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The Atmospheric Reactivity of α-Methyltetrahydrofuran

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■ Biomass-derived α-methyltetrahydrofuran (MTHF) has been proposed as an automotive fuel additive. Since MTHF is a volatile organic compound, the environmental impact of evaporation to the atmosphere needs to be considered. The major loss process of MTHF in the atmosphere is expected to occur via reaction with hydroxyl radical; hence we have conducted a study of the kinetics of the reaction OH + MTHF → products using both absolute (flash photolysis resonance fluorescence) and relative rate techniques. The absolute rate experiments were performed over the temperature range 240–400 K at total pressures of 35 Torr (4.7 kPa) argon; the relative rate experiments were conducted at 295 K in 740 Torr (99 kPa) synthetic air. The results from both techniques were in good agreement and yield $k_1 = (2.52 \pm 0.74) \times 10^{-12}$ exp-$[(650 \pm 80)/T]$ cm^3 molecule^{-1} s^{-1}, with k_1(298 K) = 2.2 $\times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Quoted errors represent 2σ from the least-squares analysis and do not include any estimate of systematic errors. The implications of these results for the atmospheric chemistry of MTHF are discussed.

Introduction

At present there is substantial interest within the automotive and petroleum industries in alternative liquid fuel formulations for powering spark-ignited internal combustion engines in automobiles and light-duty trucks. α-Methyltetrahydrofuran (MTHF) has been proposed as a biomass-derived automotive fuel extender (*1*, *2*) for reasons that include its ease of production from cellulosic biomass such as waste paper, high Btu value, good antiknock characteristics, and satisfactory performance when mixed in a 10% blend with gasoline in conventional internal combustion engines. Since MTHF is a volatile organic with a vapor pressure at 295 K of ≃75 Torr, its use as an automotive fuel additive will result in its evaporative emission to the atmosphere. Following such release, the main atmospheric fate of MTHF is expected to be reaction with OH radicals, since (by analogy with other ethers) photolysis (*3*), reaction with O$_3$ (*4*), and reaction with NO$_3$ radicals (*5*) would be negligibly slow. Thus, to assess the tropospheric lifetimes of fuel additives such as MTHF and evaluate the atmospheric impact of their emissions, accurate kinetic data on their reactivity with

OH radicals are needed. This information is also useful for modeling combustion chemistry since such reactions play an important role in the oxidation of organic compounds in combustion systems (*6*). In the case of MTHF, there is presently no experimental information on its reaction with hydroxyl radicals.

As part of ongoing experimental programs in our laboratories to assess the atmospheric reactivity of oxygenated organics, including alternative fuels and fuel additives (*7–11*), we have performed a laboratory investigation of the kinetics of reaction 1. Two sets of experiments were

$$\text{OH} + \text{MTHF} \rightarrow \text{products} \qquad (1)$$

performed, using absolute (at NIST) and relative (at Ford) rate techniques. The absolute technique used was flash photolysis resonance fluorescence at temperatures over the range 240–400 K and 35 Torr total pressure of argon. The relative technique was used at 295 K and atmospheric pressure (≃740 Torr) of synthetic air.

Experimental Section

The apparatus and experimental techniques used in both the absolute (*12–14*) and relative study (*11*, *15*) have been described in detail previously and are only briefly detailed here.
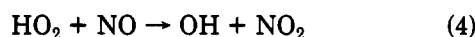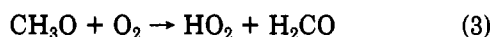
Absolute Experiments. Hydroxyl radicals were produced by the vacuum ultraviolet (λ > 165 nm) flash photolysis of H$_2$O (≃0.1 Torr) and monitored as a function of time by their fluorescence at ≃310 nm (A$^2\Sigma^+$ → X$^2\Pi$, 0–0 band) excited by a microwave discharge resonance lamp. Depending on the initial OH concentration, the fluorescence signals from 60 to 200 flash photolytic experiments were averaged to generate a kinetic decay curve suitable for least-squares analysis.

