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Gas-Phase Reaction of Methyl Isothiocyanate and Methyl Isocyanate with Hydroxyl Radicals under Static Relative Rate Conditions

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ABSTRACT: Gaseous methyl isothiocyanate (MITC), the principal breakdown product of the soil fumigant metam sodium (sodium *N*-methyldithiocarbamate), is an inhalation exposure concern to persons living near treated areas. Inhalation exposure also involves gaseous methyl isocyanate (MIC), a highly reactive and toxic transformation product of MITC. In this work, gas-phase hydroxyl (OH) radical reaction rate constants of MITC and MIC have been determined using a static relative rate technique under controlled laboratory conditions. The rate constants obtained are 15.36×10^{-12} cm^3 molecule^{-1} s^{-1} for MITC and 3.62×10^{-12} cm^3 molecule^{-1} s^{-1} for MIC. The average half-lives of MITC and MIC in the atmosphere are estimated to be 15.7 and 66.5 h, respectively. The molar conversion of MITC to MIC for OH radical reactions is 67% ± 8%, which indicates that MIC is the primary product of the MITC−OH reaction in the gas phase.

KEYWORDS: *gas-phase reaction, OH radical rate constant, MITC, MIC, SPME*

INTRODUCTION

Metam sodium (sodium *N*-methyldithiocarbamate) is the most commonly used fumigant in U.S. agriculture as a preplant treatment to control soil pathogens, nematodes, and insects.[1] Potato production in the Pacific Northwest receives half of its total use.[1] Following application in soil, over 90% of metam sodium will be converted to the actual fumigant, methyl isothiocyanate (MITC) within a few hours.[2] Because of its volatility, approximately half of the MITC in soil will be emitted into the troposphere, although this percentage varies substantially, depending on the application technology.[3]

In the lower atmosphere, reaction with hydroxyl (OH) radicals is the major degradation pathway for most organics.[4−8] The OH radical reaction rate constant of MITC has been reported in a previous study with an indication that an important product of the reaction of OH radicals with MITC is methyl isocyanate (MIC).[5] The acute exposure of MIC to humans can result in severe pulmonary damage.[9] However, no previous studies have reported the conversion percentage of MITC to MIC and the rate constant for oxidation of MIC with OH radicals.

This study examined the gas-phase OH radical reaction rate constants of both MITC and MIC at 293 ± 2 K using a relative rate method. The molar conversion ratio of MITC to MIC has also been estimated for the first time in the presence of OH radicals.

MATERIALS AND METHODS

Chemicals. MITC and MIC standards (>98%, respectively) were purchased from ChemService, Inc. (West Chester, PA). Toluene (HPLC grade), methanol (HPLC grade), *o*-xylene (certified A.C.S.), carbon tetrachloride (certified A.C.S.), sodium nitrite (certified A.C.S.) were obtained from Thermo Fisher Scientific, Inc. (Pittsburgh, PA), and *m*-xylene (anhydrous, ≥ 99%) was purchased from Sigma−Aldrich Co. LLC. (St. Louis, MO). Air (ultra zero grade), helium (balloon grade), and liquid nitrogen were obtained from Airgas, Inc. (Radnor, PA).

Source of OH Radicals. The photolysis ($\lambda \geq 300$ nm) of methyl nitrite (CH_3ONO) served as a source of OH radicals and was used in this work:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

CH_3ONO was prepared by the dropwise addition of concentrated H_2SO_4 into methanol saturated with sodium nitrite.[10] A stream of helium was passed through the reaction vessel and carried the CH_3ONO vapor passed through a trap containing 30% NaOH solution, followed by a tube containing anhydrous $CaCl_2$ to remove any H_2SO_4 and water, and finally to a condensing vessel cooled with liquid nitrogen (77 K).

Relative Rate Method. This technique is based on monitoring the loss of the test compound and one or several reference chemicals for which the OH radical rate constants are currently known, in an irradiated reaction chamber.[7] In this study, two reference chemicals, toluene and *m*-xylene, were employed.

