Indoor Air Chemistry: Formation of Organic Acids and Aldehydes

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The formation of aldehydes and organic acids was examined for the gas-phase reactions of ozone with unsaturated VOCs. Formaldehyde and formic acid were produced via the reaction of ozone with each of the three selected unsaturated VOCs: styrene, limonene, and 4-vinylcyclohexene. In addition, benzaldehyde was detected in the styrene-ozone-air reaction system, and acetic acid was found in the limonene-ozone -air system. The study also examined the gas-phase reactions involving formaldehyde, ozone, and nitrogen dioxide and found the formation of formic acid, suggesting that the nitrate radical may play an important role in converting formaldehyde into formic acid. Experiments for all the reactions were conducted by using a 4.3-m³ Teflon chamber. Since the conditions and chemicals employed in the reactions were similar to those for indoor environments, the results from this study may be extrapolated to typical indoor situations and support indications from previous studies that certain aldehydes and organic acids could be generated by indoor chemistry.

Introduction

A field study conducted at six residential houses located in a suburban New Jersey area during the summer of 1992 showed evidence that several aldehydes and formic acid could be generated via indoor air chemistry (1-3). The formation of aldehydes under indoor conditions has been also observed in a laboratory simulation study conducted by Weschler and co-workers (4). These studies suggest that dark reactions of ozone with volatile organic compounds containing unsaturated carbon-carbon bonds (herein called unsaturated VOCs) are mainly responsible for the formation of aldehydes and organic acids. In addition, the nitrate radical (NO₃) indoors, formed via the reaction of ozone (O₃) with nitrogen dioxide (NO₂), may play a role in generating secondary pollutants (2, 5) that may have adverse health effects.

To examine the formation of aldehydes and organic acids via the O_3 -unsaturated VOC reaction, three unsaturated VOCs were selected for study. They were styrene, limonene, and 4-vinylcyclohexene (4-VCH). Each has been found frequently in indoor environments (4, 6-8). Al-

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The reaction chamber was made of FEP Teflon film (DuPont Co.), having a volume of approximately 4.3 m³. The dimension of the chamber was $\approx 1.2 \times 1.2 \times 3.0$ m³. Air and reactants were introduced into the chamber through one or more of the five sampling ports. The inside

through one or more of the five sampling ports. The inside surfaces (walls) of the chamber were aged with high ozone concentrations and flushed with purified air before use. The purified air refers to zero air generated by a dynamic gas calibrator (Model 8550, Monitor Labs, Inc.). Before outdoor or room air was introduced into the calibrator, it was forced to pass through two 0.2- μ m air filters (HEPA Capsule filter, Gelman Sciences, Inc.) and several acrylic plastic jars (6.7 cm diameter, 29 cm height) filled with 6-12 mesh activated carbon. One or two jars of anhydrous CaSO₄ (10-20 mesh) were connected in series within the

though the kinetics and mechanisms of the gas-phase

reactions of O_3 with styrene and with D-limonene have

been reported (9), the formation of aldehydes and organic

acids has not been studied in detail. Aldehydes are well

known as toxic pollutants (10, 11), and organic acids may

be components of acidic aerosols which can cause respira-

tory damage (2). Indoor exposures to these organic

compounds are generally greater than outdoor exposures

because the indoor concentrations of these compounds

are higher and because individuals spend large fractions of

their time indoors (1, 2). Therefore, it is necessary to study

the potential for formation of aldehydes and organic acids

indoor organic acids and indoor formaldehyde, suggesting

the possibility that indoor formaldehyde is converted to

formic acid (2). The gas-phase oxidation of formaldehyde

may involve the participation of the NO₃ radical. To

examine this possibility, the present study included several

experiments that investigated the formation of formic acid

chosen to simulate indoor conditions. For example,

reactions were conducted under typical room temperature

for summertime conditions, and the initial concentrations

of O_3 were selected not to exceed the maximum indoor

levels of O₃ that were found in the residential houses during

the summertime (3). However, the initial concentrations

of individual unsaturated VOCs were higher than their

typical indoor levels to reduce the analytical errors.

via reactions involving O_3 , NO_2 , and formaldehyde. All experimental runs were carried out in a Teflon reaction chamber, and the experimental conditions were

A field study found a significant correlation between

in the indoor air.

Experimental Methods

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airstream to obtain low-humidity air. The chamber was flushed with purified air at least once between the experimental runs. The leakage of the chamber was examined after every 2-3 runs using a simple method. After the chamber was evacuated and sampling ports were tightly closed, the chamber was observed to have no notable expansion in volume for up to 12 h. Thus, the leakage rate of the chamber is considered to be negligible.

