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EVALUATION OF CHROMATOGRAPHIC SORBENTS USED IN AIR POLLUTION STUDIES

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SUMMARY

Laboratory and field experiments were performed to examine potential *in situ* formation of chemical substances or their decomposition on the surface of Tenax GC, XAD-2 and carbon sorbents. The effects of NO_x and ozone in air were tested for conversion of olefins plus molecular halogens into halogenated hydrocarbons. Possible reactions between ozone and olefins producing polar products on sorbent surfaces were studied. Trace quantities of halogenated hydrocarbons were produced in reactions between molecular halogens (bromine and chlorine) and 2-butene and cyclohexene but not with ethylene or propylene. These *in situ* reactions were prevented by using a sodium thiosulfate impregnated glass fiber filter in front of the sorbent cartridge to quench the reactive gases.

INTRODUCTION

An approach to the detection, identification and quantification of halogenated hydrocarbons in the ambient air has previously been described¹⁻²⁶. Ambient air was sampled using a Tenax GC cartridge technique and sample analysis employed high-resolution (glass capillary) gas chromatography-mass spectrometry-computer (HRGC-MS-COMP) methods. Many halogenated hydrocarbons have been identified and quantified in ambient air from several geographical regions throughout the Continental U.S.

In view of the potency and the broad spectrum of carcinogenic activity (in experimental animals) for the halogenated hydrocarbons identified the detection of these compounds in the atmosphere has generated considerable interest in their origin. Many of the previous studies were initiated to determine emission of halogenated hydrocarbons from stationary and fugitive sources as well as their potential formation through photochemical reaction from precursors.

In order to determine whether halogenated hydrocarbons may be present in the atmosphere from industrial sources or as products of an atmospheric chemical reaction, it was first necessary to know the extent to which these compounds may

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form at trace levels as an "artifact" of the technique employed or the sample collection process. Furthermore, the experimental methods should differentiate between homogeneous and heterogeneous reaction mechanisms.

Our primary concern has been with the use of the Tenax GC sampling cartridge which has been extensively employed for collecting organic vapor from ambient air for characterization and quantification purposes. Since the Tenax GC cartridge may concentrate reactive compounds including ozone, NO_x and, for example, molecular chlorine or bromine, *in situ* formation of artifact compounds may occur, even though inorganic gases do not appreciably accumulate on the sorbent⁸. It was the purpose of this study to further supplement previously reported observations, *i.e.*, the *in situ* formation of N-nitrosamines, and to determine whether other additional *in situ* reactions could occur on the Tenax GC sampling cartridge^{11,14}.

Since urban air often contains substantial concentrations of NO_x and ozone, we conducted a series of laboratory experiments to determine whether air containing these gases might be more effective than air containing only NO_x in converting olefins plus molecular halogens. Experiments were designed to delineate the transformation of olefins [whether adsorbed on sorbents (Tenax GC, XAD-2 and carbon) or occurring in low concentrations in air] via homogenous atmospheric reactions or heterogeneous reactions which might take place on the walls of the sample inlet tube. In addition to the halogenation of olefins, we were interested in the possibility of reactions between ozone and olefins producing polar products which also might be considered as artifacts of the collection process.

EXPERIMENTAL

Apparatus for laboratory studies

The apparatus used to determine whether air containing ozone, NO (Matheson, Coleman & Bell, East Rutherford, N.J., U.S.A.), NO_2 (Matheson, Coleman & Bell), olefins, molecular halogens and water might convert olefins to halogenated compounds on Tenax GC (35-60 mesh, Applied Science Labs., State College, Pa., U.S.A.) is depicted in Fig. 1. Nitric oxide was measured into the stream with a rotometer and a metering valve from a supply tank which contained ppm of NO and nitrogen (Scott Environmental). Ozone was generated by an ultraviolet lamp equipped with a sliding cover for obtaining different concentrations. Concentrations of NO, NO_2 and ozone were monitored with a Bendix NO_x analyzer (Model 5513802) and a Bendix ozone analyzer. Intakes for these instruments were at the same point as the intake for the Tenax GC glass cartridge sampler (6.0 cm bed length \times 1.5 cm I.D.) through which air was drawn by a Nutech Model 221-A (Nutech, Durham, N.C., U.S.A.) sampler. The sampling cartridge and the analyzer inlet tubes were centered in the air flow pattern from the reaction tube. Various levels of relative humidity in the air stream were produced by changing the temperature of the humidifier bath.

Permeation tubes (TFE) of molecular chlorine and bromine were prepared and gravimetrically calibrated with a MS-5A Mettler balance after their equilibration to a constant rate.