In the reaction chamber, the test compound (T) and the reference chemical (R) will react with OH radicals simultaneously:

$$\text{test compound (T)} + OH \rightarrow \text{products}$$

$$\text{reference chemical (R)} + OH \rightarrow \text{products}$$

The reaction kinetics will depend on the decreasing concentration of OH radicals and both the reference chemicals and the test compounds:

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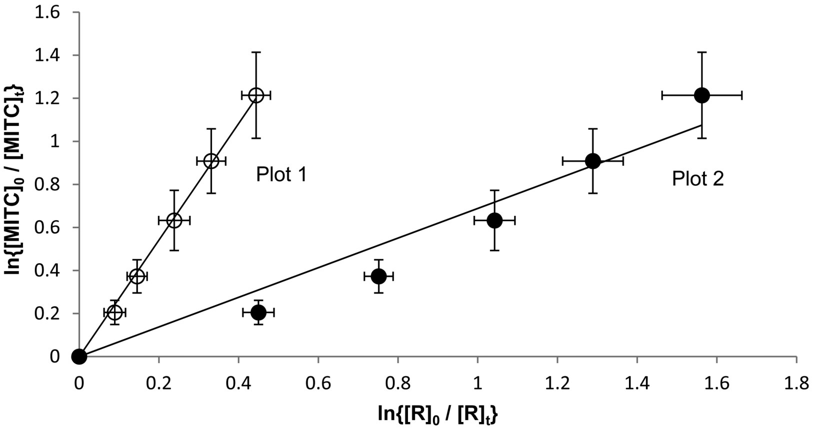

Figure 1. Plots of eq 5 for MITC using toluene (plot 1) and *m*-xylene (plot 2) as reference chemicals.

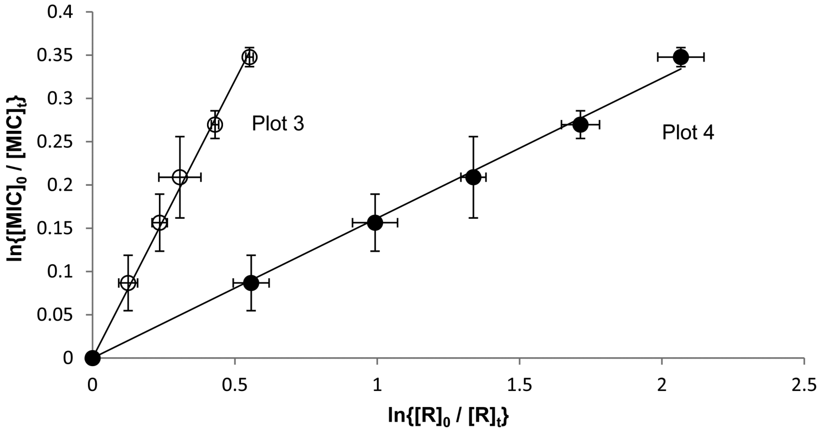

Figure 2. Plots of eq 5 for MIC using toluene (plot 3) and *m*-xylene (plot 4) as reference chemicals.

$$-\frac{d[T]}{dt} = k_1[OH][T] \tag{1}$$

$$-\frac{d[R]}{dt} = k_2[OH][R] \tag{2}$$

where k_1 and k_2 refer to the OH radical rate constants of the test compound and the reference chemical, respectively. Integrations can be made to both sides of eqs 1 and 2:

$$\int_0^c \left\{\frac{d[T]}{[T]}\right\} = -k_1[OH]\int_0^t dt \tag{3}$$

$$\int_0^c \left\{\frac{d[R]}{[R]}\right\} = -k_2[OH]\int_0^t dt \tag{4}$$

Finally, eq 5 is derived from the combination of eqs 3 and 4:

$$\ln\left\{\frac{[T]_0}{[T]_t}\right\} = \frac{k_1}{k_2}\ln\left\{\frac{[R]_0}{[R]_t}\right\} \tag{5}$$

where $[T]_0$ and $[R]_0$ refer to the concentrations of the test compound and the reference chemical at the beginning time of the experiment, t = 0, respectively; $[T]_t$ and $[R]_t$ are their concentrations measured at each time point as the experiment proceeds. A plot of $\ln\{[T]_0/[T]_t\}$ versus $\ln\{[R]_0/[R]_t\}$ will yield a straight line with a slope of k_1/k_2, assuming that there are no other reactions occurring.

