Photochemistry of Thiocarbamate Herbicides: Oxidative and Free Radical Processes of Thiobencarb and Diallate

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Irradiation of thiobencarb at 300 nm in aqueous solution or as a thin film on Pyrex or silica gel yields 30 characterized or tentatively identified photoproducts of which 8 are major (>3%) as follows: thiobencarb sulfoxide; the *N*-desethyl and *N*-acetyl derivatives of thiobencarb; 4-chlorobenzyl diethylcarbamate; *N*-(4-chlorobenzyl)diethylamine; 4-chlorobenzaldehyde and the corresponding alcohol and acid. Photooxidative processes are prevalent with thiobencarb but the sulfoxide is not a major intermediate. Photocleavage of the carbon–sulfur bonds generates the 4-chlorobenzyl radical from which 4-chlorotoluene is formed in the presence of hydrogen donors and a variety of dimers are obtained in other systems. Diallate is considerably more photostable than thiobencarb and undergoes cis–trans isomerization and oxidative cleavage to 2,3-dichloro- and 2-chloroacroleins. Sulfallate and triallate also photodecompose in oxygenated water to yield chloroacroleins or other products mutagenic in the Ames *Salmonella typhimurium* TA 100 assay.

Thiobencarb (1) (Figures 1 and 2) with an *S*-chlorobenzyl substituent and the diallate isomers (**32** and **33**) (Figure 3) with an *S*-dichloroallyl moiety are important thiocarbamate herbicides. Thiocarbamates photodecompose and biodegrade by both oxidative and hydrolytic processes (Aizawa, 1982). Cleavage of the C(O)–S bond is the predominant photoreaction of several thiocarbamates in degassed hexane solution (DeMarco and Hayes, 1979). Irradiation of thiobencarb in water or as a thin film with ultraviolet (UV) light or sunlight yields the sulfoxide and products from cleavage and ring hydroxylation (Ishikawa et al., 1977). Some of the thiobencarb photooxidation reactions proceed by hydroxyl radical initiated processes (Draper and Crosby, 1981). Metabolism of sulfallate, diallate, and triallate by oxidation at the sulfur or the *S*-methylene substituent yields 2-chloroacrolein derivatives, which are potent bacterial mutagens (Schuphan et al., 1979; Rosen et al., 1980a,b; Marsden and Casida, 1982). No reports are available on the possible photoactivation of the *S*-chloroallyl herbicides to give mutagenic products.

The present study considers oxidative and free radical processes and possible mutagenic products in the photodecomposition of thiobencarb and diallate.

MATERIALS AND METHODS

Chemicals. Compounds are designated by numbers as shown in Figures 1–3. **1** and **32** + **33** were from Chem Services (Westchester, PA) and **32** and **33** were separated as previously described (Schuphan and Casida, 1979). Thiobencarb sulfoxide (**8**) was prepared from **1** by treatment with equivalent *m*-chloroperbenzoic acid in dichloromethane for 1 h and isolated by thin-layer chromatography (TLC) with hexane–acetone, 5:2 (HA). Amine **11** was synthesized by treatment of 4-chlorobenzylamine with 2 equiv of sodium hydride in tetrahydrofuran for 1 h followed by addition of 2 equivalents of ethyl iodide, stirring for 48 h, and TLC (hexane–acetone–methanol, 8:2:1). Compounds **15–20** and **30** were from Aldrich Chemical Co. (Milwaukee, WI).

Irradiation Procedures. Photolyses were carried out at 300 nm through Pyrex in a Rayonette reactor (The Southern New England Ultraviolet Co., Middletown, CT) equipped with eight RPR 3000 lamps. Solutions were 0.12 mM in organic solvents for rate determinations, 0.5 mM in water for preparative purposes, 5 mM in chloroform for trapping experiments, and 2 mg/mL in 5% tetrahydrofuran in sterile water (oxygenated by pretreatment with O_2 for 2 h) for mutagenesis assays. The solutions (1 mL) were either degassed by three cycles of freeze–pump–thaw (0.01 mm Hg) or oxygenated before or during irradiation (10 mL/min). Thin films of **1** (50 $\mu g/cm^2$) were irradiated at 300 nm as above on Pyrex (in 9 cm diameter Petri dishes with Pyrex covers) or absorbed on to silica gel 60 chromatoplates (EM Reagents, Elmsford, NY; 0.25-mm thickness without fluorescent indicator). Irradiation of photoproducts of **1** (i.e., **3**, **8**, and **16**) was carried out in water or $CDCl_3$ solution or as a thin film on Pyrex. Volatile products were trapped in 3:2 phosphoric acid–ethanol (5 mL) at ~10 °C containing 25 mg of 2,4-dinitrophenylhydrazine (DNP). Sensitized irradiations utilized 0.12 mM **32** and 1 mM biphenyl or benzophenone in benzene.

