Ozone Reactive Chemistry on Interior Latex Paint

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The heterogeneous chemistry of ozone on interior latex paint was investigated in a tube flow reactor. The emissions of several polar volatile organic compounds (VOCs) including organic acids and carbonyls (aldehydes and ketones) were measured while a glass tube coated with latex paint was exposed to clean air and ozone. Four different commercial brands of latex paint were tested. Formic and acetic acids were not found to be generated via ozone reactions; however, both were found to off-gas from the latex paints, and the off-gasing increased with increasing relative humidity. The off-gasing rates are large enough, particularly for acetic acid, to impact residential concentrations significantly. Formaldehyde was found to be produced by reactions related to the ozone concentration. There was some evidence that acetaldehyde and acetone may also be produced by processes related to the ozone concentration. A steady-state model is presented that is used to extrapolate the chamber results to a representative indoor environment. The model is based on an experimentally derived parameter termed the VOC formation factor, which is defined as the number of VOC molecules of a particular species formed via an ozone reaction divided by the total number of ozone molecules sticking to the surface. Using this model, it was found that formaldehyde production via ozone reactions is significant enough to impact indoor concentrations of formaldehyde.

Introduction

Indoor volatile organic compounds (VOCs) are of increasing concern because of their potential as irritants and carcinogens and their relation to sick-building syndrome, (*1*). For example, Molhave et al. (*2*) have found that the indoor total VOC concentration correlates with occupant irritation. Many of the VOCs that have been detected in indoor environments are present at higher concentrations than in the ambient environment, indicating that there are indoor sources for VOCs (*1*). Recent research efforts have focused on the specific sources of the VOCs. It has been shown that numerous VOC species originate from off-gasing by household products and materials (*3*). However, a new avenue of research is emerging that studies the secondary formation of VOCs via the indoor reactions of other pollutants (e.g., refs 4–6).

Weschler et al. (*7*) have found, in a laboratory chamber study, that ozone reacts with carpet to form formaldehyde, acetaldehyde, and other C_5–C_{10} aldehydes. The postulated pathway for these products is the reaction between ozone and olefins (*5, 6*). The ozone–olefin reaction yields a carbonyl and a Criegee biradical (*8*). The Criegee biradical may isomerize to an organic acid, with the isomerization rate increasing with the presence of water vapor. In a residential field study in Boston, MA, Reiss et al. (*5*) found a correlation between the removal of ozone in indoor residences and the formation of secondary polar VOCs including carbonyls and organic acids. Environmental variables including temperature and relative humidity are confounders in this relationship, but it still appears that ozone reactions may account for a measurable portion of the concentration of polar VOCs found in residential environments. In a similar study in New Jersey, Zhang et al. (*6*) found that the indoor ozone correlates with the indoor concentrations of acetaldehyde, *n*-valeraldehyde, valeraldehyde (isovaleraldehyde plus *n*-valeraldehyde), and formic acid. These carbonyl and organic acid compounds constitute about 15% of the total VOC concentration (*5*).

Latex paint is a common indoor surface, and the resins used in the latex paints in our study were all variations of vinyl polymers. Vinyl compounds have the following functional form: $CH_2{=}CHR$. The double bonds in the vinyl open as the polymer is formed; however, there are normally unreacted monomer resin-containing free double bonds. These unreacted monomers are susceptible to attack by oxidizing agents such as ozone. There are also some VOCs in latex paints such as toluene and xylene that can react with ozone (*3*), but the rates of these reactions are very slow. In this paper, we studied the reaction of ozone with several brands of interior latex paint. Several polar VOCs, including carbonyls (aldehydes and ketones) and organic acids, were measured during exposure of latex paint surfaces with ozone and clean air. From these measurements, the emission rates of the polar VOCs were calculated for each of the exposures. The emission rates for the zero-air exposure corresponds to a natural off-gasing rate of the material, while the emission rate of the ozone exposure corresponds to natural off-gasing plus formation from processes related to the ozone concentration. This process is likely to be the formation of VOCs as a result of the reaction of ozone with some constituent of the paint. Another possibility is that ozone may break down the polymer structure of the paint and may cause VOCs that were trapped in pores below the paint surface to be released. Thus, from a comparison of emission rates of the zero-air and ozone exposure experiments, any VOC products related to the ozone concentration will be quantified. Finally, a steady-state model will be presented to extrapolate the results of this chamber study to an actual residential environment.

