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Characterization of nitromethane emission from automotive exhaust

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HIGHLIGHTS

- Nitromethane was observed in diesel and gasoline engine exhausts.
- Nitromethane emission increased with increasing acceleration at low velocity.
- Nitromethane was also emitted at high vehicle velocity range.
- Nitromethane emission was enhanced when the aftertreatment was cold.
- It is likely that the NO_x reduction catalyst greatly reduced nitromethane emission.

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ABSTRACT

We carried out time-resolved experiments using a proton-transfer-reaction mass spectrometer and a chassis dynamometer to characterize nitromethane emission from automotive exhaust. We performed experiments under both cold-start and hot-start conditions, and determined the dependence of nitromethane emission on vehicle velocity and acceleration/deceleration as well as the effect of various types of exhaust-gas treatment system. We found that nitromethane emission was much lower from a gasoline car than from diesel trucks, probably due to the reduction function of the three-way catalyst of the gasoline car. Diesel trucks without a NO_x reduction catalyst using hydrocarbons produced high emissions of nitromethane, with emission factors generally increasing with increasing acceleration at low vehicle velocities.

1. Introduction

Diesel and gasoline engines are important sources of nitrogen oxides (NO_x), volatile organic compounds (VOCs), and fine particulate matter (PM) in the urban atmosphere. These pollutants not only impact air quality but also adversely affect human health (Lloyd and Cackette, 2001; Monks et al., 2009). Diesel and gasoline engine exhausts contain organic components such as polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs (nitro-PAHs), some of which are probable human carcinogens (International Agency for Research on Cancer (IARC), 1989). Nitro-PAHs also account for a major portion of the direct-acting mutagens in diesel exhaust particles (DEPs) (Rosenkranz and Mermelstein, 1983; Schuetzle, 1983; Hayakawa et al., 1997). In addition to nitro-PAHs, nitrophenols, including 4-nitrophenol, 2-nitrophenol, 2,4-dinitrophenol, and 3-methyl-4-nitrophenol, in DEPs have attracted attention because of their vasodilatory, estrogenic, and anti-androgenic activities (Taneda et al., 2004).

We recently used proton-transfer-reaction mass spectrometry (PTR-MS) for on-line measurement of gaseous nitro-organic compounds in diesel exhaust during the Japanese JE05 transient cycle (Inomata et al., 2013). On-line measurement is essential in analyzing gaseous nitro-organic compounds because artifacts due

Abbreviations used: NO_x, nitrogen oxides; VOC, volatile organic compound; NMVOC, non-methane volatile organic compound; PM, particulate matter; PAH, polycyclic aromatic hydrocarbon; nitro-PAH, nitrated PAH; IARC, International Agency for Research on Cancer; DEP, diesel exhaust particle; PTR-MS, proton-transfer-reaction mass spectrometry; GC/FID, gas chromatography with flame ionization detection; GC/MS, gas chromatography–mass spectrometry; vehicle-GASOLINE, compact gasoline passenger car with a three-way catalyst; vehicle-DOC, diesel truck with an oxidation catalyst; vehicle-DPNR, diesel truck with a PM–NO_x catalytic reduction system; vehicle-SCR, diesel truck with a urea-selective catalytic reduction system.

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to nitration of organic compounds can readily form during sampling (Levsen et al., 1988; Tremp et al., 1993). Moreover, time-resolved measurements are helpful in determining when nitro-organic compounds are generated during vehicle acceleration and deceleration, and such information will be useful for improving engine design and exhaust-gas treatment (aftertreatment) to reduce emissions of nitro-organic compounds. In the previous study by Inomata et al. (2013), three diesel trucks, each with a different type of aftertreatment, were tested on a chassis dynamometer system. Among the mononitro-organic compounds detected, nitromethane, a Group 2B carcinogen ("possibly carcinogenic to humans"; IARC, 2000), was commonly observed and found to be related to the emissions of carbon monoxide, benzene, and acetone. The emissions of other nitro-organic compounds, such as dihydroxynitrobenzenes and C_7-, C_8-, C_9-, and C_{10}-nitrophenols, depended on the vehicle and possibly the type of aftertreatment.

Seizinger and Dimitriades (1972) detected nitromethane in exhaust from vehicles burning simple hydrocarbon fuels by GC/FID, and nitromethane has been detected by GC/MS in urban ambient air in Brazil and Algeria at concentrations ranging between 1 and 9 ppbv (Grosjean et al., 1998; Yassaa et al., 2001). Our group recently carried out an on-line measurement of the nitro-organic compounds at a busy intersection in Kawasaki, a large city in Japan. Nitromethane was detected, with a diurnal variation similar to that of NO_x. Although the average nitromethane concentration during the measurement was 0.1 ppbv, the maximum was approximately 5 ppbv (Inomata et al., manuscript in preparation).