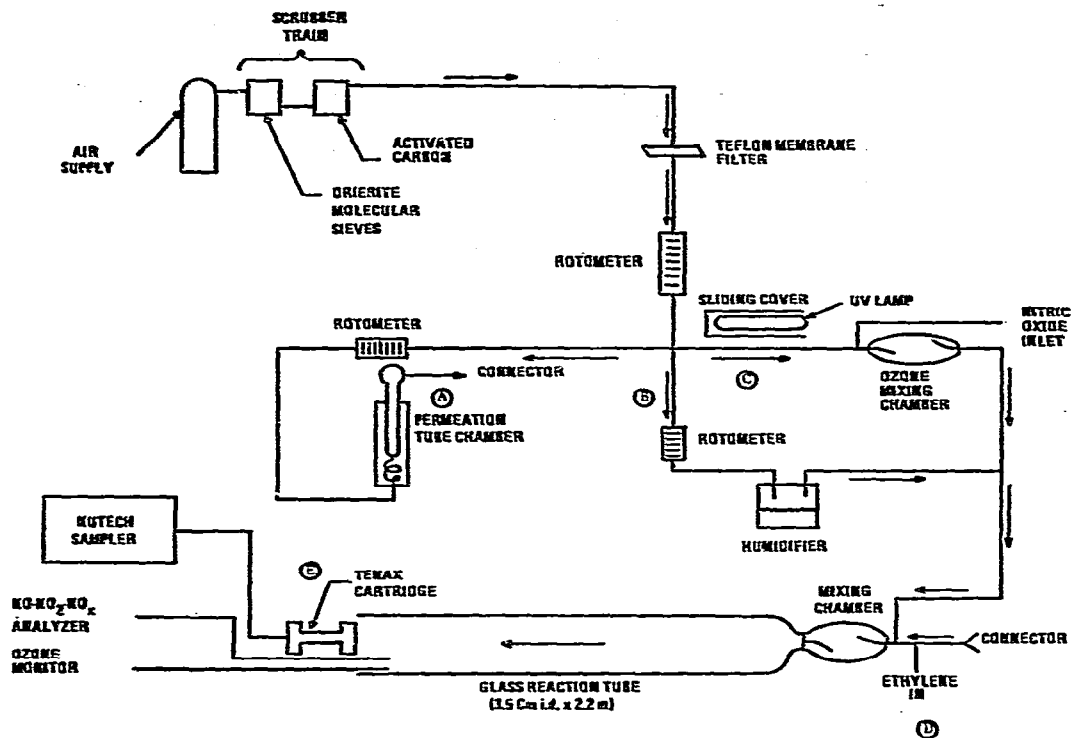


Fig. 1. Schematic of instrumentation and devices for examining *in situ* formation of halogenated hydrocarbons on solid sorbent surfaces.

Preparation of sorbent cartridges

Prior to its use, Tenax GC was purified by Soxhlet extraction for 18 h with methanol and *n*-pentane, respectively. After drying under nitrogen atmosphere, Tenax GC was heated to 150° for 2 h in a vacuum oven (12 in. of water), sized into a 35–60 range and packed into glass tubes (6.0 cm bed length × 1.5 cm I.D.). All sample cartridges were preconditioned by heating to 275° for 20 min under a helium purge of 20–30 ml/min. After cooling in precleaned Kimax® culture tubes, the containers were sealed to prevent contamination of the cartridge.

The effect of ozone on tetrachloroethylene during sampling with charcoal (SKC) tubes containing 150 mg of sorbent was examined. Tetrachloroethylene (149 ng) was loaded on charcoal sampling cartridges and known levels of ozone, NO and NO₂ in ambient air were sampled through the charcoal tube. A mixture of methanol and carbon disulfide (1:1, v/v) was used to desorb the tetrachloroethylene for subsequent analysis.

XAD-2 sorbent cartridges (3.0 cm bed length × 1.5 cm I.D.) were prepared in the same manner as Tenax, except thermal conditioning was performed at 200° for 2 h.

Sample analyses

Replicate samples and blanks were analyzed by GC equipped with flame-

ionization detection. Thermal desorption was used to transfer vapors from the cartridge sampler to the analytical system using a specially designed manifold¹⁻⁵. In a typical thermal desorption cycle, sampling cartridges were placed in the desorption chamber (275°) and helium gas was passed through the cartridge (*ca.* 20 ml/min) to purge the vapors into the liquid nitrogen cooled nickel capillary trap. After desorption (4 min), the six-port valve was rotated and the temperature on the capillary loop was rapidly raised (>150°/min). The carrier gas introduced the vapors onto the capillary gas-liquid chromatographic (GLC) column. The 100-m glass SCOT containing SE-30 stationary phase and was programmed from 30 to 240° at 4°/min. A Varian 3700 gas-liquid chromatograph was used. Hydrogen and air were 35 and 200 ml/min, respectively.

GLC with electron-capture detection and a column (Pyrex, 1.8 m × 2.5 mm I.D.) of 0.2% Carbowax 1500 on Carbowax C was used. A Fisher Victoreen Model 4400 gas-liquid chromatograph equipped with a high-temperature scandium titride electron-capture detector was used²⁷.

A Varian MAT CH-7 gas-liquid chromatograph-mass spectrometer with a 620 L computer system equipped with an inlet manifold was used for analyzing Tenax GC cartridges where structural confirmation was required. The software programs available with this system provide for reconstructed gas chromatograms and mass fragmentograms for correlation between mass spectrum number and retention time. Operating parameters for the HRGC-MS-COMP system are given in Table I. A single stage glass jet separator interfaced the SCOT capillaries to the mass spectrometer.

TABLE I
OPERATING PARAMETERS FOR GLC-MS-COMP SYSTEM

<i>Parameter</i>	<i>Setting</i>
<i>Inlet-manifold</i>	
Desorption chamber	270°
Valve	220°
Capillary trap —minimum	-195°
maximum	250°
Thermal desorption time	4 min
<i>GLC</i>	
100 m glass SCOT SE-30	30-240°, 4°/min
Carrier (He) flow	≈ 3 ml/min
Transfer line to MS	240°
<i>MS</i>	
Scan range	<i>m/e</i> 20-300
Scan range, automatic-cyclic	1 sec/decade
Filament current	300 μA
Multiplier	6.0
Ion source vacuum	<i>ca.</i> 4 · 10 ⁻⁶ Torr

Field sampling experiments

Field artifact studies were conducted in Baton Rouge, La., U.S.A., and vicinity. Table II presents the experimental design. A schematic of the configurations under examination in artifact study is given in Fig. 2. In this study, we examined

TABLE II

EXPERIMENTAL DESIGN FOR FIELD *IN SITU* REACTION STUDIES IN BATON ROUGE, La., U.S.A.

GFF-U = glass fiber filter, untreated.

Sample code	Experimental configuration*	Filter		Glass tube		Adsorbent	
		F ₁	F ₂	T ₁	T ₂	Ad ₁	Ad ₂
P1/LSA-1	A	GFF-U	GFF-U	—	+Br ₂	Tenax	Tenax
P1/LSA-2	A	GFF-U	GFF-U	—	+Cl ₂	Tenax	Tenax
P1/LSB	A	GFF-U	GFF-U	—	+DMA-d ₆	Tenax	Tenax
P2/LSA	A	GFF-U	GFF-U	—	+Br ₂	Tenax	Tenax
P2/LSB	A	GFF-U	GFF-U	—	+Cl ₂	Tenax	Tenax
P2/LSC	A	GFF-U	GFF-U	—	+DMA-d ₆	Tenax	Tenax
P3/LSA	A	GFF-U	GFF-U	—	+Br ₂	Tenax	Tenax
P3/LSB	A	GFF-U	GFF-U	—	+Cl ₂	Tenax	Tenax
P3/LSC	A	GFF-U	GFF-U	—	+DMA-d ₆	Tenax	Tenax