Reaction mixtures consisting of water vapor, MTHF, and Ar diluent were prepared manometrically in 5-L Pyrex bulbs. To avoid the accumulation of photolysis or reaction products, the gas mixtures were flowed through the reaction cell at a total pressure of 35 Torr (Ar diluent) with a typical residence time of ≃5 s. The flash lamp was operated at discharge energies of 40–125 J per flash at a repetition rate of 0.25 Hz, resulting in replenishment of the reaction mixture every few flashes. In all cases the

flash duration was negligible in comparison with the OH kinetic lifetimes. Temperature regulation of the mixtures was achieved by the passage of cooled methanol or heated oil between the outer walls of the spherical, double-walled, Pyrex reaction vessel ($\simeq$100-cm^3 volume), and the gas temperature was measured by a Chromel/Alumel thermocouple projecting into the center of this cell. The argon diluent gas had a manufacturer's stated purity of 99.998% and was used without further purification.

For the apparatus setup and flash lamp conditions used in this investigation, the initial hydroxyl radical concentration was estimated as $10^{10} < [OH]_0 < 10^{11}$ molecules cm^{-3}, based upon a comparison with previous experiments from this laboratory and with similar systems used by other workers (16, 17). Thus, the reagent concentration range of (0.3–1.5) $\times$ 10^{13} molecules cm^{-3} was high enough to assure first-order kinetic conditions with respect to the hydroxyl radical decay.

Relative Rate Experiments. Hydroxyl radicals were formed through the photolysis of methyl nitrite in air

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \qquad (2)$$

$$CH_3O + O_2 \rightarrow HO_2 + H_2CO \qquad (3)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (4)$$

Reaction mixtures consisting of a reference organic (diethyl ether or di-n-butyl ether), MTHF, and methyl nitrite diluted in synthetic air were introduced into a Teflon bag (volume $\simeq$100 L) and left to mix for at least 15 min. In the presence of OH radicals there is a competition between the reference organic and MTHF by reactions 1 and 5

$$OH + MTHF \rightarrow products \qquad (1)$$

$$OH + reference\ organic \rightarrow products \qquad (5)$$
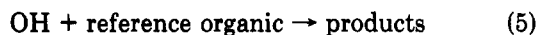
Providing that MTHF and the reference organic are lost solely by reactions 1 and 5 and that neither organic is reformed in any process, it can then be shown that

$$\ln \frac{[reactant\ organic]_{t_0}}{[reactant\ organic]_t} = \frac{k_1}{k_5} \ln \frac{[reference\ organic]_{t_0}}{[reference\ organic]_t}$$

where $[reactant\ organic]_{t_0}$ and $[reference\ organic]_{t_0}$, and $[reactant\ organic]_t$ and $[reference\ organic]_t$ are the concentrations of the reactant and reference organics at times t_0 and t, respectively, and k_1 and k_5 are the rate constants of reactions 1 and 5.

Methyl nitrite was prepared as described previously (11) and its purity was checked by FTIR spectroscopy; no observable impurities were detected. Diethyl ether and di-n-butyl ether were obtained from commercial sources at purities of at least 99% and were used as received.

Gas analyses were carried out on a Hewlett-Packard Model 5880A gas chromatograph equipped with a split/splitless injector, 30 m $\times$ 0.25 mm 5% phenyl methyl silicone column and a flame ionization detector. The initial concentrations of reactants in the Teflon bags were typically 10–20 ppm MTHF and the reference organic and 50–100 ppm methyl nitrite. The sample of MTHF used in both the absolute and the relative rate experiments was obtained at 99% purity stabilized with 1% of butylated hydroxytoluene (BHT). Before use the sample was thoroughly degassed. A GC analysis established the purity of the vapor from this sample as >99.7% with a small (<0.3%) BHT impurity.

Results

Absolute Study. At low radical concentrations, the OH fluorescence is directly proportional to the OH concen-
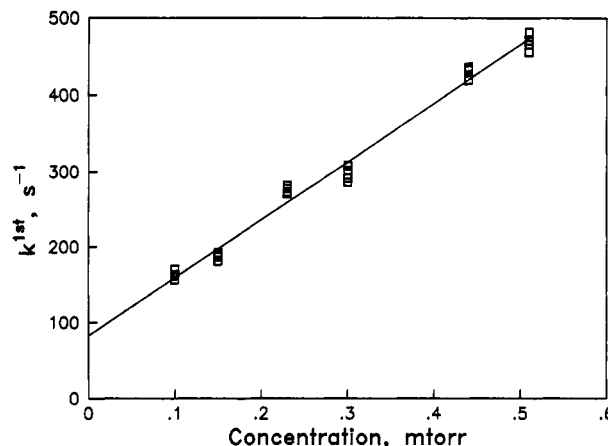