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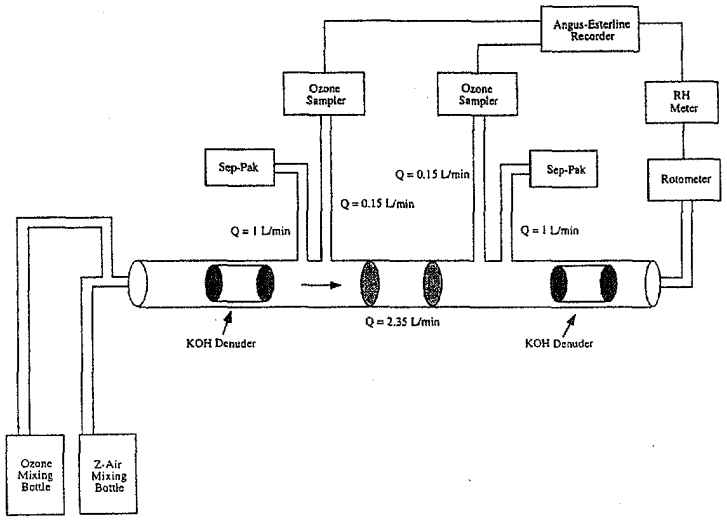

FIGURE 1. Schematic diagram of tube flow apparatus.

Materials and Methods

Description of Apparatus. Polar VOC formation via ozone reactions was measured in a laminar tube flow reactor. A schematic of the apparatus is shown in Figure 1. This represents a modification of an apparatus used to study ozone deposition onto latex paint (see ref 9). A zero-air (i.e., pure air) system is used to expose a latex paint-coated glass tube sequentially to pure air with ozone. The zero-air system is described in detail in Reiss et al. (9). The glass tube (inside diameter of 2.1 cm and length of 30 cm) was coated by standing the tube vertically and pouring the latex paint through it and allowing the excess paint to drip down to the bottom onto a towel. After about 2 h, the tube was placed horizontally on a shelf in the laboratory and allowed to dry 5 days prior to being exposed. The concentrations of polar VOCs including organic acids and carbonyls were measured before and after the latex paint test section. Also, the inlet and outlet concentrations of ozone were measured in order to determine the ozone deposition to the surface. The measurement methods for ozone, temperature, and relative humidity were described in Reiss et al. (9). For a typical experiment, a latex paint-coated tube was first exposed to zero-air for 3 h. The tube was then exposed to ozone for 3 h and then to a higher ozone concentration for 3 h. The first ozone exposure was typically between 50 and 75 ppb ozone, and the second ozone exposure was between 100 and 150 ppb ozone. The flow rate for these experiments was typically 2.5 L/min.

Modification of our apparatus was made to afford collection of organic acids and carbonyls. Organic acids were collected using potassium hydroxide (KOH) coated diffusion denuders and were analyzed using ion chromatography. Lawrence and Koutrakis (10) provide a description of this measurement method. In order to measure the organic acid production, one denuder was placed upstream of the test section, and another was placed downstream of the test section. For a typical organic acid experiment, a latex paint-coated tube was exposed to zero-air for about 18 h, and then the next day the same tube was exposed to ozone (60–110 ppb) for 18 h. The limit of detection (LOD) for formic acid was 6.6 ppb, and for acetic acid it was 1.6 ppb. Our apparatus does not allow collocated sampling. Therefore, these LODs were determined by multiplying three times the standard deviation of the laboratory blanks and using a representative flow rate and duration of experiments.

TABLE 1

Summary of Limits of Detection for Carbonyl Compounds

compound	molecular formula	LOD (ppb)
aldehydes		
formaldehyde	HCHO	1.28
acetaldehyde	CH_3CHO	0.70
acrolein	$CH_2{=}CHCHO$	0.39
propionaldehyde	CH_3CH_2CHO	0.44
crotonaldehyde	$CH_3CH{=}CHCHO$	0.89
butyraldehyde	$CH_3(CH_2)_2CHO$	0.64
benzaldehyde	C_6H_5CHO	3.20
isovaleraldehyde	$(CH_3)_2CHCH_2CHO$	0.71
n-valeraldehyde	$CH_3(CH_2)_3CHO$	1.21
n-hexaldehyde	$CH_3(CH_2)_4CHO$	2.28
ketones		
acetone	CH_3COCH_3	0.47
butanone	$CH_3COCH_2CH_3$	0.98

