at *ca.* 25°C. (B) Tenax cartridge cooled to *ca.* −15°C. Shown are the molecular ion *m/z* 256 $[M_{d_9}]^+$ and the characteristic fragment ion $[M_{d_9} - NO]^+$ at *m/z* 226.

anthene isomer[10] makes it possible to distinguish small quantities of the 3-nitrofluoranthene isomer in the presence of larger amounts of 2-nitrofluoranthene. Fig. 1 shows that 2-nitro[$^2H_9$]fluoranthene, together with much lower amounts of the 1-, 3-, 7- and 8-nitrol[$^2H_9$]fluoranthene isomers, was formed when sampling at 25°C (Fig. 1A). In contrast, all five nitrofluoranthene isomers were produced in more equal amounts when the sampling was carried out at *ca.* −15°C (Fig. 1B).

Table I gives the overall yield of the nitro[$^2H_9$]fluoranthene isomers formed for each run, together with the ratio of the 2-nitro[$^2H_9$]fluoranthene to 8-nitro[$^2H_9$]fluoranthene molecular ion intensities. This ratio reflects the relative abundance of the two types of reaction: the radical reaction which produces 2-nitrofluoranthene and the ionic electrophilic reaction which leads to the 1-, 3-, 7- and 8-nitrofluoranthene isomers[8]. At *ca.* −15°C, the overall yield of nitration ranged from <1 to *ca.* 3% and the 2-nitro[$^2H_9$]fluoranthene/8-nitro[$^2H_9$]fluoranthene ratio was <1, indicating that the reaction was largely ionic. For a sampling temperature of *ca.* 25°C, the overall yield of nitration increased to 6–8% and the 2-nitro[$^2H_9$]fluoranthene/8-nitro[$^2H_9$]fluoranthene ratio increased to 10–20. Thus the yields of the 1-, 3-, 7- and 8-nitro[$^2H_9$]fluoranthene isomers were similar at both temperatures, while the 2-nitro[$^2H_9$]fluoranthene yield increased dramatically at the higher temperature.

2-Nitro[$^2H_9$]fluoranthene was produced in an essentially identical yield in run 3, in which 10 ppm of NO_2 was added with the N_2O_5 to drive the equilibrium 1 between N_2O_5, NO_2 and NO_3 radicals towards N_2O_5. Since the concentration of NO_3 radicals was *ca.* 20 times lower in this exposure, this demonstrated that N_2O_5, and not the NO_3 radical, was the nitrating species.

Since we have observed that the reaction of fluoranthene adsorbed on glass fiber and PTFE-impregnated glass fiber filters with gaseous N_2O_5 produces the 1-, 3-, 7- and 8-nitrofluoranthene isomers and that the gas-phase reaction of fluoranthene with N_2O_5 forms exclusively 2-nitrofluoranthene, the data presented here sug-

TABLE I

THE OVERALL YIELD OF NITRATION AND THE RATIO* OF 2- TO 8-NITRO[$^2H_9$]FLUORANTHENE (2-NFL-d_9/8-NFL-d_9) FROM SAMPLING N_2O_5 AND N_2O_5 + NO_2 MIXTURES THROUGH TENAX CARTRIDGES DOPED WITH [$^2H_{10}$]FLUORANTHENE

Run No.	*Species added to chamber*	*Sampling conditions*			
		−15°C		*25°C*	
		Nitration yield (%)	*2-NFL-d_9/ 8-NFL-d_9*	*Nitration yield (%)*	*2-NFL-d_9/ 8-NFL-d_9*
1	N_2O_5 (5 ppm)**	<1	0.7	6	9
2	N_2O_5 (5 ppm)**	*ca.* 3	0.2	8	10
3	N_2O_5 (5 ppm) + NO_2 (10 ppm)***	*ca.* 2	0.1	8	20

* The ratio of the peak heights of the *m/z* 256 molecular ions for 2- and 8-nitro[$^2H_9$]fluoranthene.

** Also contained *ca.* 0.001 ppm of NO_3 radicals and *ca.* 0.5 ppm each of NO_2 and nitric acid.

*** Also contained *ca.* 0.00005 ppm of NO_3 radicals and *ca.* 0.5 ppm of nitric acid.

gest that a gas-phase reaction leading to the formation of 2-nitro[$^2H_9$]fluoranthene occurred within the Tenax cartridges. The observation that the yields of 2-nitro[$^2H_9$]fluoranthene were higher at 25°C than at -15°C is consistent with the increased amount of [$^2H_{10}$]fluoranthene anticipated to be present in the gas phase at the higher temperature. However, significant gas-phase reaction would be surprising considering the high collection efficiency of Tenax and the absence of [$^2H_{10}$]fluoranthene breakthrough under our sampling conditions, and it is possible that the 2-nitro[$^2H_9$]fluoranthene formed at 25°C resulted from an adsorbed phase radical reaction.

Clearly, the present data show that sampling gas-phase polycyclic aromatic hydrocarbons (PAH) from environmental chambers or the ambient atmosphere onto Tenax solid adsorbent in the presence of oxides of nitrogen can lead to artifact formation of nitro derivatives via reactions within the Tenax adsorbent. For sampling of PAH, we advise the use of Tenax doped with deuterated PAH to assess directly the importance of these artifact processes during such sampling.

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