* Experimental configuration given in Fig. 2.

the potential bromination, chlorination and nitrosation of endogenous atmospheric organics by employing a tandem arrangement as shown in the configuration A (Fig. 2). In this case, the ambient air was first pulled through glass fiber filters and through glass tubes followed by a tube containing the adsorbent Tenax GC. The glass tube designated as T₂ contained a permeation tube of either bromine (*ca.* 4 · 10⁻⁷ g/min), chlorine (*ca.* 1 · 10⁻⁶ g/min) or d₆-dimethylamine (7 · 10⁻⁷ g/min). Thus, molecular halogen or d₆-dimethylamine which permeated at a constant rate provided a constant sparging of the atmosphere just prior to the adsorbent bed. The corresponding

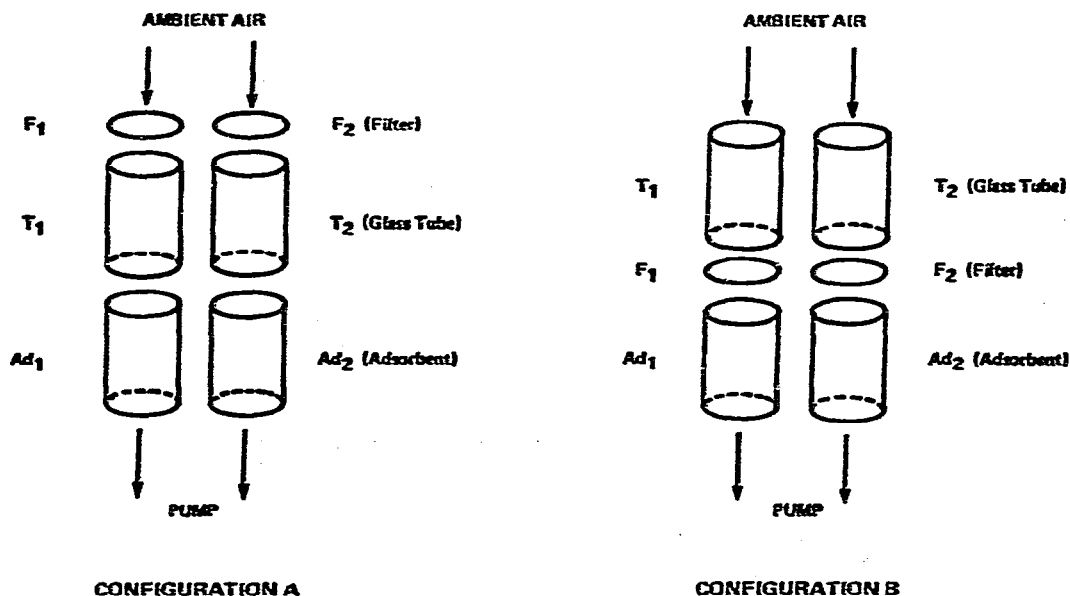


Fig. 2. Experimental sampling cartridge configurations for *in situ* reaction studies.

TABLE III
EFFECTS OF REACTANT GASES AND MOLECULAR CHLORINE ON *IN SITU* FORMATION OF HALOGENATED ETHANES ON TENAX
GC
ND = not detected.

Experiment No.	Reactant gas concentrations (ppb)							Volume sampled (l)	C ₂ H ₄ Cl ₂ detected (ng)	Remarks
	O (added)	O ₃ (excess)	NO _x	NO	NO ₂	Cl ₂	C ₂ H ₄			
1	0	0	0	0	0	86	590	16	ND	Blank control
2	0	0	0	0	0	0	0	16	ND	
3	0	0	0	0	0	86	0	16	ND	
4	0	0	0	0	0	86	590	16	ND	
5	160	160	0	0	0	86	590	16	ND	
6	250	120	130	0	130	86	590	16	ND	
7	880	880	0	0	0	86	590	16	ND	
8	1290	570	720	0	720	86	590	16	ND	
9	0	0	200	200	0	86	590	16	ND	
10	0	0	800	800	0	86	590	16	ND	
11	840	0	1720	880	840	86	590	16	ND	
12	740	740	0	0	0	86	590	16	ND	With GFF
13	1220	620	600	0	600	86	590	16	ND	With GFF
14	0	0	920	920	0	86	590	16	ND	With GFF
15	760	0	1520	760	60	86	590	16	ND	With GFF
16	--	--	--	--	--	--	--	--	840	
17	--	--	--	--	--	--	--	--	420	
18	--	--	--	--	--	--	--	--	210	For response curve

parallel arrangement served as a control (T_1). By examining independently the cartridges labeled Ad_1 and Ad_2 , it was possible to determine the endogenous organics in the atmosphere and to differentiate these from those which were formed as an *in situ* reaction on the adsorbent.

RESULTS AND DISCUSSION

Laboratory studies

A series of experiments was conducted which examined the potential *in situ* formation of chemical substances or their decomposition on the surface of the solid sorbent Tenax GC. The experimental conditions chosen were selected to allow the detection of potential *in situ* formation of organic substances under typical atmospheric conditions encountered during field sampling.

Table III presents the series of experiments which were conducted utilizing different combinations of ozone, NO_x , NO, NO_2 , chlorine and ethylene. The volume of air stream sampled was 16 l in all cases. In all experiments (experiments 1-15) with or without the presence of a glass fiber filter in front of the Tenax cartridge, no dichloroethane was detected. In experiments 16-18, standard amounts of authentic dichloroethane were loaded onto cartridges to obtain a standard curve response for the flame-ionization detector. The detection limit was *ca.* 10 ng per cartridge.

Table IV presents additional experiments on the effect of NO, NO_2 and ozone on chlorination of ethylene. In these experiments, higher concentrations of ozone were added to the extent that in some cases (experiments 19 and 22) excess ozone was present. In other experiments, high concentrations of NO and NO_2 were created to provide extreme atmospheric conditions to determine whether it was possible to produce chlorinated ethylene. As depicted in this table, no 1,2-dichloroethane or other products as the results of reactions between these reagent gases could be detected. The detection limit was *ca.* 10 ng using a flame-ionization detector.