Ozone was generated by two ozone generators: one generator built within the dynamic calibrator; the other was Model 165 by Thermo Environmental Instrument, Inc. When the chamber was filled with ozone and air (or ozonated air) and an initial ozone concentration was established, the ozonated air was analyzed for blank levels of unsaturated VOCs and aldehvdes. Afterwards, an unsaturated VOC or other reactants (NO2 and formaldehyde for the HCHO-O₃-NO₂-air system) were introduced into the chamber. If the reactant was a gaseous compound, it was released from a gas cylinder directly into the chamber. If the reactant was a liquid compound, it was injected into the chamber by adding the appropriate amount of the liquid into a glass evaporator. The evaporator was heated, and zero-grade compressed air was forced to pass through the evaporator to carry the reactant into the chamber. All tubing used for introducing and sampling compounds was made of Teflon. The mixing of reactants in the chamber was expedited by manually disturbing the chamber. Once the reactants were mixed in the chamber, measurements were made of the temperature, humidity, and concentrations of each reactant and product. Several unsaturated VOC samples and aldehyde samples were collected during each experimental run, and the ozone concentrations were measured continuously. Only one organic acid sample was collected per run. All experiments were conducted at room temperature (19.5-24.7 °C). Several relative humidity levels (10-56%) were selected to study the impact of humidity on the yield of organic acids.

Since the measurement of organic acids needed relatively long sampling duration, the blank levels of organic acids in the ozonated air could not be determined for each run. In an attempt to examine if an organic acid could be introduced into the chamber through contamination or sources other than reactions, several control runs were made. During these runs, only ozone or an unsaturated VOC (but not together) was added into the chamber.

All experiments were performed in the dark, which meant that the chamber was not exposed to UV light. Comparison experiments were performed with and without the presence of fluorescent room light, and the room light did not affect the reactions.

Measurements of O₃, Aldehydes, Organic Acids, and NO₂. The measurement procedures for O₃, aldehydes, and organic acids can be found in our previous papers (1-3). Briefly, ozone concentrations were measured with a chemiluminescent ozone analyzer (Thermo Environmental Instruments, Inc. Model 560), which was calibrated with EPA primary standard methods. A chart recorder was used for continuous recording of ozone concentration data.

Aldehyde samples were collected with dinitrophenylhydrazine (DNPH)-coated Sep-Pak C₁₈ cartridges. The typical sampling flow rate was 0.5 L/min, and the sampling duration was 20-40 min. A sampled cartridge was eluted with 4 mL of acetonitrile and analyzed by HPLC (see ref 1 for details). The precision of the method was typically $\approx 20\%$ RSD. The DNPH-coated cartridge collection efficiency was >90%. The analytical detection limit was ≈ 0.1 ng of aldehyde–DNPH derivative. This was equivalent to $\approx 2 \,\mu g/m^3$ of an aldehyde in air for typical sampling conditions.

KOH-impregnated Sep-Pak C₁₈ cartridges were used to collect organic acids. Samples were collected for 4–6 h at a flow rate between 1.0 and 1.8 L/min. After sampling, each cartridge was eluted slowly with 2 mL of HPLC-grade water and analyzed by HPLC (see ref 2 for details). The sampling cartridges had no breakthrough for both formic and acetic acids and had a collection efficiency of >92%. The precision of the method was found typically within 25% RSD. Analytical detection limits were 4 and 29 ng/injection for formic acid and acetic acid, respectively. These were equivalent to $0.2 \,\mu g/m^3$ formic acid and $1 \,\mu g/m^3$ acetic acid in the air for typical sampling conditions.

Nitrogen dioxide (NO₂) was measured by using a chemiluminescent NO/NO₂/NO_x analyzer (Model 8840, Monitor Labs, Inc.). The analyzer was calibrated with a dynamic gas calibrator (Model 8550, Minitor Labs, Inc.). Gas standards were 100.4 ppm nitric oxide (NO) in nitrogen and 0.500% nitrogen dioxide (NO₂) in air (Scott Specialty Gases).

Measurement of Unsaturated VOCs. A 1-mL air sample was taken from the reaction chamber and then directly injected to a gas chromatography system (Model 5890 Series II, Hewlett Packard Co.). The GC was equipped with a 30 m \times 0.25 mm i.d. \times 0.25 μ m film capillary column (HP-1 column) and a built-in flame ionization detector (FID). Zero-grade nitrogen (N₂) was used as the carrier gas at a flow rate of 3.00 mL/min. The oven temperature was ramped over a range of 50-250 °C. The temperatures for the detector and injection port were set at 250 and 200 °C, respectively.