The rate constant for the reaction of nitromethane with OH radicals at 296 K is $(1.6 \pm 0.1) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} (Liu et al., 1990). Thus, at [OH] $= 1 \times 10^6$ molecule cm^{-3}, the lifetime of nitromethane is calculated to be approximately 2 years. The photodissociation lifetime of nitromethane calculated with solar flux intensities at a zenith angle of 45°, however, is approximately 10 h at ground level (Taylor et al., 1980). Therefore, the photodissociation is important as a loss process of nitromethane in the atmosphere compared with the reaction with OH radicals.

Nitromethane photodissociates mainly by rupture of the C–N bond to produce a methyl radical and NO_2:

$$CH_3NO_2 + h\nu \rightarrow CH_3 + NO_2 \quad (1)$$

Because nitromethane from urban areas persists in the atmosphere during atmospheric transport, photodissociation of nitromethane can serve as a source of NO_x in remote regions. Thus we believe nitromethane has the potential to affect human health and air quality in both urban and rural regions.

Recently, several techniques were used for on-line analysis of multiple VOCs in diesel vehicle exhaust; some examples include ion-molecule reaction mass spectrometry with Hg^+ as the primary ion (Heeb et al., 2002), proton-transfer-reaction mass spectrometry (PTR-MS) (Jobson et al., 2005), selected-ion flow-tube mass spectrometry (Smith et al., 2004), supersonic jet/resonance-enhanced multiphoton ionization time-of-flight mass spectrometry (Misawa et al., 2009), and single-photon ionization time-of-flight mass spectrometry (Yamamoto et al., 2012). However, the previous studies did not discuss emissions of nitromethane. In the present work, we focused on the emission of nitromethane from automotive exhaust. We performed experiments under both cold-start and hot-start conditions, and determined the dependence of nitromethane emission as a function of vehicle velocity and acceleration/deceleration as well as the effect of various types of aftertreatment.

2. Materials and methods

2.1. Experiments with the chassis dynamometer

Experiments were carried out on a chassis dynamometer system equipped with a constant-volume sampler (DLT-1860 (40 m^3 min^{-1}) or CVS-7400T (120 m^3 min^{-1}), Horiba, Kyoto, Japan; hereafter "dilution tunnel") at the National Traffic Safety and Environment Laboratory (Yamada et al., 2011; Inomata et al., 2013). A compact gasoline passenger car (vehicle-GASOLINE), the most popular car size in Japan (Yamada, 2013), was tested in addition to diesel trucks with an oxidation catalyst (vehicle-DOC), a PM–NO_x reduction system (vehicle-DPNR), or a urea-selective catalytic reduction system (vehicle-SCR) (Inomata et al., 2013). Specifications for these vehicles are listed in Table 1. A three-way catalyst was used for aftertreatment of the exhaust gas from the gasoline vehicle. Exhaust gas was diluted, on average, by a factor of 56 (vehicle-DOC), 14 (vehicle-DPNR), 69 (vehicle-SCR), or 41 (vehicle-GASOLINE) with HEPA (high-efficiency particulate air)-filtered and charcoal-filtered air (hereafter "background air"). The background air was maintained at 298 K and 50% relative humidity. The vehicle was set on the chassis dynamometer and driven according to the Japanese JE05 transient emission test cycle (diesel trucks) or the

Table 1
Specifications of tested vehicles.

	Vehicle-DOC	Vehicle-DPNR	Vehicle-SCR	Vehicle-GASOLINE
Manufacturer	Isuzu	Hino	UD Trucks	Toyota
Engine model	KR-4HL1	N04C	GE13TB	3SZ-VE
Vehicle model	KR-NKR81EA	PH-XZU414	ADG-CG4ZL	DBA-QNC21
Engine type	L4, DI[a]	L4, DI[a]	L6, DI[a]	L4, MPI[h]
Intake air management	NA,[b] EGR[c]	Turbocharger, EGR[c]	Turbocharger, EGR[c]	NA,[b] EGR[c]
Displacement (L)	4.78	4.01	13.07	1.495
Max. power (kW rpm^{-1})	96/3000	110/3000	279/1800	80/6000
Injection system	Common rail	Common rail	Common rail	MPI[h]
Aftertreatment	DOC[d]	DPNR[f]	Urea-SCR[g]	3-Way catalyst
GVW[e] (kg)	4489	5035	24930	1050
Emission regulation	03 Japan	03 Japan	05 Japan	05 Japan
Fuel	JIS No. 2	JIS No. 2	JIS No. 2	Japanese commercial gasoline (regular)

[a] Direct injection.
[b] Natural aspiration.
[c] Exhaust gas recirculation.
[d] Diesel oxidation catalyst.
[e] Gross vehicle weight.
[f] Diesel PM-NO_x reduction system.
[g] Selective catalytic reduction.
[h] Multipoint injection.