Rate Constant Determination. The test procedures were performed in a 100 L Tedlar bag (SKC, Inc., Eighty Four, PA) with the irradiation of 9 Q-PANEL UVA-351 lamps (Q-LAB, Co., Westlake, OH). A fan was used to provide a stream of air to eliminate heating caused by the irradiation, and a temperature of 293 ± 2 K was measured around the bag. Carbon tetrachloride (CCl_4) was added as a stable tracer to demonstrate that the OH radical reaction is the predominant reaction causing the loss of the reactants in the bag. Certain amounts of CH_3ONO, CCl_4, MITC or MIC, toluene, and *m*-xylene were first injected into a glass gas sampling tube using a gastight syringe. The contents of the gas sampling tube were then passed into the Tedlar bag using a constant stream of air, which carried the volatile compounds into the bag until 90 L of air was added. The initial concentrations of each component in the bag were as follows: CH_3ONO, ~400 ppm; MITC or MIC, ~20 ppm; CCl_4, ~20 ppm, toluene and *m*-xylene, ~20 ppm.

The bag was first placed in the dark irradiation chamber for 1 h, which allowed each volatile compound to mix thoroughly. The loss of each substance in the irradiated bag was determined by sampling the bag every 10 min using a Supelco solid-phase microextraction (SPME) fiber (75 μm CAR/PDMS, Sigma−Aldrich Co. LLC.). The SPME sampling was performed for 30 s followed by 10 s desorption onto the inlet of a Hewlett−Packard 6890-5972 gas chromatography−mass spectrometry (GC-MS) system (Agilent Technologies, Inc., Santa Clara, CA) equipped with a 30 m × 0.25 mm DB-624 capillary column (Agilent Technologies). The oven temperature of the gas chromatograph was first held at 70 °C for 0.5 min; then, the temperature ramped from 70 to 150 °C at a rate of 15 °C/min. The mass spectrometer was operated in the selected ion monitoring (SIM) mode to screen mass-to-charge ratios (m/z) of 72 for MITC, 57 for MIC, 91 for toluene, 106 for *m*-xylene, and 117 for CCl_4. The MITC−OH and MIC−OH reaction experiments were replicated three times, respectively.

Conversion of MITC to MIC. A solution was prepared by dissolving the same mass of MITC and MIC in *o*-xylene. The solution was then analyzed by GC-MS to yield the peak area ratio of MITC to MIC.

RESULTS AND DISCUSSION

OH Radical Reaction Rate Constants of MITC and MIC. Samples taken and analyzed using GC-MS every 15 min for 1 h in the dark indicated that there was no significant loss of either the test compound or the reference chemicals in the Tedlar bag during this period.

When the lamps were turned on, about 50% of the initial concentration of *m*-xylene was observed to be lost within 10 min, consistent with an observation of Biermann and coworkers.[11] As discussed in this previous study, a series of complex photoreactions induced by a small amount of impurity in CH_3ONO added could be one possible reason accounting for this phenomenon.[11] Thus, for these experiments, the samples taken at 10 min after turning on the lamps were used as the time 0 samples, since samples taken earlier showed a high level of inconsistency.

Concentrations of the test compound and the reference chemicals obtained from each sampling time point during the 1 h irradiation period were plotted based on eq 5 with standard deviations from three replications (Figures 1 and 2). Relevant index of the plots is shown in Table 1.

Table 1. Index of MITC and MIC OH Radical Reaction Data Plots

plots of eq 5	reference chemical	equation	R^2
plot 1	toluene	$y = 2.71x$	0.998
plot 2	*m*-xylene	$y = 0.688x$	0.943
plot 3	toluene	$y = 0.641x$	0.996
plot 4	*m*-xylene	$y = 0.162x$	0.996

A consistent, but small curvilinear response was observed for MITC, but not for MIC, when *m*-xylene was used as the reference chemical (see Figure 1), suggesting that some additional mechanism for loss of MITC exists, in addition to reaction with OH radicals. Previous research has indicated that MITC does undergo direct photolysis, although the photochemical reaction is slower than the OH radical reaction.[12] The reason for the observed lack of linearity may be due to a small contribution from direct photolysis, since while the lamps have a maximum emission at 351 nm, this is a broad band emission and emits light of shorter wavelengths. The relatively greater loss of MITC in those plots is consistent with this suggestion.

OH radical rate constants of 5.48×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for toluene and 23.0×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for *m*-xylene reported by Atkinson were used in this study.[13] Thus, according to eq 5, multiplying the slope of a linear plot by the rate constant of its corresponding reference chemical gives the OH radical rate constant of MITC and/or MIC (Table 2).