Pure liquids (>97% purity) of the unsaturated VOCs (Aldrich Chemical Co., Inc.) were used as external standards. Chromatography-grade carbon disulfide $\left(CS_{2}\right)$ (EM Science, Inc) was used as the dilution solvent. Calibrations were made by using both gas standards and liquid standards. Gas standards were produced by adding a known amount of liquid solution into a heated glass container, which totally evaporated the liquid. The exact volume of the glass container was known. The two calibration methods showed a good agreement (${<}15\,\%~{\rm RSD}$ < the analytical precision), and the linear regression coefficients had $R^2 > 0.99$ for all calibration curves. The method precision, measured by using replicate samples, was typically < 20% RSD. The analytical detection limits were 0.04, 0.08, and 0.04 ng for styrene, limonene, and 4-VCH, respectively. These were equivalent to $40 \ \mu g/m^3$ of styrene, $82 \ \mu g/m^3$ of limonene, and $40 \ \mu g/m^3$ of 4-VCH in air (at 20 °C).

Results

Styrene-O₃-Air System. Five runs were conducted to study the reaction of O_3 with styrene. The initial conditions are summarized in Table 1. When the initial concentrations of O_3 and styrene were approximately equal, as in runs 1-4 ([O_3]/[styrene] ratio ranged from 1.8 to 2.1), the concentrations of both reactants were observed to decline as the reaction proceeded (see Figure 1, for example). When the initial concentration of styrene was

Table 1, Initial Conditions for Styrene-O₃-Air System

run	styrene	concn	jozone c	oncn	temp	humidity
no.	$(\mu mol/m^3)$	(µg/m ³)	$(\mu mol/m^3)$	$(\mu g/m^3)$	(°C)	(%RH)
1	2.89	301	5.20	249	22.7	45.6
2	3.70	385	7.40	355	22.4	17.0
3	2.75	287	4.96	238	22.5	28.4
4	2.06	215	4.44	213	21.4	56.1
5	40.6	4230	2.61	125	23.7	13.2
Conc (ug/m3)	200 150 100 50	•	the second secon		nzaldehyde' ■	*10
	0] , , , , , ,	100	200	 	300	400
			Reaction time (n	nin.)		

Figure 1. Profiles of compounds in the styrene-ozone-air system, results from run 3.



Figure 2. Profiles of compounds in the styrene-ozone-air system, results from run 5.

in large excess compared to O_3 , as in run 5 ([styrene]/[O_3] = 15.6), the styrene concentrations did not decrease while the O_3 concentrations were quickly reduced to zero (see Figure 2). Time zero in Figures 1 and 2 refers to the time when the two reactants were mixed, i.e., the start time for the reaction.

Formaldehyde and benzaldehyde were detected in the chamber air during all five runs. The concentrations of both aldehydes vs reaction time are also shown in Figure 1 for run 3 and in Figure 2 for run 5. In these figures, the concentrations of O_3 and styrene were point values, while the concentrations of formaldehyde and benzaldehyde were averaged values because aldehyde samples were collected over a time interval of 20-40 min. Thus, for an aldehyde data point in the figures, the corresponding value on the X-axis (reaction time) was the middle point of each sampling interval. In general, the concentrations of an aldehyde increased first and then started to decrease at a certain point during the reaction. The aldehyde increase indicates the accumulation of the aldehyde generated via the reaction, and the decrease may result from the deposition of the aldehyde onto the chamber surfaces or other processes that could consume the aldehyde.

The concentrations of formaldehyde and benzaldehyde measured during each run are listed in Table 2. These aldehyde concentrations are all blank-corrected and are

Table 2.	Concentrations	of Aldehydes	and	Organic	Acids
Generated	l in Styrene-O ₃ -	-Air System			

run	formaldehyde concn		benzaldehy	de concn	formic acid concn	
no.	$(\mu mol/m^3)$	$(\mu g/m^3)$	(µmol/m ³)	$(\mu g/m^3)$	$(\mu mol/m^3)$	$(\mu g/m^3)$
1	4.76	152	0.057	6.0	0.37	17.2
2	6.85	219	0.084	8.9	0.35	16.0
3	2.85	91.2	0.041	4.4	0.35	16.1
4	2.81	90.0	0.051	5.4	0.52	23.8
5	4.54	145	0.021	2.2		<0.4ª
a	Not detecte	d.				

Table 3. Initial Conditions for Limonene-O₃-Air System

run no.	limonene concn		ozone c	oncn	temp	humidity	
	$(\mu mol/m^3)$	$(\mu g/m^3)$	$(\mu mol/m^3)$	$(\mu g/m^3)$	(°C)	(%RH)	
1	1.96	266	6.21	298	19.5	46.1	
2	2.70	368	5.30	255	23.4	38.9	
3	2.18	297	4.43	212	24.5	48.5	
4	5.66	770	1.11	53.2	24.2	18.5	

Table 4. Concentrations of Aldehydes and Organic Acids Generated in Limonene-O₃-Air System

run no.	formaldehyde concn		formic aci	d concn	acetic acid concn		
	$(\mu mol/m^3)$	(µg/m ³)	$(\mu mol/m^3)$	$(\mu g/m^3)$	$(\mu mol/m^3)$	$(\mu g/m^3)$	
1	2.88	92.0	0.67	30.6	0.75	45.1	
2	2.54	81.3	0.85	39.2	0.97	58.3	
3	2.89	92.5	0.73	33.6	0.84	50.3	
4	15.9	509	0.75	34.7	0.10	5.90	

the maximum values for each run. During all five runs, the concentrations of formaldehyde were greater than those of benzaldehyde.

