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MASS SPECTRA AND ANALYTICAL CORRELATIONS OF SOME ALKYLCYCLOALKYL SULFIDES

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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MASS SPECTRA AND ANALYTICAL CORRELATIONS OF SOME ALKYLCYCLOALKYL SULFIDES

By J. E. Dooley, R. F. Kendall, and D. E. Hirsch

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MASS SPECTRA AND ANALYTICAL CORRELATIONS OF SOME ALKYLCYCLOALKYL SULFIDES

by

J. E. Dooley,[1] R. F. Kendall,[2] and D. E. Hirsch[3]

ABSTRACT

Reference mass spectra and analytical correlations for 20 alkylcycloalkyl sulfides and two dicycloalkyl sulfides are presented to provide information that will facilitate the identification of sulfur compounds occurring in natural or synthetic mixtures. Reference spectra indicate relative intensities in addition to parent and base peak sensitivities. Analytical correlations establish the ionic species that reflect major fragmentation paths for the compounds studied. Specifically, the correlations show that base peaks are formed by several different processes: (1) Cleavage of the bond α to the ring, (2) fragmentation of the alkyl chain, and (3) fragmentation of the ring plus fragment contribution from the alkyl chain. Useful correlations for determining alkyl chain length involve the $C_nH_{2n+3}S^+$ and $C_nH_{2n+1}^+$ ions. $C_nH_{2n-2}^+$ and $C_nH_{2n-1}S^+$ ions reveal the number of carbon atoms in the cyclic ring. Other important ionic species are also discussed.

alpha

INTRODUCTION

Reference mass spectra and analytical correlations are needed for structural elucidation of hydrocarbons in petroleum. Extensive spectral catalogs[4]

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[1] Chemist.

[2] Project leader.

[3] Research chemist.

All authors are with the Bartlesville Petroleum Research Center, Bureau of Mines, Bartlesville, Okla.

[4] American Petroleum Institute Research Project 44. Catalog of Mass Spectral Data. Chemical Thermodynamics Properties Center, Texas Agricultural and Mechanical University, College Station, Tex. 77840

American Society for Testing and Materials. Index of Mass Spectral Data. Committee E-14 on Mass Spectrometry, 1916 Race Street, Philadelphia, Pa. 19103

Sadtler Research Laboratories, Inc., 3316 Spring Garden Street, Philadelphia, Pa. 19104, keeps a spectral data file for many compounds and continually add to the file. To obtain spectra for a compound, one must contact Sadtler.

and established correlations for hydrocarbons (2, 9, 12-13)[5] and their heteroatom analogs (1, 3-8, 10-11, 15) confirm this need.

The Bureau of Mines, in cooperation with American Petroleum Institute Research Project 48, has recently completed a program on separation and identification of sulfur compounds in petroleum. As a result of this project, 20 alkylcycloalkyl and two dicycloalkyl sulfides were synthesized and purified to aid in spectral identifications. The mass spectra and analytical correlations presented herein should be beneficial to other spectroscopists working in the fields of petroleum and sulfur chemistry.

ACKNOWLEDGMENTS

Sixteen of the compounds reported in this investigation were prepared by Ralph Hopkins of the Bureau of Mines Petroleum Research Center, Bartlesville, Okla. The remaining six compounds were prepared by the late Professor R. W. Higgins of Texas Woman's University, Denton, Tex. We are grateful to Mr. Hopkins and Dr. Higgins for making these preparations available for study.

EXPERIMENTAL

Data were obtained on a Consolidated Electrodynamics Corporation (CEC)[6] mass spectrometer, model 21-102, modified to the equivalent of a model 21-103C. A CEC heated inlet system maintained sample vapor temperature at 135° C. The isotron temperature was 250° C. Ionizing currents of 15 and 35 microamperes were used with an ionizing voltage of 70 volts. Determinations were made at a magnetic field strength of 3110 gauss. Sensitivities of parent and base peaks are given with each spectrum.

Individual compounds were purified on a preparatory gas-liquid chromatographic (GLC) column, 11 feet in length by 3/8 inch in diameter. The column packing material was 60 to 80 mesh firebrick, coated with 10 percent Carbowax 9000. Helium flow rates (60 to 120 cc/min) and column temperature conditions (150° to 180° C) were adjusted to meet the boiling point requirements of the compounds being purified. Purity determinations were made for each sulfide, recovered from the preparatory GLC, on both polar and nonpolar GLC columns. The hydrogenolysis technique of Thompson and coworkers (17) was also used to verify purities.

DEVELOPMENT OF CORRELATIONS

Spectra for 20 alkylcycloalkyl sulfides and two dicycloalkyl sulfides are presented in tables 1 to 3. Relative intensity (RI) values, corresponding to a given mass to charge ratio (m/e), are tabulated for individual fragment ions observed in each spectrum. RI values for parent ions (ions equivalent to compound molecular weight) and base peaks (peak equivalent to the most intense ion) are underlined. Parent ions are further denoted by the symbol "P."

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[5] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

[6] Reference to specific company or brand names is made for identification only and does not imply endorsement by the Bureau of Mines.