Table V presents experiments employing various concentrations of standard pollutants and a mixture of olefins. Other olefins which might be more reactive were used to determine whether any halogenated hydrocarbons might be formed. The olefin mixture consisted of ethylene (10 ppm), propylene (9.92 ppm), 1-butene (12.8 ppm), *cis*-2-butene (7.82 ppm) and *trans*-2-butene (8.40 ppm). The flow-rate was 250 ml/min into the mixing chamber prior to the reaction tube. Thus the various concentrations of olefins indicated in Table V were produced. These olefin concentrations and the relative proportions remained the same for all experiments (Table V). Molecular chlorine was introduced from a permeation tube (Metronix) which had been calibrated to determine its permeation rate.

Again, no dichloroethane was detected in these experiments (Table V). However, 2,3-dichlorobutane (racemic and meso forms) were detected. Their formation also occurred in the absence of standard pollutants (experiment 3). Indicated in this table are the relative amounts of each product based upon peak height response to the flame-ionization detector. These results suggest that small quantities of chlorinated substances may be produced when molecular chlorine and 2-butenes (with or without standard pollutants) are presented to a Tenax GC sampling cartridge.

TABLE IV

EFFECT OF NO, NO₂, AND O₃ ON CHLORINATION OF ETHYLENERelative humidity → 50%, no GFF was used, sampling rate = 1 l/min and all reactants and Cl₂ were introduced at beginning of flight tube.

Experiment No.	O ₃ Added (ppb)	O ₃ Excess (ppb)	NO _x (ppb)	NO (ppb)	NO ₂ (ppb)	Cl ₂ (ppb)	C ₂ H ₄ (ppm)	Vol. sampled (l)	1,2-Dichloroethane (ng)
19	840	840	0	0	0	86	2.04	16	0
20	900	0	900	0	900	86	2.04	16	0
21	0	0	840	840	0	86	2.04	16	0
22	1020	520	500	0	500	86	2.04	16	0
23	600	0	1320	720	600	86	2.04	16	0

TABLE V

EFFECTS OF STANDARD POLLUTANTS, MOLECULAR CHLORINE AND OLEFINS ON IN SITU FORMATION OF HALOGENATED COMPOUNDS ON TENAX GC

Experiment No.	Reactant gas concentration (ppb)										Volume sampled (l)	2,3-DCB (rac.) detected Peak height (cm)	2,3-DCB (Meso) detected Peak height (cm)	C ₃ H ₆ Cl ₂ (ng)	C ₃ H ₄ Cl ₂
	O ₃ (added)	O ₃ (excess)	NO _x	NO	NO ₂	Cl ₂	C ₂ H ₄	C ₃ H ₆	C ₄ H ₆	C ₄ H ₈					
1	0	0	0	0	0	86	581	577	744	455	488	0	0	0	0
2	0	0	0	0	0	86	581	577	744	455	488	0	0	0	0
3	0	0	0	0	0	86	581	577	455	488	744	10.2	8.2	0	0
4	120	0	0	0	0	86	581	577	744	455	488	6.0	4.8	0	0
5	860	860	0	0	0	86	581	577	744	455	488	2.9	2.9	0	0
6	0	0	200	200	0	86	581	577	744	455	488	2.9	2.2	0	0
7	0	0	940	940	0	86	581	577	744	455	488	6.8	5.5	0	0
8	200	0	200	0	200	86	581	577	744	455	488	6.5	5.4	0	0
9	920	0	920	0	920	86	581	577	744	455	488	7.3	5.9	0	0

Table VI presents experiments concerning the effect of NO, NO₂ and ozone on the chlorination of olefins (581 ppb* ethylene, 577 ppb propylene, 744 ppb 1-butene, 455 ppb *cis*-2-butene and 488 ppb *trans*-2-butene were the chamber concentrations). Ethylene, propylene and 1-butene did not yield detectable chlorinated hydrocarbons (detection limits \approx 10 ng using flame ionization). On the other hand, significant quantities of 2,3-dichlorobutane (racemic and meso) were detected. In the absence of ozone, NO_x, NO and NO₂ molecular chlorine and 2-butene did react immediately in front of the Tenax GC cartridge or in the front of the flight tube to produce dichlorobutane mixtures (experiment 17). On the other hand, the addition of NO to the reaction between chlorine and 2-butene appeared to suppress the chlorination reaction (experiment 12). In cases in which ozone was added or ozone plus NO, NO₂, low yields of chlorinated butanes were found.

Experiments 18–22, 24 and 28–31 were conducted in which the olefins were introduced at the beginning of the flight tube and sampling was conducted using a glass fiber filter impregnated with 10% sodium thiosulfate in front of the Tenax GC cartridge. In all of these experiments, regardless of the concentration of ozone, NO_x, and NO₂, no chlorinated products were detected. These experiments are contrasted with experiments 23 and 27 which a glass fiber filter was used which had not been impregnated with sodium thiosulfate.

The capacity of filters which have been impregnated with 10% sodium thiosulfate was tested using an ozone concentration of 200 ppb. A volume of 400 l of air was pulled through the filter. The filter was then placed in-line with the ozone monitor and no ozone was detected. The filter was not tested to its breakthrough limit since field sampling does not generally exceed a sampling volume of 200 l and ozone levels seldom exceed 200 ppb.

The reaction products from the reactions between NO, NO₂ and ozone, chlorine and butene appeared to increase when the glass wool plug used to anchor the Tenax was removed or when the glass fiber filter on the intake to the Tenax cartridge was removed. The presence of the glass wool and glass fiber filter thus appeared to decrease the amount of artifact seen, in contrast to observations on the *in situ* reactions or the formation of N-nitrosamines¹⁴. These observations indicate that the artifact reactions occur on the Tenax sorbent to a significant extent since yields as high as 300 ng were observed.

Furthermore, an additional artifact apparently occurred as indicated by the presence of a polar compound during GC. In Table VI the amount of polar material formed based upon peak height is given for the various experiments conducted. The polar material was identified subsequently by GC-MS to be propionic acid. Traces of acetone, acetic acid, acetaldehyde, propionaldehyde and methyl ethyl ketone were also detected. Formation of the major polar compound was also prevented using a sodium thiosulfate impregnated filter. New artifacts as the result of the impregnation of the glass fiber filter with sodium thiosulfate were not observed.