Figure 1. Plot of k^{1st} versus α-methyltetrahydrofuran concentration at 298 K.

tration and the first-order rate expression can be integrated to obtain

$$F_t = F_{t_0} \exp[-k^{1st}(t - t_0)] =$$
$$F_{t_0} \exp[-(k_0 + k_1[MTHF])(t - t_0)]$$

$$\ln [F_t/F_{t_0}] = -(k_0 + k_1[MTHF])(t - t_0)$$

where F_t and F_{t_0} are the OH radical fluorescence intensities at times t and t_0 respectively, k^{1st} is the total first-order decay rate, k_0 is the first-order rate constant for OH removal in the absence of reactant (attributed to diffusion out of the viewing zone and reaction with possible impurities in the argon diluent gas), and k_1 is the bimolecular rate constant for the reaction of OH with MTHF. Values of k^{1st} were determined for various reactant concentrations by weighted linear least-squares analysis of the experimental OH fluorescence decay curves and ranged from 20 to 1000 s^{-1}. Values for k_1 were then determined from linear least-squares analyses of plots of the OH decay rate versus the reactant concentration.

In all experiments, exponential decays of the resonance fluorescence signal were observed over at least 3 half-lives and the measured decay rates demonstrated a linear dependence on the reactant concentration. Variation of the flash energy by a factor of 3 had no observable effect on the measured rate constants, suggesting the present work to be free from complications arising from secondary reactions involving reactant photofragments. Figure 1 shows the data obtained at 298 K. The linear least-squares analysis of the data is indicated by the line drawn in Figure 1 and yields a value for the bimolecular rate constant of $k_1 = (2.27 \pm 0.17) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Quoted errors are 2σ from the statistical analysis. Similar analysis of the data obtained at other temperatures yielded the following values of k_1 (expressed in units of 10^{-11} cm^3 molecule^{-1} s^{-1}): 240 K, 3.77 $\pm$ 0.47; 273 K, 2.58 $\pm$ 0.22; 330 K, 1.83 $\pm$ 0.25; 360 K, 1.50 $\pm$ 0.30; 400 K, 1.16 $\pm$ 0.23. While it is difficult to quantify possible systematic errors, we estimate an additional uncertainty of 5–10% for such contributions in the present work.

Relative Rate Study. The relative rate technique relies on the assumption that both the reactant and reference organics are removed solely by reaction with hydroxyl radicals. To test this assumption, mixtures of methyl nitrite with MTHF, diethyl ether, and dibutyl ether were prepared and left in the dark. In all cases there was no evidence of any reaction of the organic species with methyl nitrite, in the absence of ultraviolet light, over the typical time periods used in this work. Additionally, to test for the possible photolysis of the reactants used in the present
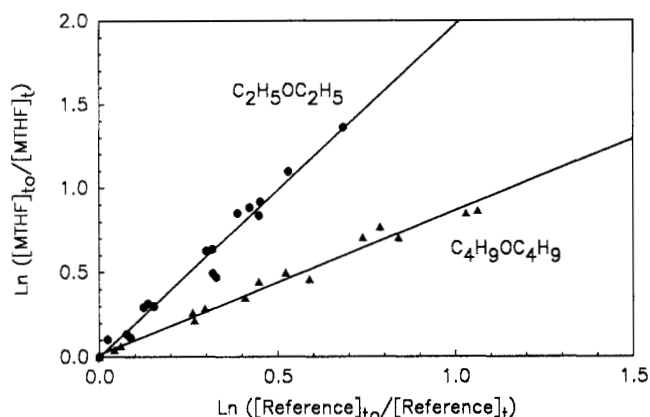
Figure 2. Plot of ln ([MTHF]$_{t_0}$/[MTHF]$_t$) versus ln ([reference]$_{t_0}$/[reference]$_t$) using diethyl ether (●) and di-n-butyl ether (▲) as references.

Figure 3. Arrhenius plot for k_1; (●) absolute rate data; (▲) relative rate data.

work, mixtures of the reactants in synthetic air in the absence of methyl nitrite were irradiated by using the black lamps surrounding the Teflon bag. GC analyses of samples before and after irradiation were indistinguishable, indicating that photolysis of the reactants was unimportant.

