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Study on Origins of Particle-associated Nitrotriphenylenes: Isomer Distribution in Direct Emissions and in Secondary Formations

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Introduction

In recent years, the possibility of atmospheric formation of nitrotriphenylenes (NTPs), including the strongly mutagenic isomer 2-nitrotriphenylene (2-NTP), was suggested from the characteristics of seasonal and locational occurrences of ambient NTPs. Since 2-NTP has much higher mutagenic activity than 1-nitropyrene (1-NP) and 2-nitrofluoranthene (2-NF), which are the most abundant nitro-PAH in the atmosphere, and concentrations of 2-NTP comparable to those of 1-NP and 2-NF have been observed in airborne particles, the contribution of 2-NTP to atmospheric mutagenicity is expected to be significant. In view of their influence on human health, it is of great importance that more detailed data about the environmental occurrence of NTPs are obtained.

In this study, the formation of 1-nitrotriphenylene (1-NTP) and 2-NTP via gas-phase OH or NO₃ radical-initiated reaction of triphenylene is shown for the first time using a flow reaction system. We also conducted diesel exhaust particles (DEP) sampling and determined the concentration of NTPs in DEP using GC/MS and HPLC analysis. Furthermore, the isomer distribution of NTPs obtained from the laboratory nitration of triphenylene was contrasted with that observed in ambient particles and DEP.

Experimental Section

A 30-L Pyrex flow reactor (5 cm ID × 15 m length) with black-light or fluorescent-light lamps was employed for gas-phase OH or NO₃ radical-initiated reactions of triphenylene. Any reaction products were collected on a polyurethane foam (PUF) plug (5 cm OD × 7 cm length) throughout the reaction, at a total gas-flow rate of 0.7 L min⁻¹ for 72 h. OH radicals were generated by photolysis of HONO, which was prepared by reaction of sodium nitrite with gaseous hydrochloric acid. The resulting HONO had a concentration of ca. 700 ppbv; a by-product was NO₂ (ca. 40 ppbv), which can act as a nitration reagent for triphenylene, and thus no further NO₂ was added to the system. NO₃ radicals were generated by the reaction of 10 ppmv NO₂ and 5 ppmv O₃.

The exhaust emissions of a diesel-powered vehicle (a 1988 Nissan Civilian with a diesel engine of model U-BW40, 3465 cc displacement volume) were collected under idling conditions. The fresh exhaust was vigorously mixed with ambient air, which was negligibly polluted, in a 25-m³ dark dilution chamber using a large fan. The generated DEP were immediately collected using an open-face air sampler (Kimoto Electric, Model 120) on quartz fiber filters (Advantec MFS, QR100) at flow rate of 900 L min⁻¹.

Airborne particles were collected at the rooftop level of a three-story building approximately 10 m above ground level at Osaka Prefecture University, Sakai, Osaka, Japan. The sampling campaigns were performed using high-volume air samplers (Kimoto Electric, Model 120) on quartz

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fiber filters (Advantec MFS, QR100), at a flow rate of 1500 L min⁻¹, during September 3 and 6, 2001, and September 2 and 3, 2002, with a regular collection time of 3 h per filter; thus, 31 sample filters were obtained.

Both the reaction products collected on the PUF plugs and the soluble organic fraction (SOF) of the filter samples were extracted with benzene/ethanol (3/1, v/v) or dichloromethane under sonication. The SOF was washed with NaOH and H₂SO₄ or fractionated using preparative HPLC on a silica gel column. And then, an aliquot of the sample solution concentrated to 0.5 mL was subjected to chemiluminescence detection HPLC or GC/MS analysis.

Results and Discussion

Table shows the isomer distribution of NTPs formed via OH or NO₃ radical-initiated reactions in the gas-phase, in DEP, and in ambient airborne particles. More 2-NTP than 1-NTP was formed in the OH radical-initiated reaction: the observed 2-NTP/1-NTP ratio was 1.25. In contrast, the main product of the NO₃ radical-initiated gas-phase reaction was 2-NTP, with only trace amounts of 1-NTP formed. Since the amount of 1-NTP formed was smaller than the quantification limit of the HPLC system, the 2-NTP/1-NTP ratio in the NO₃ radical-initiated reaction could not be determined precisely, but is known to be greater than 1.5. The gas-phase formation of nitro-PAH via OH or NO₃ radical-initiated reactions involve addition of OH or NO₃ radical at the carbon atoms of highest electron density, followed by ortho-addition of NO₂ and loss of water or nitric acid. In triphenylene, the carbon at the 1-position is the most electron-rich; therefore, the preferential formation of 2-NTP over 1-NTP in the gas-phase radical-initiated reaction is consistent with the reported mechanisms.

Table also shows the concentration ratios of 1-NTP and 2-NTP to 1-NP in DEP and in the airborne particles. In all the DEP samples, 1-NTP and 2-NTP were detected for the first time, as well as 1-NP, the nitro-PAH most commonly found in emissions. The observed concentration of 1-NP in DEP ranged from 21 to 37 pmol mg⁻¹. Concentrations of DEP-associated 1-NTP and 2-NTP ranged from 1.5 to 7.7 pmol mg⁻¹ and 0.28 to 5.4 pmol mg⁻¹, respectively, and were much lower than the concentration of 1-NP. The concentration ratios of 1-NTP/1-NP and 2-NTP/1-NP in DEP were 0.13 and 0.08, respectively, while the mean concentration ratios of 1-NTP and 2-NTP to 1-NP associated with airborne particles were higher, at about 0.25 and 0.37, respectively. That is, the values of 1-NTP/1-NP and 2-NTP/1-NP in ambient air are higher than those in DEP by factors of about 2 and 5, respectively. The fact that higher concentration ratios of 1- and 2-NTPs to 1-NP are observed in airborne particles than in DEP implies that the source of airborne 1-NTP and 2-NTP is not only direct emissions from diesel-powered vehicles but also atmospheric nitration of triphenylene. The concentration ratio of 2-NTP/1-NTP in DEP was 0.59, but the mean 2-NTP/1-NTP ratio in the atmosphere was > 1.6, which is higher than that found in DEP by a factor of 3. This result implies that significant amounts of airborne 2-NTP are selectively formed via radical-initiated reactions, as in the flow chamber experiment, resulting in a high 2-NTP/1-NTP value.

Thus, the radical-initiated reactions of gas-phase triphenylene should be a significant source of airborne NTPs, although which radical participates significantly in the atmospheric formation of NTPs is still unknown. In order to understand the factors affecting the formation and behavior of atmospheric NTPs, further observation of ambient NTPs and triphenylene is required, taking into account typical gaseous atmospheric pollutants, such as nitrogen oxides, and meteorological parameters.

Table. Comparison of concentration ratios of selected nitroarenes in DEP, ambient airborne particles, and the products from the radical-initiated reactions.

	DEP	Airborne Particles	OH reaction	NO ₃ reaction
1-NTP/1-NP	0.13	< 0.25	-	-
2-NTP/1-NP	0.08	0.37	-	-
2-NTP/1-NTP	0.59	> 1.6	1.2	> 1.5