TABLE 1. - Mass spectral data for 10 alkylcyclohexyl sulfides

	(1-Thiaethyl) cyclohexane	(1-Thiapropyl) cyclohexane	(1-Thiabutyl) cyclohexane	(2-Methyl-1-thiapropyl) cyclohexane	(1-Thiapentyl) cyclohexane	(2-Methyl-1-thiabutyl) cyclohexane	(2,2-Dimethyl-1-thiapropyl) cyclohexane	(1-Thiahexyl) cyclohexane	(4-Methyl-1-thiapentyl) cyclohexane	(1-Thiaheptyl) cyclohexane
Alkyl substituent	Methyl	Ethyl	n-Propyl	Isopropyl	n-Butyl	s-Butyl	t-Butyl	n-Pentyl	Isopentyl	n-Hexyl
Molecular weight	130	144	158	158	172	173	172	186	186	200
Magnetic field, gauss	3110	3110	3110	3110	3110	3110	3110	3110	3110	3110
Sensitivity, divisions/micron:										
Base peak	58.99	63.41	68.99	53.42	76.99	53.80	112.39	77.71	64.50	85.09
Parent peak	38.15	37.54	37.66	35.07	38.22	32.00	29.98	33.88	36.95	32.78
n-Butane, m/e 43 peak	94.29	92.09	92.09	92.09	94.92	93.17	92.09	94.92	94.92	94.29
Ionizing current microamperes	15	15	15	15	15	15	15	15	15	15
RELATIVE INTENSITIES, M/E										
24	0.04	0.04	0.04	0.05	0.04	0.04	-	0.03	0.04	0.03
25	.20	.41	.17	.20	.16	.17	0.07	.13	.15	.11
26	4.82	7.64	4.22	4.66	3.86	4.99	1.74	3.20	3.21	2.64
27	38.68	55.14	50.95	61.61	42.17	53.36	20.75	43.59	49.35	38.58
28	6.48	8.06	6.17	6.51	7.46	8.82	3.77	6.16	6.81	6.08
29	17.22	37.34	22.58	20.39	46.63	70.52	30.81	44.52	37.45	42.85
30	.37	.84	.50	.47	1.04	1.59	.72	.97	.85	.95
31	.03	-	-	-	.02	.02	-	.02	.02	.03
32	.63	.65	.46	.70	.29	.43	.30	.27	.33	.19
33	.49	.72	.37	.56	.27	.40	.25	.22	.27	.19
34	.41	1.08	.56	.81	.49	.66	.35	.44	.53	.39
35	1.88	9.14	.66	1.13	1.16	2.41	.35	1.12	1.25	.94
36	.07	.14	.07	.11	.08	.11	.05	.05	.07	.04
37	.98	.94	.75	1.12	.48	.71	.42	.47	.56	.38
38	2.47	1.63	1.96	2.91	1.18	1.70	1.11	1.14	1.38	.82
39	36.28	30.45	34.59	40.54	27.63	40.12	22.13	27.97	33.75	23.73
40	3.96	3.22	3.78	5.23	3.00	4.07	2.55	3.57	4.13	3.01
41	66.71	59.51	76.63	94.52	67.28	93.04	51.86	76.58	91.82	72.67
42	4.18	3.57	10.74	7.31	4.31	5.25	2.68	11.68	10.79	7.84
43	3.99	3.52	26.01	56.61	6.63	4.25	1.68	26.29	40.35	32.66
44	.51	.23	.95	1.86	.25	.20	.08	.90	1.43	1.12
45	24.37	24.08	22.58	26.61	17.68	24.51	11.08	16.12	19.00	13.29
46	6.00	4.02	5.29	2.31	4.23	2.10	.89	4.15	5.25	1.90
47	15.45	12.06	17.33	16.88	16.43	13.60	5.81	12.69	15.45	8.74
48	3.51	.76	1.04	.77	.76	.43	.20	.61	.69	.50
49	4.59	.66	1.08	1.96	.96	.97	1.43	.71	.88	.64
50	3.09	1.76	1.20	1.48	.97	1.40	.76	.75	.96	.60
51	5.75	4.06	3.06	3.85	2.53	3.60	1.81	2.16	2.82	1.81
52	2.71	1.91	1.65	1.97	1.33	1.84	.86	1.22	1.52	1.04
53	14.40	13.24	11.55	14.23	10.72	14.67	6.57	10.53	13.41	9.46
54	37.25	35.73	30.52	32.90	23.90	23.56	7.31	22.04	22.64	18.94
55	82.06	73.05	69.60	75.81	71.48	82.64	27.59	75.06	94.58	77.53
56	3.98	1.40	3.48	3.92	15.61	12.84	11.08	4.21	6.54	12.93
57	.62	1.15	.70	1.09	19.85	48.52	100.00	1.37	4.82	3.98
58	4.00	5.47	3.81	6.24	3.41	5.95	5.98	2.70	3.27	2.13
59	6.00	10.73	5.94	14.31	5.30	13.00	6.91	4.99	6.05	4.17
60	1.10	7.59	5.56	12.74	5.33	14.43	3.39	6.06	6.27	6.23
61	14.05	10.35	6.33	29.09	12.17	81.04	2.99	11.21	21.48	10.90
62	1.75	4.51	.54	1.51	.72	3.13	.25	.76	1.06	.73
63	1.64	12.22	.62	1.69	.79	3.90	.26	.77	1.23	.69
64	.27	.61	.12	.15	.10	.18	.03	.12	.11	.09
65	2.19	2.51	1.77	2.08	1.50	1.90	.80	1.61	1.80	1.40
66	2.05	2.18	1.99	2.26	1.72	1.80	.69	1.72	1.75	1.51
67	88.26	99.27	89.21	99.68	75.43	65.98	18.92	73.54	67.64	62.17
68	5.15	5.66	5.19	5.82	4.49	3.90	1.16	5.11	4.90	4.12
69	1.38	1.71	1.75	2.85	1.52	2.67	1.05	11.47	13.59	4.39