Chromatography and Spectroscopy. TLC employed silica gel F-254 chromatoplates (0.25 mm, EM Reagents) with solvents specified later. Products were recovered from the gel by sonication in chloroform or methanol. Gas–liquid chromatography (GLC) utilized a glass 3% SP 2100 column (1 m, 3-mm i.d., Supelco) operated at 25 mL/min argon–methane (19:1) with temperature programming (100–200 °C, 20 °C/min) in a Hewlett-Packard 5830A instrument equipped with a ^{63}Ni electron capture detector. Peak areas were calculated by an on-line computer. Quantitation involved GLC of authentic standards and assumed similar electron capture responses to those of available standards of appropriate structure or retention time (R_t). Compound **8** is not stable on GLC and was quantitated based on the weight of material recovered from TLC.

Mass spectrometry (MS) utilized a Hewlett-Packard 5985 system with ionization by electron impact (EI, 70 eV) or chemical ionization (CI, 230 eV) with methane (0.8 torr). Masses and relative intensities are given for molecular $[M^{+\cdot}]$ or quasi-molecular ($[M + 1]^+$) ions and other important fragments. GLC–MS was carried out with a Hewlett-Packard 5840A gas chromatograph interfaced with the MS system. A cross-linked high-performance methyl silicone capillary column (10 m) was operated with temperature programming (120–220 °C, 20 °C/min) to give the reported R_t values. For detection of low molecular weight products GLC was carried out isothermally at 80 °C. Proton nuclear magnetic resonance (NMR) spectra were obtained at 300 MHz with a Bruker WM-300 wide-bore spectrometer equipped with an ASPECT 2000A

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Table I. Mass Spectral and Gas Chromatographic Data for Thiobencarb and Its Photolysis Products

compd[a]	irradiation medium[b]	EI-MS, m/z[c] [M+·]	base	other	GLC, R_t, min[d]
1	WPS	257 (100)		125 (18), 100 (24)	8.0
2	WPS	273 (52)	148	125 (48), 116 (18), 88 (42, 0 Cl)	6.4
3	WPS	271 (95)	146	157 (34), 125 (95)	8.3
4	WPS	257 (21)	125	256 ([M − 1]+, 5), 157 (38)	7.8
5	WPS	229 (75)	125	158 (30, 1 Cl)	6.9
6	S	239 (20)	100		8.8
7	WS	253 (100)			6.1
8	WPS		100	139 (52, 1 Cl), 125 (35)	dec
9	WPS	257 (25)[e]	100	125 (40)	7.2
10	WPS	241 (82)	125	182 (16, 1 Cl)	5.9
11	WPS	197 (12)	125	182 (45)	3.8
12	WS	197 (23)	125	168 (37, 1 Cl)	5.4
13	WS	211 (26)[e]	139	210 ([M − 1]+, 34), 111 (35)	5.4
14	S	183 (24)	139	182 ([M − 1]+, 26), 111 (39)	5.0
15	H donors	126 (38)	91 (0 Cl)		0.9
16	WPS	142 (85)	107 (0 Cl)	125 (36)	2.7
17	WPS	140 (72)	139	111 (58)	2.1
18	WPS	156 (70)	139	111 (28)	3.3
19[f]	W	138 (62)	121 (0 Cl)		2.9
20[f]	W	166 (56)	135 (0 Cl)		2.9
21	WS	250 (62)	125	215 (26, 1 Cl)	7.7
22	S		178 (0 Cl)	248 (38, 2 Cl), 213 (18, 1 Cl)	9.4
23	P	280 (32)	139	245 (8, 1 Cl), 125 (64)	7.8
24	W	246 (100)		211 (12, 1 Cl), 176 (80, 0 Cl)	10.2
25	WS	248 (38)	178 (0 Cl)	213 (18, 1 Cl)	7.4
26	S	250 (17)	139	215 (9, 1 Cl), 111 (41)	7.7
27	WS	158 (21)	125		3.0
28	WS	314 (46)	125		9.2
29	W	282 (6)	125	157 (15)	10.9