Potential *in situ* reaction experiments have also been conducted using ethylene and bromine. No artifacts have been observed. The detection limit for ethylene dibromide was approximately 50 ng when using flame-ionization detection. Tables VII

* Throughout this article the American billion (10⁹) is meant.

TABLE VI

EFFECT OF NO, NO₂ AND O₃ ON CHLORINATION OF OLEFINS

A = olefins introduced immediately in front of cartridge, B = olefins introduced at beginning of flight tube, GFF impregnated with 10% Na₂S₂O₃ was used, C = olefins introduced at beginning of flight tube, GFF used, D = olefins introduced at beginning of flight tube, glass wool used to anchor Tenax was removed, E = olefins introduced at beginning of flight tube.

Experiment No.	Condition(s)	O ₃ added (ppb)	O ₃ excess (ppb)	NO _x (ppb)	NO (ppb)	NO ₂ (ppb)	Cl ₂ (ppb)	2-Butene (ppb)	2,3-Dichlorobutane formed (rac.) (ng)	2,3-DCB (Meso) (ng)	Polar material (pk. hgt., cm)
10	A	860	860	0	0	0	86	943	200	165	26
11	A	860	860	0	0	0	0	954	0	0	22
12	A	0	0	840	840	0	86	936	32	27	0
13	A	880	0	880	0	880	86	936	50	32	0
14	A	100	100	0	0	0	86	943	217	185	16
15	A	100	0	100	0	100	86	942	182	147	0
16	A	200	100	100	0	100	86	942	152	115	21
17	A	0	0	0	0	0	86	943	365	320	0
18	B	200	200	0	0	0	86	943	0	0	0
19	B	220	220	0	0	0	86	943	0	0	0
20	B	200	200	0	0	0	0	954	0	0	0
21	B	200	200	0	0	0	0	954	0	0	0
22	B	0	0	0	0	0	0	954	0	0	0
23	C	200	200	0	0	0	86	943	15	10	16
24	B	200	200	0	0	0	86	943	0	0	0
25	D	200	200	0	0	0	86	943	260	210	22
26	E	0	0	0	0	0	86	943	62	40	0
27	C	200	200	0	0	0	0	954	0	0	22
28	B	0	0	200	200	0	86	940	0	0	0
29	B	200	0	200	0	200	86	940	0	0	0
30	B	400	200	200	0	200	86	940	0	0	0
31	B	200	0	400	200	200	86	940	0	0	0

TABLE VII

EFFECTS OF REACTANT GASES AND MOLECULAR BROMINE ON *IN SITU* FORMATION OF HALOGENATED ETHANES ON TENAX GC

Experiments 1-3 and 5 did not employ a glass fiber filter; experiments 4, 6, 7 used Na₂S₂O₃ impregnated glass fiber filters.

Experiment No.	Reactant gas concentrations (ppb)							Volume sampled (l)	1,2-Dibromoethane (ng)
	O ₃ (added)	O ₃ (excess)	NO	NO ₂	NO _x	Br ₂	C ₂ H ₄		
1	0	0	0	0	0	45	2000	16	0
2	0	0	0	0	0	45	2000	16	0
3	200	200	0	0	0	45	2000	16	0
4	0	0	0	0	0	45	2000	16	0
5	0	0	100	0	100	45	2000	16	0
6	140	0	0	140	140	45	2000	16	0
7	600	600	0	0	0	45	2000	16	0

TABLE VIII

EFFECTS OF REACTANT GASES AND MOLECULAR BROMINE ON *IN SITU* FORMATION OF HALOGENATED ETHANES ON TENAX GC

Experiments 1-3 and 5 did not employ a glass fiber filter; experiments 4, 6, 7 used Na₂S₂O₃ impregnated glass fiber filters.

Experiment No.	Reactant gas concentration (ppb)							Volume sampled (l)	1,2-Dibromoethane (ng)
	O ₃ (added)	O ₃ (excess)	NO	NO ₂	NO _x	Br ₂	C ₂ H ₄		
1	0	0	0	0	0	45	2000	16	0
2	0	0	0	0	0	45	2000	16	0
3	200	200	0	0	0	45	2000	16	0
4	0	0	0	0	0	45	2000	16	0
5	0	0	100	0	100	45	2000	16	0
6	140	0	0	140	140	45	2000	16	0
7	600	600	0	0	0	45	2000	16	0

and VIII present the effects of reagent gases and molecular bromine on *in situ* formation of halogenated ethanes on Tenax GC.

Table IX gives the effects of standard pollutants, molecular bromine and olefins on *in situ* formation of halogenated compounds on Tenax GC. For the combination of reactive gases plus the olefin mixture as listed in experiments 1-16, no 2,3-dibromobutane was detected.

These results suggest that the formation of 2,3-dichlorobutane is a rather unusual reaction since no other olefins appear to react with molecular chlorine and bromine in the presence or absence of criteria pollutants. The incorporation of sodium thiosulfate into the glass fiber filter may provide a new avenue for eliminating potential *in situ* formation reactions as a result of the presence of molecular halogens and/or ozone. It would be interesting to conduct further studies in light of these new observations to see whether the *in situ* formation of nitrosamines can be eliminated or suppressed by the incorporation of sodium thiosulfate or an equivalent material into the filter prior to analysis.

TABLE IX

EFFECTS OF STANDARD POLLUTANTS, MOLECULAR BROMINE, AND OLEFINS ON *IN SITU* FORMATION OF HALOGENATED COMPOUNDS ON TENAX GC

A glass fiber filter impregnated with $\text{Na}_2\text{S}_2\text{O}_3$ was used in each experiment. Olefin mixture = ethylene (580 ppb), propylene (580 ppb), 1-butene (740 ppb), *cis*-2-butene (455 ppb) and *trans*-2-butene (490 ppb).