The results from the organic acid measurements show that formic acid was detected in the chamber air during runs 1-4, but not detected during run 5 and a control run. The averaged concentrations (typically measured from reaction time of ≈ 5 min to 5 h) of formic acid are shown in Table 2.

Limonene-O₃-Air System. The initial conditions for the reaction of O₃ with limonene are shown in Table 3. For these conditions, formaldehyde was detected during all the experimental runs. The concentration profiles of O₃, VOC, and formaldehyde for the limonene-O₃-air systems were similar to those for the styrene-ozone-air system. However, O₃ was consumed more rapidly by limonene than by styrene. After the O₃ concentrations were reduced to ≈ 0 ppb, the limonene concentrations appeared to be stable.

The concentrations of formaldehyde generated via the reaction of O_3 with limonene are listed in Table 4. They show that the formaldehyde concentration observed during run 4 was markedly higher than that observed during the other runs. The reason for this marked difference is unknown. However, the high concentration of formal-dehyde may be related to the high initial concentration of limonene.

Both formic acid and acetic acid were detected during all four runs. The averaged concentrations of both organic acids (typically measured from a reaction time of ≈ 5 min to 4 h) are shown in Table 4. With the exception of run 4, acetic acid concentrations were higher than formic acid concentrations. A control run found that levels of formic acid and acetic acid were below the detection limits.

4-VCH-O₃-Air System. Table 5 shows the initial conditions for the six experimental runs of the 4-VCH-

Table 5. Initial Conditions for 4-VCH-O₃-Air System

run	4-VCH concn		ozone c	oncn	temn	humidity	
no.	$(\mu mol/m^3)$	(µg/m ³)	$(\mu mol/m^3)$	$(\mu g/m^3)$	(°C)	(%RH)	
1	4.35	471	4.34	208	24.5	39.4	
2	5.47	592	6.11	293	24.4	21.6	
3	2.86	310	4.10	197	24.2	30.1	
4	3.81	412	3.74	180	23.5	10.4	
5	4.01	434	3.82	184	23.5	11.8	
6	15.7	1694	3.69	177	24.1	21.5	

Table 6. Concentrations of Aldehydes and Organic Acids Generated in the 4-VCH-O₃-Air System

	formaldehy	de concn	formic acid concn		
run no.	(µmol/m ³)	(µg/m ³)	(µmol/m³)	(µg/m ³)	
1	1.08	34.7	0.49	22.5	
2	1.14	36.4	1.00	46.0	
3	0.78	25.1	0.19	8.9	
4	0.79	25.2	0.31	14.1	
5	0.79	25.2	0.41	19.0	
6	0.75	23.9	0.40	18.6	

Table 7. Initial Conditions and Concentrations of HCOOH Generated in $HCHO-O_3-NO_2$ -Air System

				run		
		1	2	3	4	5
нсно	$(\mu g/m^3)$	0ª	540	58.4	289	475
	$(\mu mol/m^3)$	0	18.0	1.95	9.62	15.8
O ₃	$(\mu g/m^3)$	0	213	150	127	129
-	$(\mu mol/m^3)$	0	4.44	3.13	2.65	2.69
NO_2	$(\mu g/m^3)$	598.0	0.0	114	58.0	570
-	$(\mu mol/m^3)$	13.00	0.00	2.48	1.30	12.4
temp	(°C)	23.2	24.2	24.1	24.5	24.7
humidity	(%RH)	14.7	30.1	28.7	19.2	14.8
нсоон	$(\mu g/m^3)$	ND^b	ND	3.50	5.20	6.70
	$(\mu mol/m^3)$	ND	ND	0.08	0.11	0.15
an the	compound m	a not a	ddad in	to the al	ambar b	ND not

detected.

 O_3 -air system. The concentration profiles of the reactants demonstrate that the concentrations of O_3 decreased rapidly as the reaction proceeded during all six runs. Decays of 4-VCH concentrations were observed for runs 1-5 but not for run 6, which had an initial concentration of 4-VCH in large excess of the O_3 initial concentration.

The formation of both formaldehyde and formic acid was observed during all six runs. The concentrations of both products are shown in Table 6. Formic acid was measured typically from a reaction time of ≈ 5 min to 4 h. The highest concentration of formic acid was found in run 2, while no formic acid was detected in a control run.