[a] For structures, see Figures 1 and 2. [b] W = water; P = pyrex; S = silica gel. [c] Major fragments identified in Table III. Unidentified fragments with number of chlorine atoms indicated based on chlorine isotope cluster. [d] Methyl silicone (10 m); 120–220 °C; 20 °C/min; He at 1 mL/min. Isothermal at 80 °C for 15. Compounds with the same R_t appear in different regions on TLC. [e] CI-MS data: 9, 258 ([M + 1]+, 100), 141 (42), 125 (15); 13, 212 ([M + 1]+, 100). [f] As methylated derivatives.

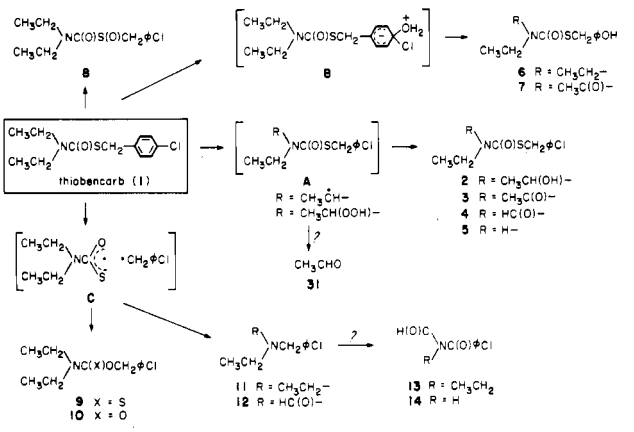

Figure 1. Photoreactions of thiobencarb in oxygenated chloroform or water solution to yield products containing both the aryl and amine moieties.

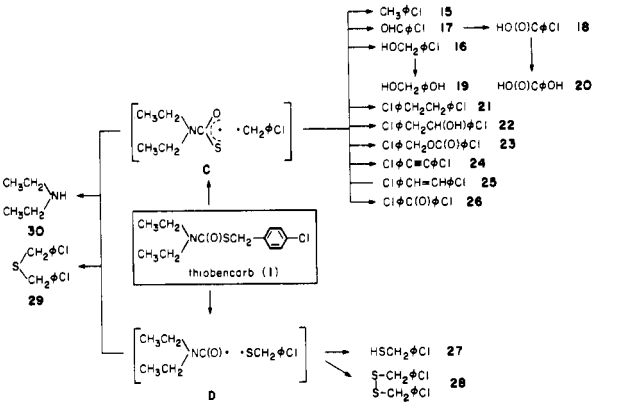

Figure 2. Photoreactions of thiobencarb in oxygenated chloroform or water solution to yield products containing either the aryl or the amine moiety.

computer. Samples were dissolved in $CDCl_3$ and chemical shifts (δ) are reported as ppm downfield from tetramethylsilane. UV spectra were recorded in cyclohexane with a Perkin-Elmer 576 ST spectrophotometer.

Mutagenesis Assays. *Salmonella typhimurium* strain TA 100 was used for standard Ames assays (Ames et al., 1975) adding aliquots (50–500 μL) of the irradiated aqueous solutions to the culture plates. Mutagenic activity values in this assay are 113, 104, and 224 revertants/nmol for 2-chloroacrolein, 2,3-dichloroacrolein, and 2,3,3-trichloroacrolein, respectively (Rosen et al., 1980b).

