

DETECTION AND THIN-LAYER CHROMATOGRAPHY OF SULFUR COMPOUNDS

I. SULFOXIDES, SULFONES AND SULFIDES

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INTRODUCTION

A number of feeding and metabolic studies of pesticidal sulfones and sulfoxides in our laboratory has prompted the need to investigate various detecting reagents and thin-layer chromatography as to their possible utility for subsequent differentiation, identification and separation of the above moieties.

Recent literature has focused on the ever expanding utility of dimethyl sulfide, specifically, as a radioprotective agent¹, preservative for red-blood cells and tissues²⁻⁴, vehicle for steroids⁵, proteins⁶, drugs^{7,8}, and agricultural toxicants⁹. Other sulfoxides, as well as sulfones and sulfides exhibit a broad spectrum of applications, *e.g.*, as insecticides¹⁰⁻¹², fungicides¹³⁻¹⁴, herbicides¹⁵⁻¹⁶, synergistic agents^{17,18}, and rocket fuels¹⁹.

The metabolic oxidation-reduction interrelationships of R_2S , R_2SO and R_2SO_2 respectively, have also been well documented²⁰⁻²⁸.

Sulfoxides have been detected on paper by Dragendorff's reagent²⁹, molybdophosphoric acid³⁰, and hydriodic acid³⁰, on thin-layer chromatograms by permanganate-sulfuric acid³¹ and separated by column^{32,33} and gas chromatographic techniques³⁴. They have also been determined classically by prior reduction with hydriodic acid^{35,36} and titanous chloride³⁷, as well as titrated directly as bases in acetic anhydride³⁸.

Sulfones have been separated by column³⁹ and gas chromatography^{40,41}, and detected on paper⁴² and columns⁴³ by Ehrlich's and N-(1-naphthyl)-ethylene diamine reagents, respectively.

Sulfides have been detected on paper⁴⁴, columns⁴⁵ and thin-layer chromatograms⁴⁶ utilizing potassium iodoplatinate, a gold-iodide complex and, Rhodamine 6G, respectively. Gas chromatographic techniques^{47,48} have also been employed for the separation of sulfides.

EXPERIMENTAL

Preparation of chromatoplates

The silicic acid chromatoplates were prepared according to the method of MORLEY AND CHIBA⁴⁹. Silica gel DF-5* was applied on (8 × 8 in.) glass plates to a

* Obtained from Camag, Muttenz, Switzerland.

thickness of 280 μ . After air drying, the plates were activated in an oven at 75° for 30 min. Acetone solutions (1–2 μ l containing 5–10 μ g) of test substance were applied along a line 2.5 cm from the lower end of the plate and developed by the ascending method, till the solvent front was about 13 cm from the starting line. After evaporation of the solvent, the spots were located on the plate by spraying with one of the chromogenic reagents, then exposure of the plates to ammonia vapors.

The developing solvent systems utilized were:

- (A) 2.5 % acetone in benzene.
- (B) Toluene-ethyl acetate (1:1).

Detecting reagents were:

- (1) TCNE reagent: 2 % tetracyanoethylene in benzene.
- (2) DDQ reagent: 2 % 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in benzene.
- (3) Chloranil: 1 % tetrachloro-*p*-benzoquinone in benzene.
- (4) N,2,6-Trichloro-*p*-benzoquinoneimine: 2 % solution in ethanol.
- (5) Gibbs reagent: 2 % 2,6-dibromo-N-chloro-*p*-benzoquinoneimine in benzene.

Materials

Compounds 1, 14, 21, 33, 35, 41–43, chloranil and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone were obtained from J. T. Baker Chem. Co., Phillipsburg, N.J., USA; compounds 2,3,5,7,8,11–13, 15, 16, 19, 20, 22, 23, 28, 32, 39, 40, 45, and 46 were obtained from K & K Laboratories, Inc., Plainview, N.Y., USA; compounds 4, 9, 10, 24–27, 30, 31, 34, 36–38 and 44 from Aldrich Chemical Co., Milwaukee, Wisc., USA; compound 29 from FMC Corporation, Middleport, N.Y., USA; tetracyanoethylene, N,2,6-trichloro-*p*-benzoquinoneimine, and 2,6-dibromo-N-chloro-*p*-benzoquinoneimine from Eastman-Kodak Laboratories, Rochester, N.Y., USA; compounds 6, 17 and 18 from Wateree Chemical Co., Lugoff, S.C., USA.