Experiment No.	Reactant gas concentration (ppb)							Volume sampled	2,3-Dibromobutane (ng)
	O_3 (added)	O_3 (excess)	NO	NO_2	NO_x	Br_2	(l) Olefin mixture		
1	0	0	0	0	0	0	+	28	0
2	0	0	0	0	0	45	+	28	0
3	140	140	0	0	0	45	+	28	0
4	0	0	120	0	120	45	+	28	0
5	0	0	0	120	120	45	+	28	0
6	0	0	100	120	220	45	+	28	0
7	800	800	0	0	0	45	+	28	0
8	760	0	760	0	760	45	+	28	0
9	540	0	260	540	800	45	+	28	0
10	700	0	0	700	700	45	+	28	0
11	1200	600	0	600	600	45	+	28	0
12	700	700	0	0	0	45	+	28	0
13	600	400	0	200	200	45	+	28	0
14	600	0	150	600	750	45	+	28	0
15	0	0	600	0	600	45	+	28	0
16	0	0	0	0	0	45	+	28	0

Table X presents the series of experiments which was conducted utilizing different combinations of ozone, NO_x , NO, NO_2 , chlorine, and cyclohexene. The volume of air stream that was sampled in all cases was 16 l. In experiments 1-6 the Tenax GC cartridges were loaded with the olefin equivalent to a level of 90 ppb. In all of these experiments where the cyclohexene had been loaded on the Tenax GC cartridge no formation of 1,2-dichlorocyclohexane or other artifact was detected (Table X). Experiments 8-16 utilized a cyclohexene permeation tube plus a molecular chlorine permeation tube which were housed in the permeation tube chamber (point A, Fig. 1). Thus, the molecular chlorine plus cyclohexene entered and travelled together down the glass reaction tube to the Tenax GC cartridge at E (Fig. 1). In these experiments the quantity of cyclohexene was almost an order of magnitude greater than in the previous experiments.

In experiments 8-16 approximately 100-120 ng of 1,2-dichlorocyclohexane was measured when molecular chlorine was present with cyclohexene regardless of whether ozone, NO, or NO_2 was added.

A replicate cartridge representing the conditions under which 1,2-dichlorocyclohexane was expected to form was submitted for mass spectral analysis. The mass spectral data confirmed the presence of 1,2-dichlorocyclohexane. In addition, another compound was identified as cyclohexene-2-one. The formation of this compound, however, occurred only when ozone was also added to the air stream (Table X).

TABLE X

EFFECT OF O₃, NO, NO₂ AND MOLECULAR CHLORINE ON *IN SITU* REACTIONS WITH CYCLOHEXENE USING TENAX GC AS THE SAMPLING SORBENT

Experiments 1-6 utilized Tenax GC cartridges loaded with cyclohexene and purged with Cl₂; experiments 8-16 utilized a cyclohexene permeation tube in line with a Cl₂ permeation tube and experiments 17-20 involved loading of cyclohexene onto the Tenax GC cartridge and sampling in the presence of criteria pollutants as indicated with Cl₂. Sampling volumes were 16 l in all cases.

Experiment No.	Standard inorganic pollutants (added) (ppb)			Cl ₂	Cyclohexene (ppb)	1,2-Dichlorocyclohexane (ng)	Other "Artifacts"
	O ₃	NO	NO ₂				
1	0	0	0	104	90	0	—
2	100	0	0	0	90	0	—
3	100	0	0	104	90	0	—
4	700	0	0	104	90	0	—
5	0	300	350	104	90	0	—
6	220	0	200	104	90	0	—
7	0	0	0	104	0	0	—
8	0	0	0	0	818	0	—
9	0	0	0	104	818	100	—
10	160	0	0	104	818	110	Cyclohexen-2-one
11	0	0	0	0	0	0	—
12	180	0	0	104	818	120	Cyclohexen-2-one
13	0	0	0	104	818	110	—
14	140	0	0	104	818	120	Cyclohexen-2-one
15	100	0	100	104	818	100	Cyclohexen-2-one
16	0	100	0	104	818	100	—
17	0	0	0	104	818	110	—
18	100	0	0	0	818	0	Cyclohexen-2-one
19	720	0	0	0	818	0	Cyclohexen-2-one
20	720	0	0	104	818	120	Cyclohexen-2-one

Additional experiments were performed (17-20) which involved the loading of cyclohexene onto the Tenax GC cartridge at a considerably higher concentration as indicated in Table X. Again, 1,2-dichlorocyclohexene and cyclohexene-2-one were detected.

These experiments indicate that 1,2-dichlorocyclohexene as well as cyclohexene-2-one could be formed; particularly when higher concentrations of cyclohexene were used. This also probably accounts for the observations in the first series of experiments where formation of 1,2-dichlorocyclohexane and cyclohexene-2-one may have been below the detection limit for the flame-ionization detection.

The potential chlorination of cyclohexene in the absence and presence of ozone and other standard pollutants was also studied using a sampling cartridge containing XAD-2 sorbent. Traces of 2,3-dichlorobutane were found with XAD-2 (Table XI).

Sampling of atmospheres containing 1 ppm of ozone, NO or NO₂ with a charcoal tube containing tetrachloroethylene did not deplete the levels of tetrachloroethylene; however, traces of 2,3-dichlorobutane were detected (Table XII).

Field studies

Three different atmospheric conditions were chosen to conduct field *in situ*

TABLE XI

EFFECT OF CRITERIA POLLUTANTS AND MOLECULAR CHLORINE *IN SITU* REACTIONS WITH OLEFINS USING XAD-2 AS THE SAMPLING SORBENT

Experiment No.	Standard inorganic pollutants (ppm)			Cl ₂ (ppb)	Olefin mixture* (ppb)	2,3-Dichlorobutane (ng) (formed)
	O ₃	NO	NO ₂			
1	0	0	0	90	B(744), P(577), E(581), B2(940)	30
2	1	0	0	90	B(744), P(577), E(581), B2(940)	20
3	1	0	1	90	B(744), P(577), E(581), B2(940)	20
4	0	1	0	90	B(744), P(577), E(581), B2(940)	20
5	0	0	0	90	B(744), P(577), E(581), B2(940)	0

* See Table XII.

TABLE XII

EFFECT OF O₃, NO, NO₂ AND MOLECULAR CHLORINE ON *IN SITU* REACTIONS WITH OLEFINS USING SKC-107 CHARCOAL AS THE SAMPLING SORBENT

Olefin mixture: 744 ppm 1-butene, 577 ppm propylene, 581 ppm ethylene, 940 ppm butene-2. In each case 16 l was sampled.