For carbonyl measurements, two ports, before and after the test section, draw off 1.0 L/min air. This air is pumped through a 2,4-dinitrophenylhydrazine– (DNPH) silica Sep-Pak cartridge (Millipore Corporation). A detailed description of this measurement method is given by Tejada et al. (11). Also, Arnts and Tejada (12) note that ozone interferes with the analysis. To eliminate these interferences, copper tubing coated with potassium iodide was placed upstream of the cartridge to act as an ozone scrubber. The limits of detection (LODs) are shown in Table 1. Only acetone had consistently measurable blank values. Thus, these LODs were determined by multiplying three times the standard

deviation of the lowest HPLC standard and assuming a typical flow rate and experimental duration.

Homogeneous versus Heterogeneous Chemistry. It is not known whether the VOC formation in residences is effected via homogeneous or heterogeneous chemistry or both. However, Reiss et al. (5) have shown, via a mathematical model, that ozone can react homogeneously with some indoor unsaturated hydrocarbons to account for about 20% of the ozone removal. Ozone also reacts homogeneously with nitric oxide, especially when gas appliances are present (5), but this reaction does not produce VOCs. However, it is known that ozone deposits on surfaces at significant rates (see refs 9 and 13). Our apparatus is designed to test only the heterogeneous reactions as the residence time in the test section is too short for homogeneous reactions to be significant. This can be shown by reaction kinetic principles given rate constants for ozone reactions of compounds known to off-gas from latex paint such as xylene and toluene (3). Thus, all values reported in this paper represent a lower limit for ozone-generated pollutants as homogeneous production and production from heterogeneous reactions on other surfaces are not taken into account.

Reaction Kinetic Calculations. We are interested in determining the rate of VOC formation as a function of ozone deposition in order to extrapolate our laboratory results to actual residential environments. Thus, we first need to quantify the ozone deposition. This can be done using the concept of the mass accommodation coefficient, which is defined as the number of "sticks" of a molecule colliding with a surface divided by the total number of collisions. Reiss et al. (9) present a method for determining the mass accommodation coefficient, α, of latex paint in a tube flow reactor. The mass accommodation coefficient in combination with knowledge of indoor air flows can be used to extrapolate chamber deposition results to predict ozone deposition in indoor residences (see refs 9 and 14). Since not all ozone "sticks" to the surface result in the formation of a single VOC constituent, it is necessary to define an additional parameter, κ, which we will refer to as the VOC formation factor. This parameter is defined as the number of molecules of a specific VOC constituent formed on the surface divided by the total number of "sticks" of ozone to the surface. The VOC formation factor is specific to each of the VOC molecules that is formed through ozone reactions. It is conceivable that this factor will be greater than unity if a single ozone molecule were to initiate a chain reaction resulting in the formation of multiple VOC molecules. The VOC formation factor was determined from our experimental data by dividing the total number of ozone molecules that deposited in the chamber by the total number of molecules of a particular VOC that is attributed to ozone formation. The emission rate attributable to ozone reactions can be determined from the emission rate of an ozone exposure minus the emission rate of the corresponding zero-air exposure. The emission rate may decrease with time, so this procedure provides a lower bound to the amount of VOC formed that is attributable to ozone reactions.

At steady state, the ozone flux across the boundary layer to the surface must be equal to the VOC flux across the boundary layer to the core region (defined as the area away from the room away from the surface boundary layer), modified by κ, which reflects the fraction of the ozone flux converted to VOC molecules, as follows:

$$J_s^{VOC} = \kappa J_s^{O_3}$$

This condition will be true even if some of the VOC molecules that are formed are adsorbed back onto the surface provided that there is an adsorption–desorption steady state. The ozone flux to the surface can be determined from the deposition velocity as follows:

$$K_{d_i} = J_s^{O_3}/[O_3]$$

where K_{d_i} is the deposition velocity corresponding to a particular surface. Cano-Ruiz et al. (14) developed a mathematical model for determining deposition velocities as a function of the nature of the air flow in the residence. They considered four possible air flow scenarios: (a) forced laminar convection parallel to a flat plate, (b) laminar natural convection flow along an isothermal vertical plate, (c) laminar natural convection flow in an enclosure, and (d) homogeneous turbulence in an enclosure. We will use the first and fourth scenarios as they are most likely to be present during the summer when the ozone is highest (9).