RESULTS

Identification of Thiobencarb Photoproducts. The MS fragmentation patterns and GLC R_t values of the photoproducts are given in Table I. Reaction mixtures were routinely inspected by GLC–MS (EI and CI) before and after treatment for 30 min with diazomethane in ether. *Caution*: diazomethane is a hazardous chemical and precautions are necessary in its use. Where feasible, individual products were isolated (TLC) (Table II) and characterized by MS (direct insertion) and NMR. Minor products (<3%) (Table I) were tentatively identified by

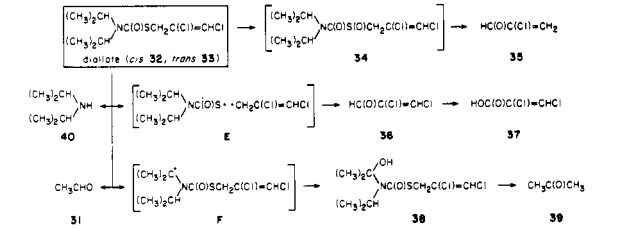

Figure 3. Photoreactions of diallate in oxygenated chloroform or water solution.

Table II. Yields and Chromatographic Properties of Major Photoproducts Formed on Irradiation of Thiobencarb in Water (W), on Pyrex (P), and on Silica Gel (S)

photoproduct[a]	yield, %,[b] with indicated irradiation medium			chromatographic property	
	W	P	S	GLC, R_t, min,[c]	TLC, R_f (system)[d]
3	46	36	6	8.3	0.32 (HE)
5	18	2	3	6.9	0.18 (HE)
8	3	1	2	dec	0.26 (HA)
10	9	18	62	5.9	0.23 (HE)
11	2	11	19	3.8	0.13 (HA)
16	4	14	6	2.7	0.38 (HA)
17	14	21	8	2.1	0.50 (HE)
18	6	8	2	3.3	0.18 (HA)

[a] Yields of other products <1%. [b] Irradiations to 40–60% conversion and yields based on percentage of 1 reacted. The yields include products with either the aryl or amine moiety and with both the aryl and amine moieties and as such may total more than 100%. [c] GLC conditions given in footnote *d* of Table I. [d] Two developments with hexane–ether, 4:1, = HE (R_f 0.48 for 1) or hexane–acetone, 5:2, = HA (R_f ~0.8 for 1).

Table III. Important Fragments in Mass Spectrometric Analysis of Thiobencarb Photoproducts

fragment (R^+)	*m/z*
$(C_2H_5)_2NC(O)$	100
ClC_6H_4	111
$C_2H_5(CH_3CHOH)NC(O)$	116
$ClC_6H_4CH_2$	125
$ClC_6H_4C(O)$	139[a]
$ClC_6H_4CH_2O$	141[b]
$C_2H_5[CH_3C(O)]NC(O)S$	146
$C_2H_5(CH_3CHOH)NC(O)S$	148
$ClC_6H_4CH_2S$	157
$ClC_6H_4CH_2N(C_2H_5)CH_2$	182[c]
$(C_2H_5)_2NCH_2C_6H_4$	162 (CI)
$(C_2H_5)_2NHCH_2C_6H_4Cl$	198 (CI)

[a] 8 gives an unidentified fragment of the same mass. [b] 5 gives an unidentified fragment of the same mass. [c] 10 gives an unidentified fragment of the same mass.

TLC fractionation of the photolysates followed by GLC–EI-MS of the appropriate bands. Criteria for interpretation of the MS data are given in Table III. In the cases of **3**, **5**, and **10** the photoproducts isolated and characterized were then used as authentic standards. Photoproducts **8** and **15–17** were characterized by cochromatography and spectroscopic comparison with standards. **18–20** were identified by cochromatography after methylation. Diethylamine (**30**) was detected by single-ion monitoring (*m/z* 73) and cochromatography with a standard. Compounds **3**, **5**, **8**, **10** and **11** were identified by EI-MS, CI-MS, and NMR as indicated below and in Tables I–III.

