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Formation of Formaldehyde from Methyl *tert*-Butyl Ether (MTBE) upon UV Irradiation

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MTBE has been used as an oxygenate in reformulated gasoline and oxyfuels in large quantities. Consequently, it has been released into the environment constantly and consistently (Brown, 1997). Therefore, concerns about its possible adverse effects to humans have been raised (Clary, 1997; Balter, 1997). Detailed reviews on possible human exposure to MTBE through atmospheric and potable water have been recently published (Brown, 1997). Among the many variability of exposure studies, the time of sampling may play an important role because MTBE is volatile and readily decomposes in UV light. The degradation products of MTBE have not yet been comprehensively identified. In the present study, the formation of carbonyl compounds, in particular formaldehyde, from MTBE by UV irradiation was investigated in order to assess possible adverse effects caused by MTBE in the environment.

Formaldehyde has been classified as a hazardous air pollutant by the United States Environmental Protection Agency (CAA, 1997). It is emitted from various materials, including building materials, cosmetic and paper products, and permanent press fabrics, as well as from combustion sources such as auto exhaust, refinery emissions, and cigarette smoke (WHO, 1987). Formaldehyde is a probable human carcinogen. It causes squamous cell carcinomas and several kinds of benign tumors in the nasal passages of mice and rats (Feinman, 1988). Therefore, it is important to study whether MTBE is an additional source of toxic formaldehyde in the environment or not.

MATERIALS AND METHODS

A preliminary photodegradation study on MTBE (99.8%) (Aldrich Chemical Co., Inc., Milwaukee, WI) was conducted using an ethanol solution. An ethanol solution (5 mL) of MTBE (4 µL/mL, 10 µL/mL, 20 µL/mL, 50 µL/mL, 60 µL/mL, 80 µL/mL, or 100 µL/mL) in a 20 mL sealed Pyrex test tube was allowed to stand under a regular home fluorescent lamp for 18 h. Carbonyl compounds formed from photodegradation of MTBE were derivatized with cysteamine to corresponding thiazolidines, which were subsequently analyzed by gas chromatography with a nitrogen/phosphorus detector using a method previously reported (Yasuhara and Shibamoto, 1989).

A flask containing 40 mL of MTBE was purged with a purified air stream at 8 mL/min for 24 h. After 24 h, 40 mL of MTBE was completely vaporized. The vapor-phase MTBE was allowed to travel through a 2 m x 0.5 mm Pyrex® glass

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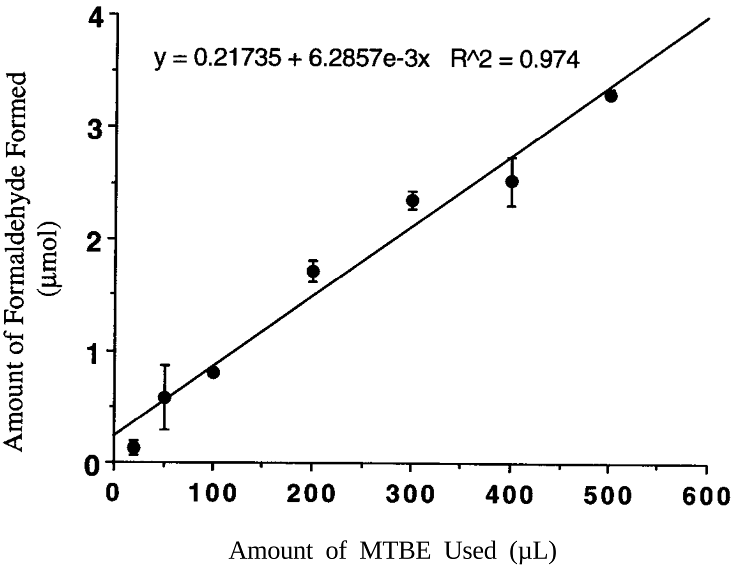

Figure 1. Amounts of formaldehyde formed from MTBE in ethanol solutions upon photon-radiation.

column which was irradiated with a regular home fluorescent lamp. The irradiated vapor-phase MTBE was purged into 250 mL deionized water containing 1.8 g of cysteamine hydrochloride (pH = 6.8), which was simultaneously and continuously extracted with 70 mL of chloroform using a simultaneous purging and extraction apparatus developed previously (Umano and Shibamoto, 1987). Carbonyl compounds formed from MTBE were derivatized to thiazolidines and subsequently analyzed by gas chromatography with a nitrogen/phosphorus detector.