We can also use some of these concepts to model the mass emission rate of the VOCs off-gasing from the latex paints during steady-state conditions. Clausen et al. (15) have shown that VOC emission from latex paint is boundary layer limited as opposed to being dependent on diffusion of the VOCs through the condensed phase of the latex paint to the paint–air interface. Nevertheless, at steady state, we do not need to be concerned about the characteristics of the boundary layer of the residence because the flux of VOC off the surface will need to equal the flux of VOC at the edge of the boundary layer releasing into the core region. It will only be necessary to adjust for the different surface areas between our chamber apparatus and the surface area of latex paint in an actual indoor environment. It should be mentioned that some researchers have developed empirical models for the change over time of VOC emission rates (e.g., refs 16 and 17). However, we did not have enough data to use any of these models.

Results and Discussion

Organic Acid Results. The organic acid results are shown in Table 2. There was no evidence of organic acid formation via ozone reactions. However, significant quantities of acetic acid and smaller quantities of formic acid off-gased from all of the paint surfaces. Also, the emission rates increased dramatically with increasing relative humidity. The relative humidity effect is best observed for latex paint brand A. Without ozone, the emission rate for experiment A4 (a low relative humidity experiment) was 1.1 μg/s, while for experiment A2 (a high relative humidity experiment), it was 60.6 μg/s. Reiss et al. (5) have observed, in a residential field study in the greater Boston area, that the acetic acid emission rate was correlated with the indoor relative humidity. To examine the effect of prior ozone exposure on the off-gasing, we can compare experiments A2 (new) and A5 (10 months), which were both high relative humidity brand A exposures. The acetic acid emission rate was significantly lower for experiment A5 while the formic acid emission rate increased a small amount.

In all but one of the experiments (experiment A5), the emission rate for acetic acid was higher for the zero-air exposure compared to the ozone exposure. One explanation for the lower emission rates of acetic acid during ozone exposure is that the mass emission rate is lowered as the

TABLE 2

Summary of Organic Acid Results

exp	surface	age (months)	RH (%)	ozone (ppb)	formic acid in[a] (ppb)	formic acid out[b] (ppb)	formic acid ER[c] (μg/h)	acetic acid in[a] (ppb)	acetic acid out[b] (ppb)	acetic acid ER[c] (μg/h)
A1	latex brand A	new	50–55	0	1.6	2.7	0.3	2.7	86.5	28.6
			45–50	65	4.1	6.3	0.6	1.4	55.5	18.4
A2	latex brand A	new	75–80	0	2.9	13.0	2.6	0.9	178.8	60.6
			80–85	78	2.2	7.2	1.3	1.0	132.8	44.9
A3	latex brand A	new	80	0	1.7	1.6	N/A[d]	11.9	146.0	45.7
			75–80	73	1.8	4.9	0.8	0.9	81.4	27.4
A4	latex brand A	10	5–23	0	1.7	2.2	0.1	2.1	5.4	1.1
			4–5	75	4.8	5.0	0.05	0.7	1.8	0.4
A5	latex brand A	10	76–84	0	3.0	17.8	3.9	2.8	63.0	20.5
			78–80	89	3.1	16.5	3.5	1.2	63.9	21.4
A6	latex brand B	new	4–5	0	0.5	3.2	0.7	0.3	3.3	1.0
			4	110	3.0	0.5	N/A[d]	0.4	2.4	0.7
A7	latex brand B	new	48–54	0	1.0	2.2	0.3	3.4	56.8	18.2
			53	88	4.6	3.3	N/A[d]	3.3	35.4	11.0
A8	latex brand B	new	46–56	0	1.7	7.2	1.4	0.0	43.9	15.0
			45–46	75	3.9	7.9	1.0	3.2	26.9	8.1
A9	latex (red) brand C	new	47–54	0	0.8	4.5	1.0	2.4	80.9	26.7
			48–56	99	5.3	8.9	1.0	1.6	33.7	11.0

[a] The flow rate to the inlet denuder was 2.85 L/min. [b] The flow rate to the outlet denuder was 1.85 L/min. [c] ER, emission rate. [d] The emission rate could not be calculated because the outlet measurement was lower than the inlet measurement.

tube is exposed, and thus, the mass emission rate is lower during the ozone exposure because it was always done after the zero-air exposure. Future experiments should test this hypothesis by alternating the order of the zero-air and ozone exposures. However, it should be noted that the ozone exposure was always conducted second in order to err conservatively in our estimate of the VOC production as a result of ozone exposure. Thus, one must be cautious in interpreting results of an experiment where the ozone exposure preceded the zero-air exposure.