RESULTS AND DISCUSSION

Tables I and II depict the spot colors of various classes of sulfur compounds on paper and thin-layers utilizing detecting reagents 1–5, followed by exposure of the chromatograms to ammonia vapors.

A number of general observations as to their chromogenic behavior to the variety of detecting reagents can be made.

1. Sulfoxides are more reactive than sulfones toward the detecting reagents screened both on paper and thin layers, *e.g.* sulfoxides yield immediate colors whereas the sulfones are detected after several minutes or require development at 80°. The greater chemical stability of the sulfone group as compared to the lower oxidized state (sulfoxides) is well recognized^{50–53}. Sulfoxides have been found to form strong hydrogen bonds with alcohols⁵⁴ and phenols^{54–56} in addition to forming complexes with iodine⁵⁷, iodine cyanide⁵⁸ and antimony pentachloride⁵⁹. Sulfones, conversely, are weaker bases (poorer donors) due to the net decrease in the electron density on the sulfur and oxygens⁵⁷.

2. The substituted *p*-benzoquinone type detectors, *e.g.* DDQ reagent (detector 2) and chloranil reagent (detector 3) were more sensitive than the halogenated quinoneimine detectors. The Gibbs reagent and N-2,6-trichloro-*p*-benzoquinoneimine, with the DDQ reagent being the detector of choice for the differentiation of sulfoxides,

TABLE I
SPOT COLORS OF SULFUR COMPOUNDS ON WHATMAN NO. 1 PAPER
Designation of colors: B = blue; Bn = brown; C = crimson; G = green; Gr = grey; L = lilac; O = orange; sl = slow (2-3 min); T = tan; V = violet; wk = weak; Y = yellow.

Class of compound	Detecting reagents									
	Before NH ₃ exposure					After NH ₃ exposure				
	1*	2	3	4	5	1	2	3	4	5
Sulfoxides										
Alkyl	C-T	O-C	Y	Y	Y-O	—	Y-O	B-Gr	Y (wk)	Bn
Aryl	C-T	O-C	Y	Y	Y-O	—	Y-O	B-Gr	Y (wk)	Bn
Cyclic	C-T	O-C	Y-G	Y-G	Y	—	Y-O	L	Y (wk)	Bn
Sulfones										
Alkyl	L**	V**	L**	—	—	Y	T	Gr (wk)	—	L
Aryl	L**	V**	L**	—	—	Y	T	Gr (wk)	—	L
Cyclic	L**	V**	L**	—	—	Y	T	Gr	—	L
Sulfides										
Alkyl	Y (sl)	T	Bn	T	Y (wk)	—	—	—	—	O
Aryl	Y (sl)	T	Bn	T	Y (wk)	—	—	—	—	O
Cyclic	Y	T	Bn	Bn	Y	—	—	—	—	Y-O
Sultones										
Thiols (alkyl)	—	V (sl)	—	—	—	Y	B-G	—	—	—
	—	—	—	—	T (wk)	—	Y-T (wk)	—	Y (sl)	Y (wk)

* For key detecting reagents 1-5, see text.

** Colors developed after heating at 80° for one minute.

TABLE II
SPOT COLORS OF SULFUR COMPOUNDS ON SILICA GEL DF-5 PLATES
Designation of colors: B = blue; Bk = black; Bn = brown; C = crimson; d = deep; G = green; L = lilac; O = orange; P = purple; Pk = pink; R = rose; sl = slow (2-3 min); T = tan; V = violet; W = white; wk = weak; Y = yellow.