HCHO-O₃-NO₂-Air System. The initial concentrations of formaldehyde (HCHO), O₃, and NO₂ are listed in Table 7, along with the values for temperature and relative humidity. During run 1, only NO₂ was added to the chamber. The concentrations of NO₂ were observed to decay slowly over the 400-min sampling period. The NO₂ decay can be considered to be a result of wall effects, and the first-order rate constant for this decay was determined to be 2.1×10^{-4} min⁻¹. No organic acids were found during this run.

During run 2, HCHO and O_3 were present, and NO_2 was absent. The concentrations of O_3 were observed to decay slowly and the concentrations of HCHO did not change significantly over a period of 320 min from the time when the two compounds were mixed in the chamber. The O_3 decay during this run can be considered mainly due to the O_3 wall effect because the decay had a first-order rate constant of 2.2×10^{-4} min⁻¹, which approximately equals the rate constant for the O_3 wall effect. The rate constant for the O_3 wall effect was obtained through other two runs during which only O_3 was added to the chamber: 2.02×10^{-4} and 2.15×10^{-4} min⁻¹, respectively (average = 2.09×10^{-4} min⁻¹). Organic acids were not found during this run.

All three reactants were used in runs 3–5. Formic acid (HCOOH) was detected in the chamber. The HCOOH concentration measured from the reaction time of 0 to that of 5 h can be found in Table 7. It is observed that NO_2 concentrations decreased markedly during runs 3 and 4, while O_3 concentration was stable. The concentrations of both O_3 and NO_2 decreased markedly during run 5.

Discussion

Rate Constant for O_3 -Unsaturated VOC Reactions. Since the reactions were conducted under static conditions, the O_3 that was initially introduced into the chamber was consumed by the following reactions:

$$O_3 + \text{wall} \rightarrow \text{loss of } O_3$$
 (1)

$$O_3 + VOC \rightarrow product$$
 (2)

Hence

$$-d[O_3]/dt = (k_1 + k_2[VOC])[O_3]$$
(3)

where k_1 and k_2 are the rate constants for reactions 1 and 2, respectively. [O₃] and [VOC] represent O₃ and VOC concentrations, respectively. When the VOC concentration was in a large excess compared to the initial O₃ concentration, the VOC concentration remained essentially constant throughout the reaction, and eq 3 simplifies to eq 4

$$-(d \ln [O_3])/dt = k_1 + k_2[VOC]$$
(4)

Then a pseudo-first-order decay of O₃ would be observed, and the slope of a straight-line plot of ln [O₃] vs reaction time equals $(k_1 + k_2[VOC])$. k_1 , the rate constant for O₃ wall effect, was measured separately $(k_1 = 2.09 \times 10^{-4}$ min⁻¹, HCHO-O₃-NO₂-Air System). Thus, the secondorder rate constant k_2 for the reaction of O₃ with each VOC can be obtained using k_1 and [VOC].

Among the five experimental runs for the reaction of O_3 with styrene, run 5 had the largest $[VOC]/[O_3]_{initial}$ (=15.6) and the styrene concentrations remained constant (see Figure 2). The decay of O_3 concentration was first order, i.e., the plot of ln $[O_3]$ vs reaction time t was a straight line (linear regression $R^2 = 0.996$), and the slope = $k_1 + k_2$ - $[VOC] = 1.286 \times 10^{-1} \text{ min}^{-1}$. Hence, the second-order rate constant k_2 for the reaction of O_3 with styrene was 7.9 $\times 10^{-17} \text{ cm}^3$ molecule⁻¹ s⁻¹ (at 297.4 K).

Similar calculations were performed for the reactions of O₃ with limonene and with 4-VCH to calculate the second-order rate constants, using runs 4 and 6, respectively. Both plots of ln [O₃] vs t had $R^2 > 0.99$. The second-order rate constant for the reaction of limonene with O₃ was 3.5×10^{-16} cm³ molecule⁻¹ s⁻¹ at 297.3 K, and that for the reaction of 4-VCH with O₃ was 2.7×10^{-16} cm³ molecule⁻¹ s⁻¹ at 296.7 K.



Figure 3. Chemical structures of the three selected VOCs.