For determining the rate of loss of chemicals in the atmosphere from OH radical reactions, the concentration of OH radicals is required. Since the OH radical concentration varies at different times in a day, an average concentration of 8.0×10^5 molecules cm^{-3} is commonly utilized for estimating the rate of OH radical reactions.[5] The calculated half-lives of MITC and MIC using this average concentration are shown in Table 3.

Photolysis is also observed when MITC is exposed to midsummer sunlight, with a half-life on the order of 30 h of continuous exposure (including nighttime).[12] While direct comparisons using these results are only approximate, the results of the previous study on photolysis of MITC and the present study indicate that OH radical reactions are about twice as important as direct photolysis for transformation of MITC. MIC was also observed during the photolysis reactions, although it presumably went through a photochemically produced intermediate, methyl isocyanide, which was then oxidized to MIC.[14] The possibility that the OH radical was created during the direct photolysis studies also cannot be excluded.

Table 2. OH Radical Reaction Rate Constants of MITC and MIC

test compd	reference chemical	k_1/k_2[a]	k_1 ($\times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1})	k_1 ($\times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1})[b]
MITC	toluene	2.71	14.9 ± 2.66	15.4
	m-xylene	0.688	15.8 ± 2.98	
MIC	toluene	0.641	3.52 ± 0.152	3.62
	m-xylene	0.162	3.73 ± 0.0823	

[a] OH radical rate constant ratio, mean value from three replications using each reference chemical. [b] Average OH radical rate constants, mean value from three replications and for each of the two reference chemicals.

Table 3. Estimated Half-lives of MITC and MIC

test compd	half-life (h)[a]
MITC	15.6
MIC	66.5

[a] Half-lives calculated by using the average OH radical rate constants in Table 2 and an average OH radical concentration of 8.0×10^5 molecules cm^{-3}.

Molar Conversion Ratio of MITC to MIC. At the same weight per volume concentration, the GC peak area ratio of MITC to MIC was determined to be 1.98 to 1. The calculated disappearance rate of MIC in the first 30 min of the irradiation of the MIC−OH reaction was approximately 14%. Since the MIC formed in the MITC−OH reaction also reacts with OH radicals to degrade at the same time, a correction of 14% should be made to the increased peak area of MIC measured during the first 30 min irradiation period of MITC−OH reaction. Thus, molar conversion ratio of MITC to MIC can be calculated by combining their peak area ratio, molecular weights (M_r) and the changed peak area (ΔA_{peak}) of MITC and MIC obtained in the first 30 min of the irradiation, respectively:

$$\text{Molar conversion ratio} = \frac{\Delta A_{\text{peak(MIC)}} \times (1 + 14\%) \times 1.98}{\Delta A_{\text{peak(MITC)}}} \cdot \frac{M_{\text{r(MITC)}}}{M_{\text{r(MIC)}}} \quad (6)$$

Finally, a molar conversion ratio of MITC to MIC during the first 30 min irradiation period of the MITC−OH reaction is estimated to be 67% ± 8% based on eq 6, indicating that MIC is a primary product of MITC in the OH radical reaction.

OH radical reaction rate constants measured in this work are 15.36×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for MITC and 3.62×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for MIC. The result of MITC is comparable to that of the former work done by Sommerlade, employing a smog chamber−mass spectrometer system.[5] Results obtained in this work demonstrate that MIC is a primary transformation product of MITC and it disappears approximately 4 times slower than MITC in the presence of OH radicals. Due to the large consumption of metam sodium in U.S. agriculture[1] and the important health concern of MIC,[9] this study will provide useful information for the exposure assessments for use of the fumigant metam sodium and other pesticides in which MITC serves as the active fumigant.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS USED

MITC, methyl isothiocyanate; MIC, methyl isocyanate; OH radical, hydroxyl radical; SPME, solid-phase microextraction; GC-MS, gas chromatography−mass spectrometry; T, test compound; R, reference chemical; $[T]_0$, concentration of test compound at the beginning time of the experiment; $[R]_0$, concentration of reference chemical at the beginning time of the experiment; $[T]_t$, concentration of test compound measured at each time point as the experiment proceeds; $[R]_t$, concentration of reference chemical measured at each time point as the experiment proceeds; k_1, hydroxyl radical reaction rate constant of test compound; k_2, hydroxyl radical reaction rate constant of reference chemical; R^2, coefficient of determination; ΔA_{peak}, changed peak area; M_r, molecular weight

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