3: CI-MS 272 ($[M + 1]^+$, 100, 1 Cl, and corresponding $[M + 29]^+$, 22, and $[M + 41]^+$, 12), 125 (50, 1 Cl); NMR δ 1.14 (CH_3CH_2, t), 2.37 (CH_3CO, s), 3.72 (CH_3CH_2, q), 4.02 ($ArCH_2$, s), 7.20 (ClC_6H_4). **5**: CI-MS 230 ($[M + 1)^+$, 50, 1 Cl), 141 (54, 1 Cl), 125 (100, 1 Cl); NMR δ 1.16 (CH_3CH_2, t), 3.27 (CH_3CH_2, m), 4.10 ($ArCH_2$, s), 7.25 (ClC_6H_4). **8**: CI-MS 274 ($[M + 1]^+$, 6, 1 Cl), 157 (62, 1 Cl), 125 (80, 1 Cl), 100 (100); NMR δ 0.95 (CH_3CH_2, t), 1.19 (CH_3CH_2, t), 3.20 (CH_3CH_2, m), 3.34 (CH_3CH_2, m), 4.20 ($ArCH_2$, dd), 7.29 (ClC_6H_4). **10**: CI-MS 242 ($[M + 1]^+$, 46, 1 Cl), 198 (18, 1 Cl), 141 (100, 1 Cl), 125 (96, 1 Cl); NMR δ 1.17 (CH_3CH_2, t), 3.29 (CH_3CH_2, m), 5.09 ($ArCH_2$, s), 7.2–7.3 (ClC_6H_4). **11**: CI-MS 198 ($[M + 1)^+$, 100, 1Cl, and corresponding $[M + 29]^+$, 8), 162 (22); NMR δ 1.05 (CH_3CH_2, t), 2.52 (CH_3CH_2, q), 3.53 ($ArCH_2$, s), 7.28 (ClC_6H_4, s).

Photolysis of Thiobencarb in Solution (Tables I and II). Products detected on irradiation of **1** in aqueous solutions (40% conversion) from which oxygen was excluded by continuous flushing with argon were **9**, **21**, **24**, **25**, and **27–29**. On photolysis of **1** in chloroform, **16–18** formed as major products, *p*-chlorotoluene (**15**) in small yield, and the DNP derivative of acetaldehyde (**31**) was obtained on trapping (discussed later). The oxygenated chloroform photolysis proceeded at 0.05 mM h^{-1} whereas degassed solutions reacted 4-fold slower. Several solvents were examined to determine the effect of H donors on the photolysis. In all cases the reaction was faster in efficient proton donors, i.e., 60% reaction in toluene vs. 10% in benzene. In toluene substantial yields were obtained of bibenzyl [183 ($[M + 1]^+$, 100)], suggesting radical abstraction processes. The reaction rates were ~5% greater in $CHCl_3$ vs. $CDCl_3$ and CH_3OH vs. CD_3OD; the increased value in protio solvents was consistent but not quantitatively reproducible.

Photolysis of Thiobencarb as a Thin Film. Photodegradation of **1** on silica gel proceeds to ~40% conversion in 48 h, yielding the major products shown in Table II with additional minor compounds given in Table I. On irradiation of thin films on silica gel through a close-fitting quartz cover (to restrict oxygen access), the same product distribution is observed but with smaller yields of **10** and **11**; no attempt was made to analyze other products.

Photolysis of **1** as a thin film on Pyrex is slower than on the gel (28% conversion in 48 h), but the same major products are formed (Table II). Compounds detected in smaller yields on Pyrex are **2**, **4**, **9**, and **23**.

Photolysis of Thiobencarb Photoproducts. Compound **3** is quite resistant to photodecomposition in water. The sulfoxide (**8**) is rapidly degraded (20× faster than **1** on irradiation in solution or as a thin film on Pyrex), yielding mainly the cleavage products **16–18** (in water and on Pyrex) and radical products **15** (in $CDCl_3$) and **21** (in water). Photooxidation in solution and as a thin film readily converts alcohol **16** to aldehyde **17**, which in turn is oxidized to acid **18**.

Photolysis of Diallate. **32** exhibits ϵ = 16 000 at λ_{max} 212 nm and ϵ = 540 at 300 nm. Irradiation of **32** results primarily in isomerization to **33** (Figure 3), identified by NMR and GLC–MS comparisons with authentic material. This isomerization takes place at similar rates in hexane, water, or $CDCl_3$ (0.75 mM h^{-1}). The rate is increased 10-fold in the presence of the sensitizer benzophenone and to a lesser extent by biphenyl, but several unidentified products are also obtained.