Carbonyl Compound Results. Table 3 shows a summary of the carbonyl compound experiments. The raw results and mass emission rates are shown in Table 4. Several brands of paint were tested including a non-white paint (see experiment C8). The relative humidity was varied throughout the experiments because it is known that relative humidity affects ozone deposition (*18*). Also, experiments C9 and C10 were run as replicates. This table only includes formaldehyde, acetaldehyde, and acetone because only a few samples showed detectable quantities of any of the higher weight compounds. Formaldehyde does appear to off-gas from latex paint. This is particularly true for latex paint brand C. Formaldehyde is not listed as a paint ingredient (although due to proprietary concerns we were not able to obtain listings of all compounds that are used). It is possible that air oxidation of the paint polymer could produce formaldehyde. For several of the experiments, we also observed small quantities of acetaldehyde and acetone off-gasing from the latex paints. However, the results for these compounds were not consistent. Some of the experiments did not show any off-gasing. This was also true for the replicates (C9 and C10). The formaldehyde results were consistent between the two experiments, but the acetaldehyde and acetone results were not consistent. The inconsistency in the acetaldehyde and acetone results may be due to the small quantities that were detected. This suggests a conclusion that off-gasing of these species, if it occurs, is likely to be small.

In several of the experiments, we observed the production of a secondary pollutant from an ozone–latex paint reaction, as evidenced by the increase in the emission rates

TABLE 3

Summary of Carbonyl Compound Experiments

exp	surface	age (months)	RH (%)	ozone (ppb)	deposition (%)
C1	latex paint brand A	new	24–26	0	
			18–20	55	75
			31–35	105	77
C2	latex paint brand A	13	40–43	0	
			48–52	71	4
			46–50	151	2
C3	latex paint brand B	new	28–30	0	
			26–28	49	44
			20–24	113	48
C4	latex paint brand B	14	10–16	0	
			12–16	49	26
			6–8	147	30
C5	latex paint brand C	new	52–54	0	
			50–53	61	74
C6	latex paint brand C	new	53–55	0	
			36–39	56	80
			35–37	112	77
C7	latex paint brand C	1	35–40	0	
			38–40	61	45
			32–35	110	42
C8	latex paint (red) brand C	new	21–25	0	
			22–28	62	50
			22–26	119	52
C9	latex paint	new	54–58	0	
			51–53	65	66
			52–54	112	56
C10	latex paint brand D	new	50–52	0	
			48–52	63	80
			52	112	73
C11	latex paint brand D	2	20	0	
			27	52	59
			18–20	101	48

of these compounds when the latex paint tubes were exposed to ozone. For experiments C4–C11, excess formaldehyde was produced from the introduction of ozone to the air stream. For a few of the experiments, the emission rate is linear with ozone (although there were not enough data points to conduct an adequate statistical analysis). Figure 2 shows this linear relationship for experiment C8. The ozone flux to the latex paint surface in the chamber is greater than a typical ozone surface flux in an actual residential environment, and the nonlinearity in deposition

TABLE 4

Summary of Raw Results from Carbonyl Experiments[a]