TABLE 1. - Mass spectral data for 10 alkylcyclohexyl sulfides--Continued

	(1-Thiaethyl) cyclohexane	(1-Thiapropyl) cyclohexane	(1-Thiabutyl) cyclohexane	(2-Methyl-1-thiapropyl) cyclohexane	(1-Thiapentyl) cyclohexane	(2-Methyl-1-thiabutyl) cyclohexane	(2,2-Dimethyl-1-thiapropyl) cyclohexane	(1-Thiahexyl) cyclohexane	(4-Methyl-1-thiapentyl cyclohexane	(1-Thiaheptyl) cyclohexane
Alkyl substituent.............	Methyl	Ethyl	n-Propyl	Isopropyl	n-Butyl	s-Butyl	t-Butyl	n-Pentyl	Isopentyl	n-Hexyl
	RELATIVE INTENSITIES, M/E (CONTINUED)									
70...........................	0.23	1.95	0.21	0.32	0.16	0.29	0.14	12.26	76.28	0.55
71...........................	2.61	2.84	3.02	3.98	2.37	3.68	1.86	17.38	24.88	2.11
72...........................	1.25	.61	.62	1.13	.54	1.10	.44	1.30	1.63	.58
73...........................	4.58	8.67	10.79	18.82	6.60	13.60	3.57	7.52	6.66	6.14
74...........................	7.27	.87	2.40	5.34	1.08	2.10	1.17	1.48	1.59	1.08
75...........................	1.68	7.54	3.10	8.23	1.15	12.03	11.08	2.77	2.08	1.59
76...........................	.70	1.34	3.33	6.47	.36	.87	.65	.44	.43	.30
77...........................	3.13	3.96	16.58	31.61	2.15	3.48	1.66	2.03	2.31	1.73
78...........................	.85	.90	1.45	2.03	.68	.87	.37	.61	.69	.52
79...........................	4.31	4.76	5.58	7.26	3.98	5.40	2.14	4.00	4.57	3.59
80...........................	1.03	1.38	1.41	2.68	1.34	2.36	1.19	1.38	1.55	1.30
81...........................	16.04	21.11	23.20	36.99	22.93	34.25	10.80	23.94	27.25	21.58
82...........................	100.00	100.00	100.00	100.00	100.00	60.52	58.34	100.00	100.00	100.00
83...........................	41.04	37.80	46.03	47.63	49.48	68.05	39.22	57.33	68.45	61.01
84...........................	2.70	2.42	3.06	3.37	3.19	4.55	2.54	3.73	4.81	10.54
85...........................	2.07	1.85	1.71	2.18	1.55	1.93	.80	1.64	1.96	13.76
86...........................	.43	.39	.44	.65	.42	.63	.28	.44	.49	1.21
87...........................	19.37	1.75	2.61	3.23	4.47	3.39	.97	5.62	10.62	8.08
88...........................	1.30	1.47	.22	.35	2.06	2.24	.42	.41	.74	1.04
89...........................	1.10	.72	3.14	3.47	3.89	5.00	1.25	.67	2.57	2.35
90...........................	.06	.10	.62	.69	2.27	2.41	.17	.04	.15	.16
91...........................	.06	.08	.36	.33	14.50	13.90	.53	.09	.21	.17
92...........................	-	.08	.05	.06	.84	.82	.03	-	-	-
93...........................	.04	.08	.06	.04	.71	.69	.03	.07	.08	.08
94...........................	-	.04	-	-	.04	.03	-	-	-	-
95...........................	.14	.42	2.16	.08	2.27	.12	.08	2.59	3.66	2.33
96...........................	.04	.04	.21	.04	.27	.06	.04	.34	.62	.35
97...........................	.36	.24	.19	.23	.20	.24	.44	.26	.30	.27
98...........................	.08	.06	.04	.08	.05	.07	.05	.07	.05	.27
99...........................	.32	.37	.26	.41	.24	.37	.14	.35	.37	.30
100..........................	.08	.06	.05	.06	.04	.07	.02	.15	.11	.06
101..........................	1.30	13.40	.25	.59	.80	.86	.13	1.14	.79	.83
102..........................	.21	.95	.42	.60	.10	.09	-	8.43	4.33	.13
103..........................	.12	.77	.30	.17	1.04	1.21	.02	31.21	10.20	.39
104..........................	-	.05	.04	.04	.32	.16	-	3.85	1.65	.04
105..........................	-	.02	.02	.03	.16	.09	-	12.78	11.76	.04
106..........................	-	-	-	-	-	-	-	.83	.79	-
107..........................	-	-	-	-	-	-	-	.53	.54	-
108..........................	-	-	-	.05	-	-	-	.02	.04	-
109..........................	.05	.04	.04	.81	.07	3.50	.03	.09	.16	.10
110..........................	.04	.04	-	.11	.04	.48	.03	.04	.06	.04
111..........................	.11	.11	.05	.08	.04	.10	.07	.07	.11	.10
112..........................	.04	-	-	-	.04	.04	.14	.04	.06	.08
113..........................	.13	.16	.22	.30	.19	.21	.10	.20	.21	.26
114..........................	.08	.52	.84	3.33	1.22	2.07	5.45	1.48	2.05	1.56
115..........................	5.81	18.64	29.53	47.90	18.92	19.77	10.44	19.27	18.51	17.69
116..........................	.45	1.79	5.84	5.48	6.82	6.38	21.69	7.14	10.63	13.72
117..........................	.29	.93	2.14	2.56	2.74	4.71	7.15	4.14	3.43	45.17
118..........................	.02	.08	.32	.26	.43	.57	1.39	.65	.70	4.76
119..........................	-	-	.05	.04	.12	.44	.31	.22	.16	10.20
120..........................	-	-	-	-	-	-	.02	-	-	.77
121..........................	-	-	-	-	-	-	-	-	-	.41
122..........................	-	-	-	-	-	-	-	-	-	.02
123..........................	-	-	-	-	-	.06	.03	-	-	.04

124	-	-	.02	.03	-	-	-	-	-	-
125	-	-	.02	.09	-	-	.02	-	-	-
127	.05	-	-	-	.07	.08	-	.05	.06	-
128	.04	-	-	-	.04	-	-	-	.05	-
129	.25	.36	4.59	.28	13.53	3.39	.07	6.06	10.16	5.81
130	64.67P	.04	.42	.10	1.28	.29	-	.75	2.77	.74
131	5.53	-	.25	.05	.72	.18	-	.44	.74	1.42
132	3.13	-	.02	-	.06	-	-	.04	.14	.18
133	.24	-	.03	-	.03	-	-	-	.03	.12
134	.02	-	-	-	-	-	-	-	-	-
135	-	.03	-	.05	-	-	-	-	-	-
142	-	.04	-	-	-	.30	-	-	-	-
143	-	.26	.11	13.11	.87	100.00	-	7.64	7.93	1.05
144	-	59.20P	.04	1.28	.10	9.66	-	.76	.79	.13
145	-	5.82	-	.65	.05	4.94	-	.42	.42	.15
146	-	2.64	-	.06	-	.41	-	.04	.03	-
147	-	.24	-	-	-	.03	-	-	-	-
153	-	-	-	-	-	-	.04	-	-	-
156	-	-	.06	.12	-	-	-	-	-	-
157	-	-	.29	.31	.04	4.78	2.89	.54	.95	5.38
158	-	-	54.59P	65.65P	-	1.02	.33	.08	.12	.61
159	-	-	5.97	7.23	-	.29	.14	.04	.05	.31
160	-	-	2.74	3.40	-	.05	-	-	-	.03
161	-	-	.25	.32	-	-	-	-	-	-
162	-	-	-	.03	-	-	-	-	-	-
168	-	-	-	-	-	-	.06	-	-	-
170	-	-	-	-	.06	.07	-	-	-	-
171	-	-	-	-	.36	.20	-	.06	.42	.61
172	-	-	-	-	49.64P	59.48P	26.67P	.03	.11	.08
173	-	-	-	-	6.02	7.16	2.91	-	.03	.04
174	-	-	-	-	2.55	3.09	1.40	-	-	-
175	-	-	-	-	.26	.31	.14	-	-	-
176	-	-	-	-	.02	-	-	-	-	-
184	-	-	-	-	-	-	-	.09	.08	-
185	-	-	-	-	-	-	-	.52	.43	.08
186	-	-	-	-	-	-	-	43.59P	57.29P	.04
187	-	-	-	-	-	-	-	5.82	7.65	.03
188	-	-	-	-	-	-	-	2.33	2.93	-
189	-	-	-	-	-	-	-	.26	.33	-
197	-	-	-	-	-	-	-	-	-	.03
198	-	-	-	-	-	-	-	-	-	.06
199	-	-	-	-	-	-	-	-	-	.56
200	-	-	-	-	-	-	-	-	-	38.53P
201	-	-	-	-	-	-	-	-	-	5.51
202	-	-	-	-	-	-	-	-	-	2.11
203	-	-	-	-	-	-	-	-	-	.25
METASTABLE PEAKS (X = PRESENT, 0 = UNDETECTED)										
25.3	X	X	X	X	X	X	X	X	X	X
26.8	X	X	X	X	X	X	X	X	X	X
28.7	X	X	X	X	X	X	X	X	X	X
29.5	0	0	0	0	X	X	X	0	0	0
36.4	X	X	X	X	X	X	X	X	X	X
37.1	X	X	X	X	X	X	X	X	X	X
38.8	X	X	X	X	X	X	X	X	X	X
39.1	0	0	X	X	0	0	0	X	X	X
40.7	X	X	X	X	X	X	X	X	X	X
42.6	0	0	X	X	0	0	0	X	X	X
46.5	X	X	X	X	X	0	0	X	X	X
55.4	X	X	X	X	X	X	X	X	X	X
66.0	X	X	X	X	X	X	X	X	X	X