Table 8. HCHO Yields (%) from Reactions of O_3 with Unsaturated VOCs

			ru	ın		
	1	2	3	4	5	6
styrene-O3-air	165 148	185 94	$104 \\ 132$	136 1430	174	
4-VCH–O ₃ –air	25	21	27	21	21	20

The reported rate constant k_2 for the gas-phase reaction of O₃ with styrene is $(2.16 \pm 0.46) \times 10^{-17}$ cm³ molecule⁻¹ s⁻¹ at 296 ± 2 K (12) and 3.0×10^{-17} cm³ molecule⁻¹ s⁻¹ at 303 K (13). In the presence of carpets, the rate constant for the reaction of O₃ with styrene was found to be higher: 3.3×10^{-16} cm³ molecule⁻¹ s⁻¹ at room temperature (4). The reported k_2 for the reaction of O₃ with D-limonene is 6.4×10^{-16} cm³ molecule⁻¹ s⁻¹ at 295 ± 1 K (14). Considering the fact that the derived rate constant values are influenced by experimental techniques and parameters such as initial concentrations of the organics and O₃ (9), the rate constants obtained in this study are in good agreement with the reported values.

In previous studies, no k_2 has been reported for the reaction of 4-VCH with O_3 . The present study found that the k_2 for the 4-VCH- O_3 reaction was similar to that found for the limonene- O_3 reaction. This is consistent with the similarity in the chemical structures for the two VOCs. Both limonene and 4-VCH have two unsaturated carbon-carbon bonds (C=C): one is contained in the cyclohexene ring and the other is in the branch chain (see Figure 3). Among the three selected unsaturated VOCs, styrene has only one C=C in its molecule to react with O_3 , which is consistent with it having the smallest rate constant.

Yields of Aldehydes. If the yield of a product can be simply defined as the ratio (as percentage) of the molar concentration of the product to the concentration of a reactant having the lowest molar concentration among all the reactants (i.e., $100 \times [product]/[reactant]_{smallest}$), the yields of formaldehyde (HCHO) via the reactions of O₃ with styrene, with limonene, and with 4-VCH can be compared, as shown in Table 8.

It has been reported that when the concentration of an unsaturated VOC is not in a large excess of the O_3 concentration, the reaction stoichiometry is not unity (9). As shown in Table 8, the HCHO yields changed upon the variations of initial concentrations for the different runs. In summary, the HCHO yields were $153 \pm 33\%$, $125 \pm 28\%$, and $23 \pm 3\%$ for the reaction of O_3 with styrene, limonene (result from run 4 excluded), and 4-VCH, respectively. These values indicate that one molecule of O_3 reacting with one molecule of styrene or one molecule of HCHO, while a molecule of O_3 reacting with one molecule of 4-VCH produced less than one molecule of HCHO. The greater than 100% HCHO yields may result from further reactions involving the Criegee biradical.

Benzaldehyde was also detected in the styrene- O_3 -air system (Table 2, at much lower concentrations than

Table 9. HCOOH Yields (%) from Reactions of O_3 with Unsaturated VOCs

	run						
	1	2	3	4	5	6	
styrene–O3–air limonene–O2–air	12.9 34.1	9.4 31.6	12.7 33.5	$25.1 \\ 68.0$	0		
4-VCH–O ₃ –air	11.3	18.3	6.7	8.2	10.8	10.9	

HCHO). Upon reviewing the chemical structures of limonene and 4-VCH (see Figure 3), each compound has an unsaturated carbon-carbon double bond in its cyclohexene ring. Ozone can attack this unsaturated carbon-carbon bond to open the cyclohexene ring, resulting in the formation of long-chain aldehydes. Thus, other longer-chain aldehydes besides formaldehyde could be expected to be produced in the limonene-O₃-air system or the 4-VCH-O₃-air system. Unfortunately, these potential products could not be measured due to the limitation of the analytical method.

Yields of organic acids. Yields of formic acid (HCOOH) were calculated for the O₃-unsaturated VOC reactions, and the results are summarized in Table 9. Since acetic acid (CH₃COOH) was also identified in the limonene-O₃-air system, similar calculations were performed to obtain the CH₃COOH yields, and the results were 38.5%, 36.0%, 38.4%, and 8.3% for runs 1-4, respectively. The mean HCOOH yields for the reactions of O₃ with the three unsaturated VOCs were $12 \pm 9\%$ for styrene, $42 \pm 17\%$ for limonene, and $11 \pm 4\%$ for 4-VCH. The mean CH₃COOH yield was $30.3 \pm 14.7\%$ for limonene and 0 for the other two compounds.

For the styrene– O_3 -air system, run 5 had a HCOOH yield of zero. Perhaps this was due to the very different initial concentrations of both reactants: highest styrene concentration but lowest initial O_3 . On the other hand, the lowest humidity level in run 5 was a possible reason for the zero yield of HCOOH. The following reaction sequence has been suggested for the formation of an organic acid via O_3 -unsaturated VOC reactions (15):



$$\begin{array}{ccc} R & I \\ - & & \\ + & + & H_2O \longrightarrow R - & C - OH + & H_2O \end{array}$$

Reaction 7 suggests that the organic acid yield increases with increases in humidity, resulting from the Criegee biradical reaction with water vapor (H_2O serves as a catalyst). This can be inferred from the relationship between humidity and HCOOH yields. The plot of the HCOOH yields vs humidity levels for the five runs demonstrates that an increase in humidity could lead to an increase in HCOOH yield (see Figure 4). This is consistent with the HCOOH-humidity relationship observed from our field study, i.e., the indoor concentrations



Figure 4. HCOOH yields vs humidity for the styrene-ozone-air system.

of formic acid was significantly and positively correlated with indoor humidity levels (2).