		formaldehyde			acetaldehyde			acetone		
exp	ozone (ppb)	in (ppb)	out (ppb)	ER (μg/h)	in (ppb)	out (ppb)	ER (μg/h)	in (ppb)	out (ppb)	ER (μg/h)
C1	0	0.8	1.9	0.18	0.5	3.4	0.69	1.5	2.0	0.16
	55	0.7	1.7	0.19	0.4	2.4	0.53	2.1	2.0	N/A
	105	0.9	1.9	0.18	0.7	2.8	0.55	2.2	2.4	0.06
C2	0	1.1	1.8	0.14	0.03	0.2	0.04	0.8	0.3	N/A
	71	1.3	1.9	0.13	0.5	1.0	0.16	1.6	2.0	0.18
	151	1.3	1.9	0.13	0.3	0.5	0.07	0.6	2.3	0.69
C3	0	2.0	7.3	0.95	0.5	0.4	N/A	0.0	0.1	0.02
	49	3.1	6.2	0.58	0.8	0.8	N/A	3.8	1.8	N/A
	113	2.8	7.8	0.96	0.9	1.6	0.20	1.6	0.8	N/A
C4	0	0.5	1.5	0.16	0.0	0.1	0.02	1.7	1.7	0.01
	49	0.6	4.4	0.68	0.6	1.2	0.14	1.5	2.4	0.32
	147	1.1	5.7	0.83	0.6	2.2	0.42	2.4	5.2	0.97
C5	0	1.8	14.5	2.42	0.6	0.5	N/A	1.2	0.0	N/A
	61	3.7	28.5	4.96	0.4	1.4	0.30	3.6	1.6	N/A
C6	0	1.0	20.5	3.45	0.6	1.4	0.22	0.9	0.8	N/A
	56	1.3	26.4	4.29	0.6	2.9	0.58	1.1	1.1	0.00
	112	2.1	35.5	6.29	1.0	4.5	0.97	1.5	1.6	0.01
C7	0	0.7	4.3	0.68	0.1	0.3	0.06	0.3	2.1	0.68
	.61	1.5	9.7	1.64	0.7	0.6	N/A	2.9	6.4	1.35
	110	5.0	19.3	2.86	2.7	2.4	N/A	7.0	2.3	N/A
C8	0	2.5	3.6	0.21	0.5	0.4	N/A	0.2	0.3	0.03
	62	2.3	11.1	1.71	1.0	1.3	0.09	3.9	1.1	N/A
	119	2.9	20.0	3.32	0.8	1.0	0.04	3.5	1.1	N/A
C9	0	0.5	0.9	0.07	0.0	1.1	0.34	0.3	0.5	0.05
	65	0.8	2.0	0.26	0.0	0.9	0.27	0.0	0.4	0.31
	112	0.8	3.1	0.46	0.4	2.6	0.66	1.9	1.3	N/A
C10	0	1.9	2.1	0.05	0.4	2.0	0.43	1.6	1.8	0.07
	63	1.9	3.4	0.30	1.5	1.4	N/A	3.3	2.6	N/A
	112	3.2	6.0	0.56	2.3	1.7	N/A	4.6	1.6	N/A
C11	0	0.3	2.5	0.38	0.0	0.1	0.03	0.1	0.4	0.09
	52	1.1	4.0	0.58	0.8	1.4	0.15	2.0	0.5	N/A
	101	1.0	5.0	0.77	0.8	1.3	0.14	3.0	2.2	N/A

[a] ER, emission rate. N/A, not applicable.

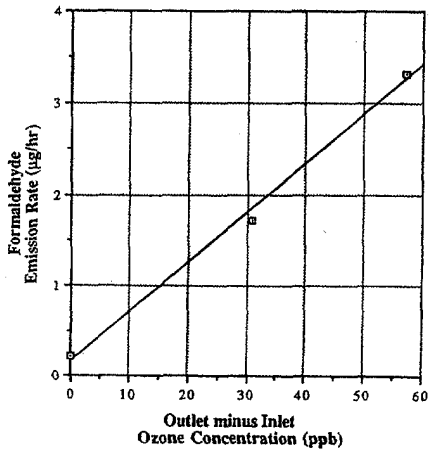

FIGURE 2. Outlet minus inlet ozone concentration versus formaldehyde emission rate for experiment C8.

usually begins at higher ozone fluxes. This suggests that the formaldehyde production via ozone–latex paint reactions in a residence may also be linear with respect to ozone concentration. Latex paint brand C showed the most formaldehyde production. The red brand C paint showed similar formaldehyde production to the white brand C latex paint, indicating that the pigment may not be a factor in the reactivity. Latex paint brand D also showed some excess production but less than brand C. Brand B may have some reactivity, but the results are inconsistent. Brand A did not show any reactivity and also showed very little formaldehyde off-gasing. Thus, it is clear that there are significant differenes among the different brands of paint. These paints are all based on vinyl polymers, but details about the formulations were not available because this information is proprietary. The cause of these differences in reactions is important for future research where more sophisticated techniques to study chemistry may be available.

Several of the experiments (C2, C4, C5, and C6) showed production of acetaldehyde via the ozone–latex paint reaction. Figure 3 shows a plot of ozone outlet minus inlet concentration versus the emission rate of acetaldehyde for experiment C4. Two experiments (C2 and C4) showed acetone production. The fact that fewer experiments showed acetaldehyde and acetone production as compared to formaldehyde production may be a result of the low concentrations that were being measured, and thus, any changes may be difficult to distinguish from experimental error. Changes in these smaller values may not be measurable with our apparatus. Nonetheless, if ozone reacting on latex paint truly forms acetaldehyde and acetone, it does so in small quantities.