Reaction of OH radicals with organic compounds in the presence of oxygen forms HO$_2$ and organic peroxy radicals, RO$_2$. The subsequent chemistry of these radicals is complex, but they are not expected to react with any of the reference or reactant organics used in this work. A further potential complication following irradiation of the gas mixtures is the formation of products that interfere with the gas chromatographic analysis of either the reactant or reference organic. As a test for interferences caused by secondary reactions in our system, separate experiments were carried out in which mixtures of methyl nitrite and either the reactant or the reference organic were irradiated and analyses were performed to check for the formation of potentially interfering products. No such interferences were observed for the irradiation times typical of the present work (1–10 min).

Finally, to test for potential complications arising from secondary chemistry associated with ozone formation in the present work, experiments were performed with 100 ppm NO added to the gas mixtures. Results obtained with and without added NO were indistinguishable.

Figure 2 shows a plot of ln [(MTHF)$_{t_0}$/(MTHF)$_t$] versus ln [(reference)$_{t_0}$/(reference)$_t$] for both reference organics used in this work. As seen from Figure 2, both plots are linear with intercepts at the origin, within 2σ, suggesting that the present work is free from complications due to secondary chemistry. For both reference organics used, at least two separate gas mixtures were prepared and irradiated to check the experimental reproducibility; in all cases, indistinguishable results were obtained from successive experiments. Linear least-squares analysis of the data shown in Figure 2 yields rate constant ratios, k_1/k_5, of 1.97 ± 0.16 and 0.864 ± 0.065 for experiments using diethyl ether and di-n-butyl ether as references, respectively. These relative rate constants can be placed on an absolute basis by using values of 1.35×10^{-11} and 2.78×10^{-11} cm^3 molecule^{-1} s^{-1} for the rate constants of the reactions of OH radicals with the two reference ethers (7, 18) to yield $k_1 = (2.66 \pm 0.22) \times 10^{-11}$ and $(2.40 \pm 0.18) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. These values are indistinguishable and have comparable precision. Hence, we choose to quote an average of the two results with errors that encompass both sets of data; thus $k_1 = (2.53 \pm 0.31) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Quoted errors represent 2σ from the least-squares analysis and do not include any systematic
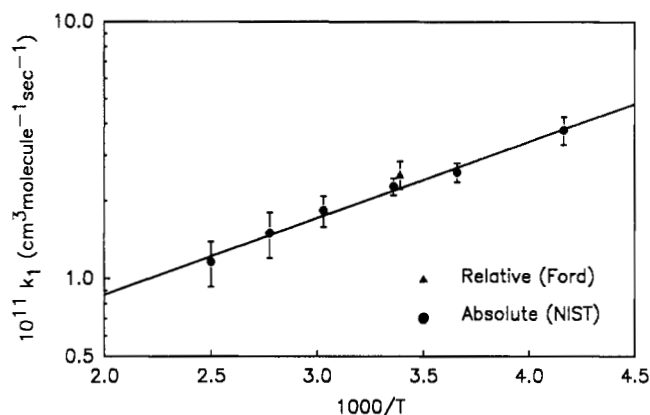
errors associated with uncertainties in the reference rate constants used to place our relative measurements on an absolute basis. While it is difficult to estimate such systematic errors, we feel that these errors could introduce an additional 10% uncertainty.

Discussion

From the rate constant ratios, k_1/k_5, measured during the present work using diethyl ether (DEE) and di-n-butyl ether (DBE) as references, we are able to calculate the relative reactivities of these reference compounds, k(OH + DBE)/k(OH + DEE) = 2.3 ± 0.4. This value is in excellent agreement with a value of 2.3 ± 0.2 for this quantity recently determined by use of relative rate techniques at Ford (11) as well as being in good agreement with the ratio of absolute rate constants measured at NIST (2.0 ± 0.2) (7). However this ratio is inconsistent with the kinetic data presented recently by Bennett and Kerr (19), which yield a ratio k(OH + DBE)/k(OH + DEE) = 1.4 ± 0.3. The cause of this discrepancy remains unclear at this time.