Photolysis of diallate as a 3:2 trans–cis mixture in oxygenated chloroform or water (5 mM) was carried out to 10% conversion. Although not isolated, diallate sulfoxide (**34**) is detected tentatively in very small yield by NMR examination (Schuphan and Casida, 1979) of $CDCl_3$ photolysates. Several photoproducts are evident on trapping as DNP derivatives (isolated by TLC, chloroform–acetone, 10:1). Acetaldehyde (**31**, DNP) (also characterized in the same way on photolysis of **1**): CI-MS 225 ($[M + 1]^+$, 100), ($[M + 29]^+$, 18). 2,3-Dichloroacrolein (**36**, DNP): CI-MS: 305 ($[M + 1]^+$, 100, 2 Cl), ($[M + 29]^+$, 12); NMR, *cis*-**36** (DNP), δ 7.62 (ClCH, s), 8.53 (ClCHC:N, s); NMR, *trans*-**36** (DNP), δ 7.38 (ClCH, s), 8.51 (ClCHC:N, s). The aromatic protons overlap for the cis and trans isomers (DNP) at 8.12 (d), 8.47 (dd), and 8.98 (d). The dichloroacrolein isomers per se are evident as prominent photoproducts in $CDCl_3$ solution with δ 9.40 (CHO, s) and 9.46 (CHO, s) for *cis*- and *trans*-**36**, respectively. The trap also contains the acetone derivative (**39**, DNP) with CI-MS 239 ($[M + 1]^+$, 100; $[M + 29]^+$, 16) and NMR δ 2.02 (CH_3, s), 2.12 (CH_3, s), and aromatics at 7.95 (d), 8.22 (dd), and 9.09

Table IV. Activation of *S*-Chloroallyl Herbicides as Mutagens in the Ames *S. typhimurium* TA 100 Assay on Irradiation at 300 nm in Oxygenated Aqueous Solution

herbicide		mutagenic activity, revertants/μg, after indicated irradiation time			
name	*S* substituent	0 h	4 h[a]	12 h	24 h
sulfallate	2-chloroallyl	<0.5	16	9	1.0
diallate	2,3-dichloroallyl	<0.1	1.9	0.5	0.2
triallate	2,3,3-trichloroallyl	<0.1	0.8	0.6	0.1
thiobencarb	4-chlorobenzyl	<0.05	<0.05	<0.05	<0.05

[a] Activity expressed as revertants/nmol: sulfallate 3.6, diallate 0.51, and triallate 0.24.

(d). Trace amounts of 2-chloroacrolein (**35**, DNP) are detected by CI-MS 271 ($[M + 1]^+$, 100, 1 Cl; $[M + 29]^+$, 9). Other minor products detected in the photolysate (GLC-MS) are as follows: **37**, 141 ($[M + 1]^+$, 100, 2 Cl); **38**, 285 ($[M^{+\cdot}]$, 32, 2 Cl), 176 (100), 109 (22, 2 Cl); **40**, 102 ($[M + 1]^+$, 100) identified by single ion monitoring at m/z 101 (EI-MS) and 80 °C.

The 4-h aqueous photolysates of sulfallate, diallate, and triallate were extracted with cyclohexane and inspected by GLC–MS revealing ~5% reaction of sulfallate and <1% conversion for the other compounds. The major product from sulfallate appears to be its thiocarbamate analogue: CI-MS 192 ($[M + 1]^+$, 100; $[M + 29]^+$, 12). Minor products tentatively characterized are 2-chloroacrylic acid [CI-MS 107 ($[M + 1]^+$, 100), 89 $[M - 17]^+$, 22)] and **35** [detected by single ion monitoring at m/z 90 (EI-MS)]. Indirect evidence for conversion of sulfallate to **35** comes from observing an unidentified minor product [CI-MS 183 ($[M + 1]^+$, 100, 2 Cl), 165 ($[M - 17]^+$, 26), 147 ($[M - Cl]^+$, 82)], appropriate for a reduced form of a dimer from **35**.