The effect of aging may be manifested as a decrease in the ozone deposition. Reiss et al. (9) observed that the ozone mass accommodation coefficient decreased by about an order of magnitude for several tubes that were about 1

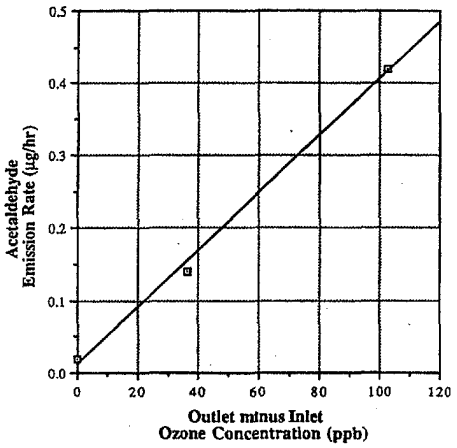

FIGURE 3. Outlet minus inlet ozone concentration versus acetaldehyde emission rate for experiment C4.

year old. The particular deposition mechanism that results in the VOC formation will determine how the decrease in deposition affects VOC production. We do not have enough data to determine the rate at which the VOC formation factor decreases with time. This is an area for future research. Another potential factor that should be investigated is the paint film thickness. Clausen et al. (*15*) showed that the film thickness of the paint, which was not controlled in this study, influences the VOC off-gasing rates of several compounds. The effect of paint film thickness on VOC formation via ozone reactions should be investigated.

Extrapolation of Model Results to Indoor Environments. Using the model developed above, we can extrapolate the results from this laboratory study to actual indoor air environments. The key variable is the VOC formation factor (κ). The VOC formation factors for the carbonyl experiments are shown in Table 5. Reiss et al. (*5*) conducted a residential field study in the Boston, MA, area where 24–h average indoor and outdoor carbonyl concentrations and emission rates were measured. We will compare the emission rate of carbonyls from the latex paint to the total carbonyl emission rate to determine the significance of the ozone–latex paint reaction. The summer data from this study will be used as ozone is most prevalent during the summer. These researchers found the following averages among the nine homes that were sampled: (a) indoor formaldehyde concentration, 16.1 ppb; (b) outdoor formaldehyde concentration, 2.4 ppb; (c) formaldehyde emission rate, 2.3 $\mu g/m^3$; (d) outdoor ozone concentration, 26.3 ppb; (e) air exchange rate, 2.6 h^{-1}; and (f) average residence volume, 350 m^3. [Several other assumptions were also necessary to apply the Cano-Ruiz et al. deposition model. These include (a) indoor air flow, 10 cm/s (ref 14), which is used to determine the boundary layer thickness; (b) turbulence intensity, 1 s^{-1} for $m = 2$ (ref 14); (c) typical mass accommodation coefficient for latex paint, 5×10^{-6} (ref 9).] We will use a surface to volume ratio (A/V) of 3.3 m^{-1} (20). By examining the descriptions of the residences sampled in this study, we estimate the A_p/V to be about 1.0 m^{-1}, where A_p is the surface area of only the latex paint. For a high end value of κ (0.25), the calculated source emission rate of formaldehyde is 0.25 $\mu g/s$ for laminar flow and 0.35 $\mu g/s$ for turbulent flow, which is 10.9% and 15.2%, respectively, of the formaldehyde emission rate measured by Reiss et al. (*5*). For a low-end value of κ (0.03), the source emission rate of formaldehyde is 0.029 $\mu g/s$ for laminar flow and 0.041 $\mu g/s$ for turbulent flow, which is 1.3% and 1.8%, respectively, of the measured formaldehyde emission rate. We can use the model in a more general sense by calculating the source emission rate of VOCs produced by an ozone reaction as a function of κ. A plot of the VOC formation factor versus the formaldehyde emission rate for laminar and turbulent flow is shown in Figure 4, given the assumptions listed above.