TABLE 2. - Mass spectral data for 10 alkylcyclopentyl sulfides

	(1-Thiaethyl) cyclopentane	(1-Thiapropyl) cyclopentane	(1-Thiabutyl) cyclopentane	(2-Methyl-1-thiapropyl) cyclopentane	(1-Thiapentyl) cyclopentane	(2-Methyl-1-thiabutyl) cyclopentane	(3-Methyl-1-thiabutyl) cyclopentane	(2,2-Dimethyl-1-thiapropyl) cyclopentane	(1-Thiahexyl) cyclopentane	(1-Thiaheptyl) cyclopentane
Alkyl substituent.............	Methyl	Ethyl	n-Propyl	Isopropyl	n-Butyl	s-Butyl	Isobutyl	t-Butyl	n-Pentyl	n-Hexyl
Molecular weight.............	116	130	144	144	158	158	158	158	172	186
Magnetic field.........gauss..	3110	3110	3110	3110	3110	3110	3110	3110	3110	3110
Sensitivity, divisions/micron:										
Base peak..................	72.82	63.57	55.62	56.22	64.93	65.73	67.55	101.41	73.73	77.52
Parent peak................	38.35	29.60	28.48	34.20	35.67	32.99	33.65	25.65	33.01	32.41
n-Butane, m/e 43 peak.......	96.97	77.52	77.52	93.17	94.92	96.97	93.17	77.52	94.92	94.92
Ionizing current microamperes..	15	35	35	15	15	15	15	35	15	15
	RELATIVE INTENSITIES, M/E									
24...........................	0.04	0.08	0.06	0.05	0.04	0.04	0.03	0.03	0.04	0.04
25...........................	.28	.59	.31	.23	.21	.18	.13	.12	.14	.13
26...........................	4.18	8.54	5.72	4.58	5.19	4.77	3.16	2.10	3.60	3.21
27...........................	21.68	44.39	48.82	47.97	46.19	41.55	35.46	17.32	42.13	40.84
28...........................	3.43	6.52	6.28	4.12	7.59	7.18	4.46	3.56	5.31	6.26
29...........................	3.01	23.19	10.79	5.48	43.64	50.29	30.22	25.76	35.07	38.55
30...........................	.07	.52	.26	.14	1.02	1.14	.70	.62	.78	.84
31...........................	.16	.08	.10	.06	.04	.04	.05	.05	.05	.06
32...........................	.73	.66	.52	.59	.44	.48	.32	.33	.29	.27
33...........................	.57	.85	.56	.58	.37	.43	.30	.32	.26	.25
34...........................	.42	1.25	.74	.70	.61	.62	.44	.39	.50	.48
35...........................	.99	9.81	.66	1.15	1.63	2.18	.59	.31	1.29	1.27
36...........................	.11	.19	.11	.10	.15	.09	.09	.05	.05	.06
37...........................	1.72	1.55	1.47	1.48	.86	.88	.90	.67	.64	.55
38...........................	4.37	3.26	4.15	4.19	2.52	2.52	2.82	1.95	2.00	1.58
39...........................	38.35	35.44	47.99	49.96	39.83	41.55	43.59	27.33	36.30	32.22
40...........................	6.95	5.88	4.95	7.71	6.44	5.72	6.69	3.98	6.10	5.50
41...........................	71.16	62.66	100.00	100.00	100.00	97.09	100.00	59.81	100.00	100.00
42...........................	4.79	4.18	15.97	8.06	6.19	5.23	7.02	3.42	18.28	11.96
43...........................	1.91	1.95	40.21	68.99	5.48	2.48	14.93	1.21	30.54	41.28
44...........................	.60	.21	1.44	2.36	.27	.14	.59	.08	1.09	1.41
45...........................	25.06	24.80	28.18	25.90	24.33	23.05	21.95	11.66	19.30	17.56
46...........................	6.68	4.60	6.98	2.44	5.55	2.00	5.43	1.10	4.72	4.01
47...........................	14.49	11.86	23.17	16.13	24.28	14.53	21.91	2.05	18.37	18.09
48...........................	3.84	.50	1 12	.51	1.11	.38	2.60	.22	.80	.66
49...........................	8.41	.61	1.25	1.57	1.42	.84	1.97	1.35	1.02	.96
50...........................	1.44	.85	.74	.70	.84	.88	.82	.62	.51	.48
51...........................	2.29	1.74	1.65	1.62	1.81	1.93	1.68	1.22	1.41	1.35
52...........................	.68	.63	.62	.59	.70	.74	.62	.41	.56	.60
53...........................	9.01	6.98	7.07	6.01	7.54	6.44	6.88	3.27	6.67	6.88
54...........................	.85	.74	.88	.78	1.76	1.12	1.33	.61	1.22	2.02
55...........................	2.84	4.00	4.41	6.26	14.98	14.92	13.14	6.67	13.70	25.49
56...........................	.24	.29	.34	.52	25.15	12.36	18.35	12.74	1.38	18.40
57...........................	.89	1.36	.79	.84	41.30	43.31	44.86	100.00	1.53	5.50
58...........................	3.74	6.35	5.31	6.66	5.17	5.71	4.39	6.09	3.22	2.80
59...........................	7.86	14.45	11.47	19.31	10.72	15.41	8.05	8.99	8.16	7.53
60...........................	.88	9.41	8.17	15.71	9.83	14.61	6.42	7.48	9.53	10.42
61...........................	9.74	9.60	5.02	51.15	13.62	100.00	4.57	1.82	11.86	12.81
62...........................	1.11	5.99	.82	1.57	1.13	4.29	.58	.49	1.07	1.05
63...........................	1.47	27.72	1.00	2.91	1.20	5.06	.69	.38	.98	.94
64...........................	2.84	1.25	.27	.26	.22	.25	.18	.12	.19	.15
65...........................	3.15	4.99	4.20	4.11	3.76	3.45	3.33	1.81	3.19	2.92
66...........................	3.84	3.87	4.07	4.58	3.56	3.35	2.97	1.64	2.97	2.76
67...........................	49.18	49.33	56.89	55.02	53.74	38.01	60.58	13.14	44.64	41.30
68...........................	100.00	100.00	99.80	77.42	98.98	34.44	61.71	27.13	77.80	69.49
69...........................	48.84	40.99	62.03	59.39	75.45	65.17	83.90	41.84	85.58	77.92