Mutagenesis of Photolyzed *S*-Chlorallyl Thiocarbamates. Mutagenic photoproducts are evident on irradiation of sulfallate, diallate, and triallate but not of thiobencarb in oxygenated aqueous medium (Table IV). The mutagens are transient, with the highest potency at 4-h irradiation time. The mutagenic activities at 4 h are equivalent to 3% conversion of sulfallate to 2-chloroacrolein, 0.5% of diallate to 2,3-dichloroacrolein, and 0.1% of triallate to 2,3,3-trichloroacrolein (Table IV).

DISCUSSION

Thiobencarb readily photodecomposes to at least 30 products formed mostly by oxidation reactions but also by radical abstraction and recombination processes (Figures 1 and 2). This large number of photoproducts was not anticipated from previous studies (Ishikawa et al., 1977; Draper and Crosby, 1981). Primary excitation gives rise to species in which either the benzylic C–S or carbonyl C–S bonds are cleaved (C and D) to generate the radicals involved in subsequent reactions. In the absence of oxygen these radical intermediates recombine to yield dimers or are quenched by hydrogen abstraction from the solvent or from thiobencarb-related materials. In the presence of oxygen, radicals such as A, C, and D rearrange or ultimately yield oxidized products. Thus, the major product in aqueous solution and on Pyrex is **3**, presumably formed by secondary reaction of radical A with oxygen to give the hydroperoxide followed by water elimination to yield the carbonyl compound. Pair C can recombine to give **1**, isomerize to **9**, or drift, resulting in the formation of **15** and **21**. Alternatively, C or similar pairs arising from **9** or **10** can lose CO_2 or COS to yield **11**. The chlorobenzyl radical (C) can scavenge oxygen leading to **16–18**. Some of the radical products may also form via **8** based on direct examination of its photoproducts and on analogy with a study on a related thiocarbamate (Draper and Crosby, 1984) and the known propensity of sulfoxides toward cleavage (Khait et al., 1981). Radical pair D can also recombine or undergo dimerization and H-abstraction reactions.

Recombination of radicals (i.e., formation of **11**) is in general a more important process in the solid phase than in solution. **11** may form from radical pair C or more likely from **10** since the yields are decreased when oxygen access is restricted. Reaction of **1** to yield **9** and subsequent oxidation to **10** has no literature precedent, to our knowledge. However, peracids readily oxidize dithiocarbamates at the thiono sulfur (Segall and Casida, 1983). Attempts to isolate and firmly characterize **9** were unsuccessful due to its low yield and similar chromatographic behavior to **1** in all systems examined. Amine **11**, also suggested earlier as a minor photoproduct of thiobencarb in solution (Ishikawa et al., 1977), is an important product in thin films and may serve as an intermediate in formation of **13** by oxidation of the *N*-benzyl group.

N-Dealkylation of thiobencarb to **5**, found in all systems examined here, is previously reported (Draper and Crosby, 1981) as a process mediated by hydroxyl radicals. **2** may be the precursor for **5** and acetaldehyde (**31**). Ring hydroxylated and dechlorinated cleavage products (**19** and **20**), also noted earlier (Ishikawa et al., 1977), are not formed via a hydroxyl radical that attacks thiobencarb without loss of chlorine (Draper and Crosby, 1981). Phenols **19** and **20** may arise via B and thiocarbamate **6** by photonucleophilic reaction with water. Alternatively, expulsion of Cl^- can give rise to a radical cation that then adds water (Ruzo et al., 1975). A host of other photoproducts from **1**, i.e., *N*-formyl compounds **4** and **12** and dimeric products such as **22**, **24**, and **25**, undoubtedly arise from minor secondary or tertiary processes.

Diallate reacts principally by cis–trans isomerization, but it also undergoes oxidation and radical reactions at both the *N*-alkyl and *S*-dichloroallyl substituents (Figure 3). Oxidation of the dichloroallyl group yields chloroacroleins **35** (presumably via sulfoxide **34**) and **36** (perhaps via radical pair E). S-Oxidation is not a major photoprocess for diallate or the yield of **35** would be greater than that of **36** (Schuphan and Casida, 1979).

Photooxidation of sulfallate, diallate, and triallate generates 2-haloacrolein derivatives or related compounds that have high mutagenic activity (Rosen et al., 1980b). The higher mutagenicity of photolysates from sulfallate than from diallate or triallate is probably the result of its greater reactivity in processes leading to haloacrolein formation. These aldehydes are undoubtedly fugitive compounds under environmental conditions.