TABLE 5
Summary of Reaction Kinetic Parameters

		VOC formation factor		
exp	ozone (ppb)	HCHO	CH_3CHO	CH_3COCH_3
C1	55	0.0	N/A[a]	N/A
	105	0.0	N/A	N/A
C2	71	0.0	0.13	0.34
	151	0.0	0.03	0.77
C3	49	0.0	0.0	N/A
	113	0.0	0.01	N/A
C4	49	0.23	0.04	0.07
	147	0.09	0.04	0.06
C5	61	0.28	0.02	N/A
C6	56	0.11	0.03	0.0
	112	0.17	0.03	0.0
C7	61	0.17	N/A	0.06
	110	0.24	N/A	N/A
C8	62	0.25	0.01	N/A
	119	0.26	0.0	N/A
C9	65	0.02	N/A	0.02
	112	0.03	0.02	N/A
C10	63	0.03	N/A	N/A
	112	0.03	N/A	N/A
C11	52	0.03	0.01	N/A
	101	0.04	0.01	N/A

[a] N/A denotes that the VOC formation factor was negative, which is a nonphysical result that usually occurred when low concentrations were being measured.

We can also examine the effects of the natural off-gassing of the VOCs from the latex paint surface. In the above model for the ozone reactions, we were able to adjust for the aging effect by use of a mass accommodation coefficient for an aged surface. However, for the off-gasing, we cannot make adjustments for the age of the paint. Nonetheless, our estimates will be valid for new paints. The largest off-gasing was observed for acetic acid. For a typical new paint, we observed an off-gasing of 0.011 $\mu g/s$ from our chamber, which after adjusting for differences in the surface area of the chamber and a typical residence (see above) translates into an emission rate of 168 $\mu g/s$ in a residence. This is a very high emission rate compared to the average of 10.4 $\mu g/s$ observed in a summer field study by Reiss et al. (*5*). This indicates that freshly coated paints will result in a very large indoor acetic acid concentration in an actual residence. For the two aged experiments, we observed an emission rate of about 0.0057 $\mu g/s$ for the high relative humidity experiment and 3.1×10^{-4} $\mu g/s$ for the low relative humidity experiment. This translates into 86 and 4.6 $\mu g/s$, respectively, for an indoor residence. The high relative humidity emission rate gives an unrealistically high indoor emission rate, about eight times what was observed in the field study. It may be that latex paints age faster in actual residences. This could occur because there is more air

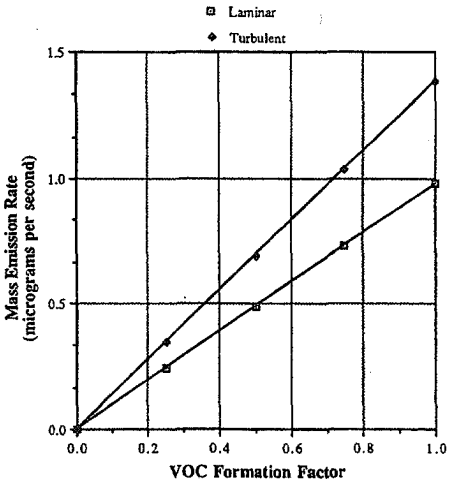

FIGURE 4. VOC formation factor versus formaldehyde mass emission rate for laminar and turbulent flow given assumptions listed in the text.

flow across the surface of latex paints in residences than our tubes in the laboratory. For formaldehyde, an average new paint emission rate was 0.0014 μg/s, which gives an indoor emission rate of 21 μg/s. The emission rate for an aged paint or a new paint for some brands was 2.8×10^{-4} μg/s, which gives an indoor emission rate of 4.2 μg/s. The average emission rate for formaldehyde observed by Reiss et al. (5) was about 2.3 μg/s. Thus, the formaldehyde concentrations will also be higher after application of an interior latex paint.

Conclusions

Formaldehyde was observed to be formed when latex paint surfaces were exposed to ozone. There was some evidence that acetaldehyde and acetone were also formed during ozone exposures. The formaldehyde production is sufficient enough to impact indoor formaldehyde production measurably. We also observed significant quantities of several of the carbonyls and organic acids off-gasing from the latex paints. The mass emission rates of the off-gasing from new latex paints were significantly higher than the total mass emission rate observed in a residential field study. A mechanism involving the ozonation of impurities in the vinyl resin of the paint is proposed for the production of the polar VOCs. Future research in this area should concentrate on determining the effect of aging, film thickness, and brand of latex paint on these processes. Also, given that the reactions studied in this paper only account for up to about 30% of the ozone deposition, future work should aim toward explaining what happens to the rest of the ozone.

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Glossary

A	surface area of the residence
A_p	latex paint surface area of the residence
$J_s^{O_3}$	ozone flux to surface
J_s^{VOC}	VOC flux from surface
K_d	deposition velocity
V	volume of residence

Greek Symbols

κ	VOC formation factor

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