70	2.74	2.27	3.55	3.41	4.33	3.74	4.95	2.46	25.38	4.57
71	3.00	3.51	4.22	4.29	3.56	3.66	3.48	2.32	31.12	3.00
72	1.48	1.25	1.17	1.47	1.02	1.07	.91	.57	2.20	.97
73	11.05	9.70	10.10	13.41	8.48	7.92	6.56	3.01	6.50	5.85
74	6.72	2.35	7.45	10.74	4.70	4.01	3.64	2.50	3.93	3.14
75	1.59	5.93	4.27	9.35	1.42	13.64	5.53	11.66	3.30	2.07
76	.57	.50	5.79	7.48	.51	.91	.56	.70	.55	.46
77	.11	.33	30.99	42.76	.19	.71	.43	.57	.30	.49
78	.08	.05	1.57	2.04	.09	.06	.09	.03	.05	.09
79	.09	.11	1.65	1.96	.28	.09	.39	.04	.25	.39
80	.03	.02	.11	.08	.05	-	.09	-	.05	.10
81	.26	1.40	8.93	.18	9.02	.26	23.15	.13	9.06	8.20
82	.09	.15	.73	.09	.95	.09	1.89	.08	.91	1.90
83	.07	.07	.16	.09	.26	.17	.26	.10	.31	9.14
84	.22	.20	.21	.19	.20	.18	.16	.10	.17	13.34
85	.96	1.12	1.47	1.47	1.56	1.25	1.44	.55	1.52	24.95
86	.15	.15	.19	.19	.25	.17	.18	.09	.22	1.77
87	16.31	1.58	3.31	1.82	4.84	1.86	3.42	1.42	5.55	8.00
88	3.40	1.23	.21	.18	2.17	1.51	1.12	.31	.39	1.00
89	.95	.53	3.21	2.30	5.84	4.33	4.25	1.08	.74	3.19
90	.16	.07	.19	.14	5.04	1.87	3.02	.16	.04	.21
91	.03	.06	.19	.14	31.58	10.89	14.12	.45	.09	.22
92	.01	-	-	.02	1.84	.64	.86	.04	-	.01
93	.06	.04	.04	.05	1.33	.58	.67	.04	.03	.04
94	-	-	-	-	.08	.05	.04	-	-	-
95	.06	.08	.07	1.43	.31	3.33	.34	.03	.18	.24
96	.03	.04	-	.13	.08	.36	.05	.02	.08	.08
97	.68	.55	.48	.51	.45	.43	.38	.22	.47	.49
98	.12	.09	.09	.06	.10	.06	.08	.04	.10	.09
99	.73	.79	.78	1.00	.80	.71	.63	.30	.73	.70
100	.18	.87	1.35	3.41	1.95	1.40	2.78	4.17	2.16	2.33
101	26.96	57.32	54.07	6.73	63.95	26.45	34.28	7.05	52.68	52.15
102	1.70	5.04	10.13	9.64	17.25	8.86	21.40	23.79	22.41	20.69
103	1.25	2.80	3.36	3.63	5.86	4.64	6.19	4.85	38.69	6.30
104	.08	.22	.48	.42	.91	.60	1.19	1.27	5.83	1.12
105	-	.03	.06	.05	.18	.20	.24	.20	20.83	.22
106	-	-	-	-	-	-	-	.02	1.41	-
107	-	-	-	-	-	-	-	-	.90	-
108	-	-	-	-	-	-	-	-	.05	-
109	-	-	-	-	-	.05	.04	-	.09	.06
110	-	-	-	-	-	-	-	-	.04	.03
111	-	-	.05	.09	-	-	.04	-	.02	.07
112	-	-	-	.02	-	-	.03	-	-	-
113	.05	-	.07	-	.04	.02	.07	-	.05	.09
114	.03	-	-	-	.04	-	.09	-	.05	.13
115	.34	1.11	23.17	6.25	16.59	.21	45.96	.12	16.96	16.72
116	52.67P	.08	2.28	.87	1.58	.08	4.51	.03	1.66	4.49
117	3.88	.06	1.14	.35	.89	.09	2.26	-	1.44	48.85
118	2.47	-	.10	.05	.08	-	.20	-	.13	5.28
119	.16	-	-	-	-	-	.03	-	.07	16.33
120	.02	-	-	-	-	-	-	-	-	1.25
121	-	-	-	-	-	-	-	-	-	.69
122	-	-	-	-	-	-	-	-	-	.04
123	-	-	-	-	-	-	-	-	-	.04
127	-	.04	-	-	-	.05	-	-	.02	.06
128	-	.04	-	-	.04	.15	-	-	-	.02
129	-	.28	.23	23.55	9.50	90.86	3.79	.03	1.19	1.61
130	-	46.56P	.04	1.99	1.23	7.97	.47	.03	.15	.15
131	-	3.99	-	1.11	.50	4.73	.21	-	.13	.66
132	-	2.29	-	.09	.05	.31	-	-	-	.06
133	-	.18	-	.02	-	.02	-	-	-	.04