Reactions Involving HCHO, O_3 , and NO_2 . The field experiments showed that indoor formic acid was significantly correlated to indoor formaldehyde, but the indoor formaldehyde was mainly derived from direct indoor emission sources, not from the chemical formation via reaction 5 (2). One of the plausible explanations for the correlation between HCOOH and HCHO was indoor air chemistry: perhaps HCHO can be oxidized to HCOOH through gas-phase reactions under indoor conditions.

Although O₃ is a very powerful oxidizing agent and can oxidize unsaturated VOCs into aldehydes and organic acids with relatively fast reaction rates, its direct reaction with HCHO is quite slow. The reported rate constant for the reaction of HCHO with O_3 is $\leq 2.1 \times 10^{-24}$ cm³ molecule⁻¹ $s^{-1}(9)$, 7 orders of magnitude smaller than the rate constant for the reaction of styrene with O_3 . In the present study, the direct reaction between O_3 and HCHO was examined through run 2 (for the HCHO-NO₂-O₃-air system, Table 8), and the results indicate no HCOOH formation. Thus, indoor HCHO is not likely to be oxidized directly by indoor O₃. However, HCOOH was found in the chamber air when HCHO, NO₂, and O₃ were all added into the chamber (runs 3-5, Table 8). Using calculation procedures similar to those for the reactions of O_3 with unsaturated VOCs, the HCOOH yields via the reactions involving HCHO, NO_2 , and O_3 were estimated as 0% from runs 1 and 2, 3.9%from run 3, 8.9% from run 4, and 5.3% from run 5. It is seen that the HCOOH yields via the reactions involving HCHO, NO₂, and O₃ were lower than those via reactions between O₃ and unsaturated VOCs.

In attempt to propose possible mechanisms for the formation of HCOOH via reactions involving HCHO, NO₂, and O₃, we start with reactions 8 and 9 that have been suggested to be a potential source of nitric acid (HNO₃) and peroxy radicals indoors (5):

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \tag{8}$$

$$NO_3 + HCHO \rightarrow HNO_3 + HCO$$
 (9)

As shown in reaction 8, the nitrate radical (NO₃) may be generated by the reaction of O₃ with NO₂ (16, 5). It may react with HCHO, producing HNO₃ and the HCO radical (reaction 9), which could react with oxygen molecule to produce the HO₂ radical (summarized in ref 17):

$$HCO + O_2 \rightarrow HO_2 + CO \tag{10}$$

The HO_2 radical may react with HCHO (17):

Then the HOCH₂O₂ radical formed via reaction 11 may undergo one or more of the following reactions to form HCOOH (17):

$$HOCH_2O_2 + HOCH_2O_2 \rightarrow HCOOH + CH_2(OH)_2 + O_2$$
(12)

$$\mathrm{HOCH}_{2}\mathrm{O}_{2} + \mathrm{HO}_{2} \rightarrow \mathrm{HCOOH} + \mathrm{H}_{2}\mathrm{O} + \mathrm{O}_{2} \quad (13)$$

$$HOCH_2O_2 + HO_2 \rightarrow HOCH_2O_2H + O_2$$
 (14)

$$HOCH_2O_2H \rightarrow HCOOH + H_2O$$
 (15)

$$HOCH_2O_2 + HOCH_2O_2 \rightarrow HOCH_2O + HOCH_2O + O_2$$
(16)

$$HOCH_2O + O_2 \rightarrow HCOOH + HO_2$$
 (17)

The proposed mechanisms suggest the NO_3 participation in the conversion processes from HCHO to HCOOH, in agreement with the conclusions of ref 5.

Implications to Indoor Environments. A few studies (1-4) have suggested that certain aldehydes and organic acids could be generated via indoor air chemistry. The present research studied gas-phase reactions that yielded aldehydes and organic acids under simulated indoor conditions.

An important variable that needs to be considered when studying indoor chemistry is the time scale of the reactions. Reactions have to be fast compared to the air-exchange rate. In the present study, decays of reactants were observed as soon as a reaction started for the gas-phase reaction of O_3 with each unsaturated VOC, and the formation of aldehydes was observed in <1 h after the reaction started. Thus, aldehydes could be generated even when the air infiltration rate is as high as 1 air change/h (moderate rate for most houses and buildings). Although the concentrations of individual VOCs used in the experiments are higher than expected in real indoor environments (e.g., $8-35 \,\mu\text{g/m}^3$ for limonene, see refs 18 and 6-8), the concentration of total unsaturated VOCs in an indoor environment may rival the VOC concentration used in an experimental run. The overall reaction rate may be the summation (maybe greater, maybe smaller) of the rate for the reaction of O_3 with each unsaturated VOC. Thus, we suggest that the gas-phase reaction of O3 with unsaturated VOCs can be a potential source of aldehydes and organic acids indoors.