Experiment No.	Standard inorganic pollutants (ppm)			Cl ₂ (ppb)	2,3-Dichlorobutane formed (ng)
	O ₃	NO	NO ₂		
1	0	0	0	90	60
2	1	0	0	90	20
3	0	1	0	90	20
4	1	0	1	90	20
5	0	0	0	0	0

reaction studies. The first was conducted during a time period representing the highest level of ozone, the second during a high level of NO_x and auto exhaust, and finally the third during low levels of ozone (night). Ozone and NO_x levels were also measured.

The characterization results are given in Tables XIII-XXIII. Tables XIII and XIV represent the halogenated and other selected organics which were identified in samples labeled P1/L5A-1/T₁ and T₂, respectively. The T₂ designation in all of these tables represents the adsorbent cartridge which was in line with the permeation tube containing either molecular halogen or d₆-dimethylamine. Table XIV lists a number of brominated compounds at trace levels which were not detected in the corresponding control. These were methyl bromide, ethylene dibromide, bromoform and dibromocyclohexane. Sampling in this case was conducted during the maximum ozone concentration during the day.

Tables XV and XVI present the results for the *in situ* reaction studies utilizing molecular chlorine. In this case the adsorbent cartridge which was in line with the molecular chlorine permeation tube contained traces of chlorocyclohexane, two dichlorocyclohexane isomers and three trichlorocyclohexane isomers.

Table XVII presents the results for the *in situ* nitrosation reaction study. d₆-Dimethylnitrosamine was detected in this sample.

TABLE XIII

HALOGENATED AND OTHER SELECTED ORGANICS IN P1/L5A-1/T₁ SAMPLE*

<i>Chromatographic peak No.</i>	<i>Elution temperature (°C)</i>	<i>Compound</i>	<i>Chromatographic peak No.</i>	<i>Elution temperature (°C)</i>	<i>Compound</i>
3	48	Methyl chloride	35	107	Toluene
10	61	Methylene chloride	41	117	Tetrachloroethylene
17	75	Chloroform	42	124	Chlorobenzene
20	80	Ethylene dichloride	46	134	Styrene
21	81	1,1,1-Trichloroethane	58	156	<i>m,p</i> -Dichlorobenzene
22	84	Benzene	59	160	<i>o</i> -Dichlorobenzene
28	90	Trichloroethylene			

* See Table II for experimental design.

TABLE XIV

HALOGENATED AND OTHER SELECTED ORGANICS IN P1/L5A-1/T₂ SAMPLE*

<i>Chromatographic peak No.</i>	<i>Elution temperature (°C)</i>	<i>Compound</i>	<i>Chromatographic peak No.</i>	<i>Elution temperature (°C)</i>	<i>Compound</i>
4	48	Methyl chloride	34	108	Toluene
6	51	Methyl bromide	37	114	Ethylene dibromide
11	60	Methylene chloride	39	117	Tetrachloroethylene
20	74	Chloroform	41	124	Chlorobenzene
23	80	Ethylene dichloride	44	131	Bromoform
24	82	1,1,1-Trichloroethane	46	136	Styrene
25	84	Benzene	58	159	<i>m,p</i> -Dichlorobenzene
26	85	Carbon tetrachloride	59	163	<i>o</i> -Dichlorobenzene
30	92	Trichloroethylene	65	199	Dibromocyclohexane

* See Table II for experimental design.

TABLE XV

HALOGENATED AND OTHER SELECTED ORGANICS IN P1/L5A-2/T₁ SAMPLE*

<i>Chromatographic peak No.</i>	<i>Elution temperature (°C)</i>	<i>Compound</i>	<i>Chromatographic peak No.</i>	<i>Elution temperature (°C)</i>	<i>Compound</i>
4	48	Methyl chloride	30	93	Trichloroethylene
10	61	Methylene chloride	35	107	Toluene
19	76	Chloroform	40	118	Tetrachloroethylene
22	80	Ethylene dichloride	43	124	Chlorobenzene
23	81	1,1,1-Trichloroethane	48	133	Styrene
25	85	Benzene	61	157	<i>m,p</i> -Dichlorobenzene
26	86	Carbon tetrachloride	63	160	<i>o</i> -Dichlorobenzene

* See Table II for experimental design.

TABLE XVI
HALOGENATED AND OTHER SELECTED ORGANICS IN P1/L5A-2/T₂ SAMPLE*

Chromatographic peak No.	Elution temperature (°C)	Compound	Chromatographic peak No.	Elution temperature (°C)	Compound
5	48	Methyl chloride	40	123	Chlorobenzene
12	61	Methylene chloride	43	130	Bromoform (trace)
19	75	Chloroform	44	133	Chlorocyclohexane
22	80	Ethylene dichloride	56	157	<i>m,p</i> -Dichlorobenzene
23	82	1,1,1-Trichloroethane	58	160	<i>o</i> -Dichlorobenzene
24	85	Benzene	62	167	Dichlorocyclohexane isomer
25	86	Carbon tetrachloride	67	182	Dichlorocyclohexane isomer
29	92	Trichloroethylene	70	198	Trichlorocyclohexane isomer
33	106	Toluene	71	200	Trichlorocyclohexane isomer
36	117	Tetrachloroethylene	72	205	Trichlorocyclohexane isomer

* See Table II for experimental design.

TABLE XVII
HALOGENATED AND OTHER SELECTED ORGANICS IN P1/L5B/T₂ SAMPLE*

Chromatographic peak No.	Elution temperature (°C)	Compound	Chromatographic peak No.	Elution temperature (°C)	Compound
1	44	CO ₂	10	86	Carbon tetrachloride
2	58	Acetone	11	91	1,2-Dichloropropane
3	60	Methylene chloride	12	92	Trichloroethylene
4	73	Hexafluorobenzene (e \bar{s})	13	107	Toluene
5	75	Chloroform	14	117	Tetrachloroethylene
6	79	Perfluorotoluene (e \bar{s})	15	120	Dimethylnitrosamine-d ₆ (tent.)
7	80	1,2-Dichloroethane	16	124	Chlorobenzene
8	81	1,1,1-Trichloroethane	17	157	Dichlorobenzene isomer (trace)
9	85	Benzene	18	162	Dichlorobenzene isomer

* See Table II for experimental design; e \bar{s} = external standard.