TABLE 2. - Mass spectral data for 10 alkylcyclopentyl sulfides--Continued

Alkyl substituent	(1-Thiaethyl) cyclopentane	(1-Thiapropyl) cyclopentane	(1-Thiabutyl) cyclopentane	(2-Methyl-1-thiapropyl) cyclopentane	(1-Thiapentyl) cyclopentane	(2-Methyl-1-thiabutyl) cyclopentane	(3-Methyl-1-thiabutyl) cyclopentane	(2,2-Dimethyl-1-thiapropyl) cyclopentane	(1-Thiahexyl) cyclopentane	(1-Thiaheptyl) cyclopentane
	Methyl	Ethyl	n-Propyl	Isopropyl	n-Butyl	s-Butyl	Isobutyl	t-Butyl	n-Pentyl	n-Hexyl
	RELATIVE INTENSITIES, M/E (CONTINUED)									
135	-	-	-	-	-	0.03	-	-	-	0.06
141	-	-	-	-	-	-	-	-	0.04	.03
142	-	-	0.05	0.05	-	-	-	-	-	-
143	-	-	.33	.27	0.12	5.43	0.59	2.64	5.87	.53
144	-	-	<u>51.21P</u>	<u>60.83P</u>	-	.49	.08	.28	.77	.09
145	-	-	5.16	5.96	-	.39	.03	.13	.32	.08
146	-	-	2.48	2.94	-	.04	-	-	.04	-
147	-	-	.23	.27	-	-	-	-	-	-
156	-	-	-	-	.06	.05	.04	-	-	-
157	-	-	-	-	.44	.14	.37	-	.08	4.58
158	-	-	-	-	<u>54.93P</u>	<u>50.20P</u>	<u>49.81P</u>	<u>25.30P</u>	.02	.73
159	-	-	-	-	6.05	5.50	5.53	2.75	-	.26
160	-	-	-	-	2.83	2.52	2.48	1.25	-	.04
161	-	-	-	-	.27	.24	.26	.12	-	-
170	-	-	-	-	-	-	-	-	.05	.08
171	-	-	-	-	-	-	-	-	.56	.09
172	-	-	-	-	-	-	-	-	<u>44.77P</u>	-
173	-	-	-	-	-	-	-	-	5.61	-
174	-	-	-	-	-	-	-	-	2.32	-
175	-	-	-	-	-	-	-	-	.25	-
184	-	-	-	-	-	-	-	-	-	.07
185	-	-	-	-	-	-	-	-	-	.62
186	-	-	-	-	-	-	-	-	-	<u>41.81P</u>
187	-	-	-	-	-	-	-	-	-	5.55
188	-	-	-	-	-	-	-	-	-	2.25
189	-	-	-	-	-	-	-	-	-	.25
	METASTABLE PEAKS (X = PRESENT, 0 = UNDETECTED)									
24.4	X	X	X	X	X	X	X	X	X	X
25.3	X	X	X	X	X	X	X	X	X	X
26.8	X	X	X	X	X	X	X	X	X	X
28.7	0	X	X	X	X	X	X	X	X	X
29.5	0	0	0	0	X	X	X	X	0	0
36.4	0	0	0	0	0	0	0	0	0	X
37.1	X	X	X	X	X	X	X	X	X	X
38.8	X	X	X	X	X	X	X	X	X	X
39.1	0	0	X	X	X	0	X	0	X	X
40.7	X	X	X	X	X	X	X	X	X	X
42.6	0	0	X	X	0	0	0	0	X	X
45.4	0	0	X	X	X	X	X	X	X	X
46.5	X	X	X	X	X	0	X	0	X	X
52.8	X	X	X	X	X	X	X	X	X	X
55.4	0	0	0	0	0	0	0	0	0	X
66.0	X	X	X	X	X	X	X	X	X	X

TABLE 3. - Mass spectral data for two dicycloalkyl sulfides

	Compound	
	Dicyclopentyl-thiamethane	Cyclopentyl-cyclohexyl-thiamethane
Molecular weight	170	184
Magnetic field gauss	3110	3110
Sensitivity, divisions/micron:		
Base peak	103.00	73.78
Parent peak	33.79	36.17
n-Butane, m/e 43 peak	94.29	94.29
Ionizing current microamperes	15	15
RELATIVE INTENSITIES, M/E		
24	0.03	0.04
25	.11	.13
26	.33	2.98
27	19.13	31.57
28	3.09	5.41
29	5.16	17.84
30	.12	.39
31	.06	.08
32	.30	.42
33	.23	.28
34	.33	.43
35	.34	.56
36	.03	.04
37	.63	.61
38	2.03	1.81
39	32.18	38.59
40	5.39	5.40
41	82.14	100.00
42	4.63	5.67
43	2.22	4.42
44	.12	.21
45	16.36	21.65
46	1.19	1.42
47	9.04	11.83
48	.23	.30
49	.43	.61
50	.47	.90
51	1.28	2.70
52	.49	1.36
53	5.58	12.08
54	.78	16.13
55	4.99	53.96
56	.37	2.78
57	.42	.61
58	3.28	4.11
59	8.56	8.63
60	9.92	10.27
61	2.13	4.88
62	.68	.71
63	.65	.68
64	.18	.17
65	3.81	3.64
66	4.68	4.02
67	43.15	73.00
68	51.03	24.30
69	100.00	60.41
70	5.53	3.60
71	3.50	4.27
72	1.14	1.33
73	9.47	13.65
74	4.67	3.12
75	.96	1.20
76	.44	.39
77	.15	1.90
78	.05	.57
79	.24	3.82
80	.07	1.97
81	.68	22.72
82	.16	65.46
83	.06	56.18
84	.18	3.75
85	1.60	2.14
86	.22	.60
87	2.18	3.52
88	.14	.39
89	.12	.21

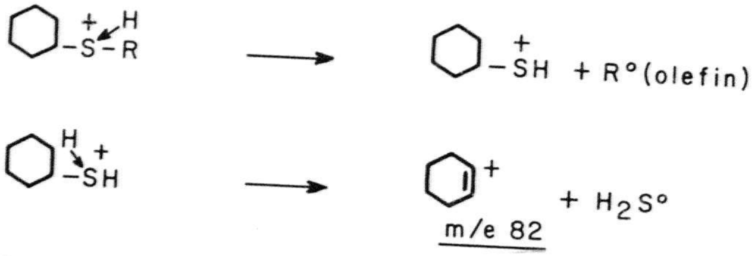
	Compound	
	Dicyclopentyl-thiamethane	Cyclopentyl-cyclohexyl-thiamethane
RELATIVE INTENSITIES, M/E (CON.)		
91	0.08	0.10
93	.12	.13
94	.10	.09
95	.65	.42
96	.07	.09
97	.46	.43
98	.11	.12
99	.83	.84
100	5.10	4.11
101	66.80	31.96
102	18.93	11.69
103	25.29	17.58
104	2.17	1.54
105	1.07	.79
106	.06	.04
107	.08	.09
108	.05	.11
109	.08	.35
110	.03	.06
111	.03	.08
112	-	.06
113	.16	.27
114	.06	3.14
115	1.27	24.69
116	.11	7.56
117	.08	13.26
118	-	1.20
119	-	.59
120	-	.04
121	.03	.09
122	-	.03
123	-	.03
124	-	.04
127	.15	.25
128	.16	.15
129	.11	.38
130	.03	.04
137	.06	-
141	2.88	4.44
142	.48	.47
143	.17	.28
144	.03	.03
150	-	.02
151	-	.09
155	-	.69
156	-	.23
157	-	.05
168	.04	-
169	.16	-
170	32.81P	-
171	3.98	-
172	1.70	-
173	.17	-
182	-	.05
183	-	.25
184	-	49.03P
185	-	6.56
186	-	2.65
187	-	.30
188	-	.02
METASTABLE PEAKS (X = PRESENT, 0 = UNDETECTED)		
24.4	X	X
25.3	X	X
26.8	X	X
28.7	X	X
36.4	0	X
37.1	X	X
38.8	X	X
40.7	X	X
45.4	X	X
46.5	X	X
52.8	X	X
55.4	0	X
66.0	X	X