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Analysis of Methyl Bromide at Ultra Low Concentration Levels

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The conditions for measuring methyl bromide concentrations in air along with calibration data using gas chromatographs with photoionization and flame-ionization detectors are given. Sensitivity for detection at very low concentrations was found to be greatest with the photoionization detector; the flame-ionization detectors were suitable for the higher concentrations used for pest control. With the photoionization detector quantities of methyl bromide down to 10 pg could be measured with an accuracy of 3.9%.

Concern about the potential chronic effects on human health of toxic gases in the atmosphere has created the need for sensitive and precise methods for analyzing these gases. For toxic compounds like fumigants, where residual quantities of the gases occasionally may be released into the atmosphere, the need for effective monitoring capability is apparent. Some methods for rapid measurement of fumigants at low levels in the atmosphere with gas chromatography have already been described (see summarized account Bond and Dumas, 1984).

The purpose of this communication is to provide further details of a procedure for increasing sensitivity and precision in the analysis of one fumigant, methyl bromide. Comparative data for two different detector systems, flame ionization, and photoionization are also given.

MATERIALS AND METHODS

The gas chromatographs used in this study were the Photovac 10 A 10 with a photoionization detector (PID), a Bendix 2300, and a Gow Mac with flame-ionization detectors (FID).

Very low concentrations of methyl bromide have been analyzed in the Photovac 10 A 10 with a PID previously described Bond and Dumas (1982). A Teflon column 2 m long, 3 mm ID, and filled with Carbopak 40/60 mesh was used with a column temperature of 32 °C and high purity air (with less than 0.1 ppm hydrocarbons) at a flow rate of 10 mL/min. Under these conditions retention time for methyl bromide was 5.7 min. Calibration standards were prepared for the high sensitivity PID, by injecting 3 μL or 300 μL of undiluted methyl bromide gas into a 12.6-L flask with sampling ports. When this gas was uniformly dispersed in the flask, aliquots of 10–30 μL were drawn by gas syringe and injected into the Photovac GC. For analysis of samples of the higher concentration the signal was attenuated 100 times. A Hewlett Packard integrator 3390A was used with the Photovac GC for computing of the data.

Higher concentration levels of methyl bromide were analyzed by the less sensitive FID in the Bendix and Gow Mac instruments. In the Bendix a nickel column 2 m long, 3 mm ID, with Chromosorb 102, 120/140 mesh, a column temperature of 110 °C, and a nitrogen carrier gas flow rate of 20 mL/min gave a retention time of 5.3 min. A Hewlett Packard 3380A integrater computed the data.

In the Gow Mac GC a stainless steel column 2 m long, 3 mm ID, and filled with Apiezon L 30% on Chromosorb W 60/80 mesh was used with a column temperature of 25 °C and a nitrogen flow rate of 10 mL/min. When the high concentration standard (300 μL methyl bromide per 12.6 L) was used, 300–1000-μL samples of standard were drawn by a syringe and injected into the GC. A Hewlett Packard 3390A integrator was used with this instrument.

Table I. Calibration Data for Methyl Bromide on the Bendix GC with a Flame-Ionization Detector

sample vol, μL	MeBr applied, ng	detector response,[a] counts	SD, counts	CV, %	MeBr calcd,[b] ng
300	30	1658	114	6.9	19.7
400	40	2365	185	7.8	30.3
600	60	3646	285	7.8	49.4
1000	100	6350	300	4.7	89.8

[a] Mean of 5 determinations. [b] Calculated using regression parameters. Calibration parameters for MeBr using least-squares regression analysis: intercept counts $-341.08^c \pm 184.36$; slope counts × ng^{-1} $66.90^c \pm 4.02$; correlation coefficient (r) 0.9932. [c] 95% confidence interval.

RESULTS AND DISCUSSION

Tables I–IV show calibration data obtained for the FID and PID. Five replicate determinations were performed for each quantity of MeBr analyzed. For the Bendix GC with FID a 5.3-min retention time was required to give good separation of MeBr from other components of the

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