Class of compound	Detecting reagents									
	Before NH ₃ exposure					After NH ₃ exposure				
	1*	2	3	4	5	1	2	3	4	5
Sulfoxides										
Alkyl	Y	O-C	Y	Y	Y-O	W	O-C	Y	Y	Y
Aryl	Y	O-C	Y	Y	Y	W	O-C	Y	Y	Y
Cyclic	Y	O-C	Y	Y	Y	W	O-C	Y	Y	Y
Sulfones										
Alkyl	Pk (sl)	L (sl)	Pk**	V (wk)	V**	Y (d)	Y-G	V	W	T
Aryl	Pk (sl)	L (sl)	Pk**	V (wk)	V**	Y (d)	Y-G	V	W	T
Cyclic	Pk (sl)	L (sl)	Pk**	V (wk)	V**	Y (d)	Y-G	V	W	T
Sulfides										
Alkyl	O-C	P-B	Y	Y-Bn	Y-Bn	—	O	P-O	Y-G	B-Bk
Aryl	O-C	P-B	Bn	Y-Bn	Y-Bn	—	O	P-O	Y-G	B-Bk
Cyclic	O-C	P-B	Y	Y-Bn	Y-Bn	—	O	P-O	T-G	B-Bk
Sultones										
Thiols (alkyl)	L (wk)	T-O	—	—	—	Y (d)	V	—	—	—
	R (sl)	W	—	—	Y	—	Y-T (sl)	—	Y (wk)	Y

* For key to detecting reagents 1-5 see text.

** Colors developed after heating at 80° for one minute.

TABLE III

 R_F VALUES OF SULFOXIDES, SULFONES AND SULFIDES ON SILICA GEL DF-5 CHROMATOPLATES

No.	Compound	2.5 % acetone- benzene	Toluene- ethyl acetate (1:1)
<i>Sulfoxide</i>			
1	Dimethyl	0.04	0.15
2	Di- <i>n</i> -propyl	0.09	0.23
3	Di- <i>n</i> -butyl	0.12	0.27
4	Di- <i>iso</i> -butyl	0.10	0.23
5	Di- <i>n</i> -amyl	0.15	0.32
6	Dihexyl	0.18	0.35
7	Diphenyl	0.19	0.37
8	Dibenzyl	0.22	0.41
9	Bis-(<i>p</i> -tolyl)	0.25	0.44
10	Bis-(<i>p</i> -chlorophenyl)	0.39	0.56
11	Tetramethylene	0.10	0.25
<i>Sulfone</i>			
12	Dimethyl	0.08	0.29
13	Diethyl	0.11	0.34
14	Di- <i>n</i> -propyl	0.15	0.38
15	Di- <i>iso</i> -propyl	0.12	0.33
16	Di- <i>n</i> -butyl	0.19	0.43
17	Di- <i>iso</i> -butyl	0.15	0.40
18	Di- <i>sec.</i> -butyl	0.16	0.40
19	Di- <i>n</i> -amyl	0.24	0.48
20	Di- <i>iso</i> -amyl	0.20	0.43
21	Divinyl	0.12	0.36
22	Diphenyl	0.28	0.54
23	Bis-(<i>p</i> -tolyl)	0.32	0.60
24	Bis-(<i>p</i> -chlorophenyl)	0.47	0.73
25	Bis-(<i>p</i> -fluorophenyl)	0.42	0.69
26	Bis-(<i>p</i> -aminophenyl)	0.05	0.30
27	Bis-(<i>m</i> -aminophenyl)	0.09	0.35
28	<i>p</i> -Chlorophenyl-methyl	0.49	0.70
29	<i>p</i> -Chlorophenyl-2,4,5- trichlorophenyl	0.47	0.77
30	<i>p</i> -Chlorophenyl-phenyl	0.41	0.69
31	<i>p</i> -Fluoro- <i>m</i> -nitrophenyl	0.45	0.73
32	Tetramethylene	0.35	0.49
<i>Sulfide</i>			
33	Di- <i>n</i> -propyl	0.54	0.70
34	Di- <i>iso</i> -propyl	0.50	0.66
35	Di- <i>n</i> -butyl	0.59	0.75
36	Di- <i>iso</i> -butyl	0.54	0.71
37	Di- <i>sec.</i> -butyl	0.53	0.71
38	Di- <i>tert.</i> -butyl	0.46	0.62
39	Di- <i>n</i> -amyl	0.64	0.80
40	Di- <i>iso</i> -amyl	0.60	0.76
41	Di- <i>n</i> -hexyl	0.68	0.84
42	Diphenyl	0.68	0.83
43	Dibenzyl	0.72	0.86
44	Bis-(<i>p</i> -chlorophenyl)	0.82	0.91
45	Bis-(<i>p</i> -aminophenyl)	0.42	0.50
46	Tetramethylene	0.56	0.74