Results from both our absolute and relative rate experiments are displayed in an Arrhenius plot in Figure 3. It is gratifying to note the excellent agreement between the results of the absolute and relative experiments at 296 ± 2 K. This agreement serves to validate the experimental techniques and shows that k_1 is invariant with pressure over the range 35–740 Torr and is unaffected by the presence of 150 Torr oxygen. Thus the Arrhenius expression derived from a fit to the absolute rate data shown in Figure 3

$$k_1 = (2.52 \pm 0.74) \times 10^{-12} \exp[(650 \pm 80)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

is appropriate for inclusion into chemical models of the atmosphere. Errors represent 2σ. Assuming an average tropospheric OH concentration of 10^6 molecule cm^{-3} (20) and using a value of $k_1 = 2.27 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, we calculate the atmospheric lifetime of MTHF to be 12 h with respect to OH attack.

To place the results from the present work in perspective we need to compare our predicted atmospheric reactivity of MTHF to the reactivities of other fuel additives currently in use. Common fuel additives include methanol, ethanol, methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), and *tert*-butyl alcohol (TBA). For simplicity we will equate the atmospheric reactivity of these species with their reactivity toward OH radicals. Using rate data from refs 9, 11, and 21, we calculate MTHF to be more reactive than CH$_3$OH, C$_2$H$_5$OH, MTBE, ETBE, and TBA by factors of 26, 6.8, 7.3, 2.8, and 21, respectively,

on a per molecule basis. Clearly, in any future plans to utilize MTHF in significant quantities as an automotive fuel additive the considerable atmospheric reactivity of this compound should be taken into account.

It is of interest to note that the measured rate constant, k_1, at 298 K in the present work is within 20% of the reactivity predicted by Atkinson's structure–activity relationship (22).

Finally, the present results can be compared with our recent determinations of the rate constants for the reactions of OH with other cyclic ethers (23). The reactivity of 1,3-dioxane was increased by about 20% upon the addition of one α-CH_3 group. The present results show that the reactivity of tetrahydrofuran, which is already more than 50% more reactive than 1,3-dioxane, is increased by about 40% upon α-CH_3 substitution. Thus, the higher reactivity observed for the four- and five-member-ring cyclic ethers appears to cause increased enhancements in substituent effects as well.

Registry No. MTHF, 96-47-9; OH, 3352-57-6.

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Atmospheric Transport of Persistent Pollutants Governs Uptake by Holarctic Terrestrial Biota

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■ The atmospheric deposition of PCBs, DDT, and lindane, governed uptake in terrestrial biota in the Scandinavian penninsula. Mammalian herbivores and predators as well as predatory insects contained higher levels of pollutants at locations where the fallout load was high than at stations where atmospheric deposition was lower, and the two variables were significantly correlated.

Introduction

Atmospheric transport of chlorinated hydrocarbons like PCB, DDT, and toxaphene (chlorinated camphenes) distributes the pollutants on a global basis (1–4). These pollutants have been found in the atmosphere of industrial regions as well as in remote areas far from urban centers, such as the Arctic and the Antarctic (2–4), and in the atmosphere over the oceans (5, 6).

Chlorinated pollutants in the atmosphere reach terrestrial environments as dry and wet deposition (7, 8). The substances exist in air as a gas or associated with particles (7, 8). Atmospheric removal, both wet and dry, is thought to occur mainly in association with particles. Scavenging by rain droplets is determined by Henry's law constant, resulting in a higher deposition at low temperatures than at high (7–9). Recently, a hypothesis has been forwarded that pesticides used in warm midlatitudal regions are transported in their gaseous state to temperate climatic regions, where they contribute to airborne fallout (9). Additionally, thereoretical models propose that pollutants in their gaseous state in the atmosphere equilibrate with water of lakes and oceans, resulting in the contamination of the water bodies (10, 11). However, no direct evidence has yet been provided that persistent pollutants originating from the atmosphere are taken up by terrestrial biota. The objective of this study was to examine if a relationship existed between deposition of pollutants from the atmosphere and uptake in terrestrial animals.

Sampling and Analytical Methods

In 1984/1985 a study regarding the atmospheric fallout of the polychlorinated biphenyls, DDT, DDE, and lindane (γ-hexachlorocyclohexane) was performed between 55° and 68° N on the Scandinavian penninsula (9). During the vegetation season several animal species were sampled, at the same 14 sampling locations. The species studied included mammalian herbivores (the voles, *Microtus agrestis*, at the stations below the Arctic Circle, and *Clethrionomys rufocanus* at stations above it), a mammalian predator (shrew, *Sorex araneus*), and an insect predator (dragonfly, *Aeschna sp.*). The mean atmospheric deposition during four sampling periods during the year was calcualted and presumed to affect uptake by the animals.