Although the formation of formic acid cannot serve as an effective indicator of the time scale for the reactions involving HCHO, O₃, and NO₂ due to the need for a large sampling volume for HCOOH detection, the decay of the reactants was observed as soon as the reactions started. Kinetic data for some key reactions proposed support the occurrence of the reactions under indoor conditions. For example, reaction 8 may occur indoors (5). This is a moderately rapid reaction, having a second-order rate constant of 3.2×10^{-17} molecule⁻¹ s⁻¹ cm³ (16), approximately equal to the rate constant for the reaction of styrene with O₃; reaction 9 has a rate constant of (3.3–8.0) $\times 10^{-16}$ molecule⁻¹ s⁻¹ cm³ (16), approximately equal to the rate constant for the limonene–O₃ reaction; reaction 10 is a rapid reaction with a rate constant of 6×10^{-12} molecule⁻¹ s^{-1} cm³ (19, 20); and reaction 11 has a rate constant of 7 $\times 10^{-14}$ molecule⁻¹ s⁻¹ cm³ (21, 22).

The indoor air chemistry needs to receive more attention in future studies. Conventionally, indoor pollutants are considered either to be derived from outdoors or to be emitted directly from indoor sources. Sinks for indoor pollutants are also simply considered to be deposition onto indoor surfaces and removal with exfiltrating air (23). The results from this research and previous studies (1-4)indicate that the conventional view is simplistic compared to the real situation. Chemical reactions occurring indoors could be complex and could affect the distribution among indoor pollutants. The chemistry of NO_x is an example. Another study reported that the relationships among indoor O₃, NO, and NO₂ were influenced by indoor air chemistry (24). The present study indicates that having NO₂ in the same indoor settings as O₃ and formaldehyde can lead to the formation of formic acid at a rate markedly higher than when only O_3 and formaldehyde are present. This is a situation which could occur in a home having a gas-operated kitchen stove during the summertime. Furthermore, surface-involved chemistry (5, 23, 25) may make the indoor chemistry issue more complex.

Also, the indoor chemistry needs to be considered when regulating a consumer compound to be used indoors. A compound may not be of concern due to its low or nontoxicity, but it may react with other indoor pollutants to generate secondary products that could produce adverse health effects.

Conclusions

The formation of formaldehyde and formic acid was observed for the gas-phase reaction of ozone with styrene, limonene, and 4-vinylcyclohexene, respectively. In addition, the formation of benzaldehyde was observed for the styrene-ozone reaction, and the formation of acetic acid was observed for the limonene-ozone reaction. The reaction of ozone with styrene and that of ozone with limonene had greater yields of both formaldehyde and formic acid than the reaction of ozone with 4-vinylcyclohexene.

The second-order rate constants for the reactions of O_3 with each of the three unsaturated VOCs at room temperature were determined. The values were 7.9×10^{-17} cm³ molecule⁻¹ s⁻¹ for styrene, 3.5×10^{-16} cm³ molecule⁻¹ s⁻¹ for limonene, and 2.7×10^{-16} cm³ molecule⁻¹ s⁻¹ for 4-vinylcyclohexene.

The gas-phase reaction of ozone with formaldehyde did not produce formic acid, while formic acid was generated via gas-phase reactions involving formaldehyde, ozone, and nitrogen dioxide. Evidence supports the hypothesis that the nitrate radical was formed *in situ* via the reaction of ozone with nitrogen dioxide. The nitrate radical probably played a significant role in the oxidation of formaldehyde into formic acid.

Since the conditions for the reactions were similar to those for indoor environments, the results may be extrapolated to actual indoor situations. They also support conclusions by previous investigators who have suggested that certain aldehydes and organic acids could be generated by indoor chemistry.

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Abbreviations and Symbols

VOC	volatile organic compound
NO_3	nitrate radical
O ₃	ozone
NO_2	nitrogen dioxide
4-VCH	4-vinylcyclohexene
HCHO	formaldehyde
DNPH	2,4-dinitrophenylhydrazine
KOH	potassium hydroxide
RSD	relative standard deviation
NO	nitric oxide
HCOOH	formic acid
CH ₃ COOH	acetic acid
t	reaction time
k_1	rate constant for reaction 1
k_2	rate constant for reaction 2
C=C	carbon-carbon double bond

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