Tables XVIII, XIX and XX represent the repeat of the *in situ* artifact study under high NO_x and auto exhaust pollution. Again, bromination chlorination and nitrosation were detected.

Tables XXI–XXIII represent the *in situ* artifact study conducted during darkness and under low ozone concentrations. In this case, the number of brominated compounds was substantially reduced while still a significant number of chlorinated compounds were found as well as the detection of d₆-dimethylnitrosamine.

Impregnation of the glass fiber filter with sodium thiosulfate prevented the trace *in situ* reactions from occurring.

TABLE XVIII

HALOGENATED AND OTHER SELECTED ORGANICS IN P2/L5A/T₂ SAMPLE*

Chromatographic peak No.	Elution temperature (°C)	Compound	Chromatographic peak No.	Elution temperature (°C)	Compound
6	50	Methyl bromide	37	112	Ethylene dibromide
11	59	Methylene chloride	39	115	Tetrachloroethylene
16A	72	Chloroform	43A	122	Chlorobenzene
18A	77	Ethylene dichloride	46	129	Bromoform
19A	82	Benzene	48	131	Styrene
19B	82	Carbon tetrachloride	61B	156	<i>m,p</i> -Dichlorobenzene
25	90	Trichloroethylene	63	161	<i>o</i> -Dichlorobenzene
32	105	Toluene	70	197	Dibromocyclohexane isomer

* See Table II for experimental design.

TABLE XIX

HALOGENATED AND OTHER SELECTED ORGANICS IN P2/LSB/T₂ SAMPLE*

Chromatographic peak No.	Elution temperature (°C)	Compound	Chromatographic peak No.	Elution temperature (°C)	Compound
4	49	Methyl chloride	45B	131	Bromoform
13	63	Methylene chloride	47	134	Chlorocyclohexane
20	76	Chloroform	64	154	Chlorophenol isomer
21A	80	Ethylene dichloride	65	157	<i>p,m</i> -Dichlorobenzene
21B	81	1,1,1-Trichloroethane	68	162	<i>o</i> -Dichlorobenzene
23A	85	Benzene	72	168	Dichlorocyclohexane isomer
23B	86	Carbon tetrachloride	78	182	Dichlorocyclohexane isomer
27	93	Trichloroethylene	82	198	Trichlorocyclohexane isomer
33	108	Toluene	83	200	Trichlorocyclohexane isomer
39	118	Tetrachloroethylene	85	207	Trichlorocyclohexane isomer
43	125	Chlorobenzene			

* See Table II for experimental design.

TABLE XX

HALOGENATED AND OTHER SELECTED ORGANICS IN P2/L5C/T₂ SAMPLE*

Chromatographic peak No.	Elution temperature (°C)	Compound	Chromatographic peak No.	Elution temperature (°C)	Compound
10	60	Methylene chloride	31	106	Toluene
16	74	Chloroform	36	117	Tetrachloroethylene
18	77	Ethylene dichloride	36A	118	Dimethylnitrosamine-d ₆
18A	78	1,1,1-Trichloroethane	40	123	Chlorobenzene
19	83	Benzene	No peak	78-180	Unknown amine (<i>m/z</i> = 30)
24	91	Trichloroethylene			

* See Table II for experimental design.

TABLE XXI

HALOGENATED AND OTHER SELECTED ORGANICS IN P3/L5A/T₂ SAMPLE*

Chromatographic peak No.	Elution temperature (°C)	Compound	Chromatographic peak No.	Elution temperature (°C)	Compound
1	45	CO ₂	9	83	1,1,1-Trichloroethane
2	53	Bromomethane (traces)	10	87	Benzene
3	59	Acetone	11	88	Carbon tetrachloride
4	63	Methylene chloride	12	95	Trichloroethylene (traces)
5	75	Hexafluorobenzene (eS)	13	118	Toluene
6	77	Chloroform (traces)	14	128	Tetrachloroethylene
7	81	Perfluorotoluene (eS)	15	136	Chlorobenzene (traces)
8	82	1,2-Dichloroethane	16	142	Bromoform

* See Table II for experimental design.

TABLE XXII

HALOGENATED AND OTHER SELECTED ORGANICS IN P3/L5B/T₂ SAMPLE*

Chromatographic peak No.	Elution temperature (°C)	Compound	Chromatographic peak No.	Elution temperature (°C)	Compound
1	61	Methylene chloride	12	118	Tetrachloroethylene
2	74	Hexafluorobenzene (eS)	13	125	Chlorobenzene
3	76	Chloroform	14	132	Bromoform (traces)
4	79	Perfluorotoluene (eS)	15	134	Chlorocyclohexane
5	81	1,2-Dichloroethane	16	158	Dichlorobenzene isomer
6	82	1,1,1-Trichloroethane	17	163	Dichlorobenzene isomer
7	85	Benzene	18	168	Dichlorocyclohexane isomer
8	86	Carbon tetrachloride	19	198	Trichlorocyclohexane isomer
9	83	Trichloroethylene (traces)	20	201	Trichlorocyclohexane isomer
10	107	Chlorocyclohexene isomer (tent.)	21	202	Trichlorocyclohexane isomer
11	108	Toluene	22	206	Trichlorocyclohexane isomer

* See Table II for experimental design.

TABLE XXIII

HALOGENATED AND OTHER SELECTED ORGANICS IN P3/L5C/T₂ SAMPLE*

Chromatographic peak No.	Elution temperature (°C)	Compound	Chromatographic peak No.	Elution temperature (°C)	Compound
1	44	CO ₂	8	83	Benzene
2	58	Acetone	9	84	Carbon tetrachloride
3	60	Methylene chloride	10	92	Trichloroethylene
4	71	Hexafluorobenzene (eS)	11	107	Toluene
5	77	Perfluorotoluene (eS)	12	117	Tetrachloroethylene
6	79	1,2-Dichloroethane	13	118	Dimethylnitrosamine-d ₆ (tent.)
7	80	1,1,1-Trichloroethane	14	159	Dichlorobenzene isomer

* See Table II for experimental design.

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