At the bottom of each table, metastable peaks are shown as measured at appropriate locations in the spectrum of each sulfide. Relative intensities of the metastable peaks are not included because many of them could not be resolved sufficiently for measurement. Rather, an appropriate symbol indicates whether a specific metastable ion may be present for any given compound.

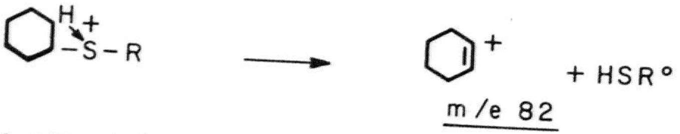
Base Peak Formation in Alkylcyclohexyl Sulfides

Eight of the 10 alkylcyclohexyl sulfides studied indicate that cleavage α to the ring, accompanied by the loss or transfer of a hydrogen atom, is preferential in base peak formation.

Two fragmentation processes may be considered in forming the base peaks at m/e 82. One process involves initial cleavage β to the ring with the transfer of a hydrogen from the alkyl chain to the sulfur, possibly producing a thiol and neutral olefin (16). This fragmentation step is followed by cleavage α to the ring accompanied by the transfer of a hydrogen from the ring to the sulfur, producing the base peak and hydrogen sulfide. This process is indicated as follows:



In a second process, cleavage occurs α to the ring with a hydrogen atom lost or transferred from the ring to produce the base peak at m/e 82 and a neutral species, possibly a thiol (16):



The neutral species cannot be proved in either case. Deuteration studies could be of value in determining the process of base peak formation.

Two alkylcyclohexyl sulfides have base peaks other than m/e 82. One of these contains a t-butyl group and the other a s-butyl group. These groups exert an influence on fragmentation and will be discussed later.

Base Peak Formation in Alkylcyclopentyl Sulfides

In six of the 10 alkylcyclopentyl sulfides investigated, base peaks in the spectra are believed to result from contributions of both ring and chain to the m/e 41 ion. The deduction is based on the two cyclopentyl sulfides (with methyl and ethyl groups for alkyl chains) having base peaks at m/e 68 (m/e 68 results from processes similar to those described above for alkylcyclohexyl sulfides). Chain lengths in these two lower molecular weight compounds are insufficient to produce an m/e 41 ion, and therefore fragmentation of the molecule favors cleavage α to the ring accompanied by loss or transfer of 1 hydrogen. The m/e 41 ion is probably produced from the ring by the process $69^+ \xrightarrow{28°} 41^+$ and, for chains with 3 or more carbons, by the processes $43^+ \xrightarrow{2°} 41^+$ and $57 \xrightarrow{16°} 41$. Metastable peaks appearing in the spectra of these compounds at approximately 24.4 ($69 \xrightarrow{28°} 41$), 39.1 ($43 \xrightarrow{2°} 41$), and 29.5 ($57 \xrightarrow{16°} 41$) could result from these processes.

Two alkylcyclopentyl sulfides have base peaks derived from the alkyl chain. These compounds have t-butyl and s-butyl groups that affect base peak formation and are similar to the exceptional fragmentation patterns noted above for alkylcyclohexyl sulfides containing t-butyl and s-butyl groups.

Prominent Ions

The more intense ions (other than the base peaks) worthy of mention occur at m/e 27, 29, 39, 41, and 67 for each compound. Relative intensities for these ions are recorded in table 4 and usually exceed 20 percent of the base peak, with exceptions noted in the table. All of these ions are typical of those found in fragmentation patterns of cycloalkanes (14).

TABLE 4. - Relative intensities of abundant ions in alkylcycloalkyl sulfides

	Relative intensities of abundant ions, m/e				
	27	29	39	41	67
CYCLOPENTYL SULFIDES					
(1-Thiaethyl)cyclopentane................	21.68	3.01	38.35	71.16	49.18
(1-Thiapropyl)cyclopentane...............	44.39	23.19	35.44	62.66	49.33
(1-Thiabutyl)cyclopentane................	48.82	10.79	47.99	100.00	56.89
(2-Methyl-1-thiapropyl)cyclopentane.......	47.97	5.48	49.96	100.00	55.02
(1-Thiapentyl)cyclopentane...............	46.19	43.64	39.83	100.00	53.74
(2-Methyl-1-thiabutyl)cyclopentane........	41.55	50.29	41.55	97.09	38.01
(3-Methyl-1-thiabutyl)cyclopentane........	35.46	30.22	43.59	100.00	60.58
(2,2-Dimethyl-1-thiapropyl)cyclopentane...	17.32	25.76	27.33	59.81	13.14
(1-Thiahexyl)cyclopentane................	42.13	35.07	36.30	100.00	44.64
(1-Thiaheptyl)cyclopentane...............	40.84	38.55	32.22	100.00	41.30
CYCLOHEXYL SULFIDES					
(1-Thiaethyl)cyclohexane.................	38.68	17.22	36.28	66.71	88.26
(1-Thiapropyl)cyclohexane................	55.14	37.34	30.45	59.51	99.27
(1-Thiabutyl)cyclohexane.................	50.95	22.58	34.59	76.63	89.21
(2-Methyl-1-thiapropyl)cyclohexane........	61.61	20.39	40.54	94.52	99.68
(1-Thiapentyl)cyclohexane................	42.17	46.63	27.63	67.28	75.43
(2-Methyl-1-thiabutyl)cyclchexane.........	53.36	70.52	40.12	93.04	65.98
(2,2-Dimethyl-1-thiapropyl)cyclohexane....	20.75	30.81	22.13	51.86	18.92
(1-Thiahexyl)cyclohexane.................	43.59	44.52	27.97	76.58	73.54
(4-Methyl-1-thiapentyl)cyclohexane........	49.35	37.45	33.75	91.82	67.64
(1-Thiaheptyl)cyclohexane................	38.58	42.85	23.73	72.67	62.17
DICYCLIC SULFIDES					
Dicyclopentylthiamethane.................	19.13	5.16	32.18	82.14	43.15
Cyclopentylcyclohexylthiamethane..........	31.57	17.84	38.59	100.00	73.00

Parent ion intensities are also abundant, the smallest of which is about 25 percent for a compound containing a t-butyl group. This is probably due to the large ionization cross section of the sulfur atom (14).