sulfones and sulfides both on paper and thin layers. DDQ has been shown to be a strong electron acceptor readily forming complexes with suitable electron donors^{60,61}. The oxidative potential of DDQ is about 1.0V compared with 0.71 V for chloranil^{62,63} suggesting the more active role of the former reagent towards complex formation. ANDERSEN⁶⁴ has indicated the utility of DDQ for the detection of aromatic amines, hydrocarbons and phenols on paper chromatograms, with the resultant color reaction being attributed to the formation of π -complexes. The hypothesis is advanced that in the case of sulfoxides (although sulfur as well as oxygen possesses a lone pair of electrons)^{57,58} complexing with DDQ may occur via oxygen, as in the previously noted complexes of sulfoxides with iodine and phenols⁵⁷.

3. The halogenated quinoneimine reagents studied in this work (detectors 4 and 5) as well as the TCNE reagent also exhibit usefulness for the differentiation of sulfoxides, sulfones and sulfides on silica gel chromatoplates, both before and following ammonia-vapor exposure. SEARLE⁶⁵ and McALLISTER⁶⁶ have indicated the ability of quinoneimine reagents to form complexes with glyoxaline-2-thiols and 2-alkylthioglyoxalines, respectively. The TCNE reagent has been previously shown to form colored complexes with a variety of aromatic hydrocarbons^{67,68}.

4. Sulfones and alkyl thiols also tested, were shown not to interfere in the differentiation of sulfoxides, sulfones, and sulfides, by the detection reagents utilized in this study.

5. The exposure of both paper and thin-layer chromatograms to ammonia vapors (after the application of the detector reagents) generally resulted in the accentuation of spots. GRAHAM⁶⁹ had previously noted the utility of ammonia exposure after the utilization of N-(*p*-dimethylaminophenyl)-1,4-naphthoquinoneimine for the detection of halogenated aromatic hydrocarbons on paper chromatograms.

Table III illustrates the R_F values of sulfoxides, sulfones and sulfides as determined in the two solvent systems on silica gel DF-5 chromatoplates. For both the 2.5 % acetone-benzene and toluene-ethyl acetate (1:1) systems the R_F relationships of the above moieties is as follows:

(a) sulfides > sulfones > sulfoxides; (b) for the substituted aryl sulfones; *p*-chlorophenyl > *p*-fluorophenyl > *p*-aminophenyl; (c) for the isomeric aminophenyl sulfones; *m*-aminophenyl > *p*-aminophenyl.

For the alkyl sulfoxides, sulfones and sulfides studied, utilizing both solvent systems, there is essentially a linear relationship when the R_F values are plotted *versus* the number of substituent carbon atoms, with the R_F values increasing with increasing chain length.

Although the separation of *n*-, *iso*-, and *tert*-butyl sulfides can be affected by both solvent systems, neither system could resolve *iso*- and *sec*-butyl sulfides or *iso*- and *sec*-butyl sulfones.

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SUMMARY

The chromatogenic and chromogenic behavior of 11 sulfoxides, 20 sulfones and 14 sulfides is described. Useful differentiation of these compounds can best be accomplished using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone or tetracyanoethylene detecting reagents. Separation has been accomplished on thin-layer chromatograms utilizing a toluene ethyl acetate (1:1) or 2.5 % acetone-benzene solvent system.

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