A Hewlett-Packard (HP) model 5980 gas chromatograph (GC) equipped with 30 m x 0.25 mm i.d. (df = 1 mm) DB-Wax bonded-phase fused silica capillary column (J & W Scientific, Folsom, CA) and a nitrogen phosphorus detector (NPD) was used. The linear velocity of the helium carrier gas was 30 cm/sec. The injector and the detector temperatures were 250 °C. The oven temperature was programmed from 60 to 200 °C at 3 °C/mm.

RESULTS AND DISCUSSION

Figure 1 shows the amounts of formaldehyde formed from MTBE in ethanol solutions upon photoirradiation. The values are mean ± standard deviation (n = 3). A linear relationship between the amount of MTBE and the amount of formaldehyde formed was obtained (R^2= 0.974). When 500 µL of MTBE was irradiated for 16 h, 3.3 µmoL formaldehyde was formed.

Because the formation of formaldehyde from MTBE upon photoirradiation was confirmed, possible formation of formaldehyde from vapor-phase MTBE by photoirradiation was investigated. Formaldehyde, butanal, and 2-butanone were isolated and identified in the photoirradiated vapor-phase MTBE. When 40 mL of MTBE was irradiated under the system described above, 2.72 ± 0.8 µmol of formaldehyde, 25.6 ± 0.5 µmol of butanal, and 12.4 ± 0.9 µmol of 2-butanone were recovered. The values are mean ± standard deviation (n = 3).

Formaldehyde is one of the most abundant volatile organic compounds in the environment. It is introduced to the environment as a result of natural processes, such as decomposition of plant residues, and from man-made sources, such as automotive exhaust. Formaldehyde is produced industrially in large quantities and used in many applications. Therefore, formaldehyde is always present in atmospheric air. For example, air concentrations of formaldehyde near the ground in coastal, mountain, or oceanic areas, ranged from 0.05 to 14.7 µg/m^3, and the majority of concentrations were within the range 0.1-2.7 µg/m^3 (WHO, 1989).

Table 1 shows a rough estimation of formaldehyde formation from MTBE emitted from various sources. The total amount of formaldehyde formed from MTBE seems insignificant because formaldehyde emitted from automobile exhaust was estimated at 35 x 10^6 Kg/year in Germany alone (Kitchens et al., 1976).

Table 1. Estimated amount of formaldehyde formed from MTBE emitted to the atmosphere. Values were calculated using the results from the present study. One gram of MTBE produced 3.06 x 10^{-5} g of formaldehyde.

Source	Total emissions of MTBE (million lb/year)	Formaldehyde (Kg/year)
Petroleum refineries	3.0*	41.6
Evaporative emissions	39†	541
Tailpipe emissions	110†	1530

* Refer to EPA (1995)

† Refer to Brown (1995)

On the other hand, the occupationally exposed populations experience far higher concentrations than do other populations (Brown, 1997). For example, estimated exposure levels in certain occupational settings ranged from 0.06 mg/m^3 in paper and paper board manufacturing to 9.96 mg/m^3 in a biology teaching laboratory (CWF, 1984).

The levels of formaldehyde recovered in the present study seem to play an insignificant role in the adverse effects caused by formaldehyde contamination. However, it should be noted that use of MTBE as an oxygenate in reformulated gasoline and oxyfuels contributes its share to the many other sources of formaldehyde in the environment.

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