A significant $C_nH_{2n+1}S^+$ (m/e 47, 61, etc.) series appears in alkylcycloalkyl sulfides although not as evident as in the thiaalkanes (3, 10). Methyl substitution on the carbon α to the sulfur atom appears to have considerable influence on the formation of this ion as shown by the large m/e 61 intensities of compounds containing isopropyl and s-butyl groups. (2-Methyl-1-thiapropyl)cyclopentane, (2-methyl-1-thiabutyl)cyclopentane, (2-methyl-1-thiapropyl)cyclohexane, and (2-methyl-1-thiabutyl)cyclohexane have considerably larger m/e 61 ions (>29 percent) than the other compounds studied. (4-Methyl-1-thiapentyl)cyclohexane also has an abundant m/e 61 (>21 percent), probably due to the location of the branching. Cook and Dinneen (3) have postulated the mechanism of formation of the m/e 61 ion observed in the spectra of other types of sulfur compounds.

Alkyl Chain Length

Cook and Dinneen (3) have proposed origins of $C_nH_{2n+2}S^+$ (m/e 48, 62, etc.) and $C_nH_{2n+3}S^+$ (m/e 49, 63, etc.) ions and have found these useful in indicating chain lengths in thiaalkanes. Their data show that a summation of these ions in thiaalkanes will establish chain length. The same correlation can be applied to alkylcycloalkyl sulfides, except that $C_nH_{2n+3}S^+$ ions alone will indicate the length of the alkyl chain. As in thiaalkanes, $C_nH_{2n+3}S^+$ ions are usually the largest when n equals the number of carbon atoms in the alkyl group. Underlined relative intensity values in table 5 indicate the cyclic sulfides which support this observation. Only two compounds fail to correlate, and both contain t-butyl groups. In view of this, if any peak in the series is >2 percent, the correlation holds; if not, it fails.

TABLE 5. - Relative intensities of ions for n in formula $C_nH_{2n+3}S^+$

	Relative intensities					
	n=1	n=2	n=3	n=4	n=5	n=6
CYCLOPENTYL SULFIDES						
(1-Thiaethyl)cyclopentane..................	8.41	1.47	0.11	0.03	-	0.16
(1-Thiapropyl)cyclopentane.................	.61	27.72	.33	.06	0.03	-
(1-Thiabutyl)cyclopentane..................	1.25	1.00	30.99	.19	.06	-
(2-Methyl-1-thiapropyl)cyclopentane........	1.57	2.91	42.76	.14	.05	-
(1-Thiapentyl)cyclopentane.................	1.42	1.20	.19	31.58	.18	-
(2-Methyl-1-thiabutyl)cyclopentane.........	.84	5.06	.71	10.89	.20	-
(3-Methyl-1-thiabutyl)cyclopentane.........	1.97	.69	.43	14.12	.24	.03
(2,2-Dimethyl-1-thiapropyl)cyclopentane....	1.35	.38	.57	.45	.20	-
(1-Thiahexyl)cyclopentane..................	1.02	.98	.30	.09	20.83	.07
(1-Thiaheptyl)cyclopentane.................	.96	.94	.49	.22	.22	16.33
CYCLOHEXYL SULFIDES						
(1-Thiaethyl)cyclohexane...................	4.59	1.64	3.13	0.06	-	-
(1-Thiapropyl)cyclohexane..................	.66	12.22	3.96	.08	0.02	-
(1-Thiabutyl)cyclohexane...................	1.08	.62	16.58	.36	.02	0.05
(2-Methyl-1-thiapropyl)cyclohexane.........	1.96	1.69	31.61	.33	.03	.04
(1-Thiapentyl)cyclohexane..................	.96	.79	2.15	14.50	.16	.12
(2-Methyl-1-thiabutyl)cyclohexane..........	.97	3.90	3.48	13.90	.09	.44
(2,2-Dimethyl-1-thiapropyl)cyclohexane.....	1.43	.26	1.66	.53	-	.31
(1-Thiahexyl)cyclohexane...................	.71	.77	2.03	.09	12.78	.22
(4-Methyl-1-thiapentyl)cyclohexane.........	.88	1.23	2.31	.21	11.76	.16
(1-Thiaheptyl)cyclohexane..................	.64	.69	1.73	.17	.04	10.20

Another useful indicator of alkyl chain length is the $C_nH_{2n+1}^+$ (m/e 29, 43, etc.) group of ions. Beginning with m/e 29, the last large intensity appearing in the series usually represents the alkyl chain length. This intensity is in excess of 20 percent for cyclopentyl sulfides and 10 percent for cyclohexyl sulfides. Supporting values are underlined in table 6. The observation is likely invalid for chain lengths larger than 6 carbons as can be noted from the decrease in intensity of ions representative of the longer chains. Some confusion could result from this correlation unless use is made in conjunction with the $C_nH_{2n+3}S^+$ observations. Methyl compounds may be determined by looking at the n=2/n=3 ratio. A ratio of less than 5 to 1 indicates S-C_1. A ratio greater than 10 to 1 denotes S-C_2. The $C_nH_{2n}^+$ and $C_nH_{2n+1}S^+$ ions (discussed above) may be useful in determining chain lengths greater than C_5.

TABLE 6. - Relative intensities of ions for n in formula $C_nH_{2n+1}^+$

	Relative intensities					
	n=2[1]	n=3	n=4	n=5	n=6	n=7
CYCLOPENTYL SULFIDES						
(1-Thiaethyl)cyclopentane...............	3.01	1.91	0.89	3.00	0.96	0.73
(1-Thiapropyl)cyclopentane..............	23.19	1.95	1.36	3.51	1.12	.79
(1-Thiabutyl)cyclopentane...............	10.79	40.21	.79	4.22	1.47	.78
(2-Methyl-1-thiapropyl)cyclopentane......	5.48	68.99	.84	4.29	1.47	1.00
(1-Thiapentyl)cyclopentane..............	43.64	5.48	41.30	3.56	1.56	.80
(2-Methyl-1-thiabutyl)cyclopentane.......	50.29	2.48	43.31	3.66	1.25	.71
(3-Methyl-1-thiabutyl)cyclopentane.......	30.22	14.93	44.86	3.48	1.44	.63
(2,2-Dimethyl-1-thiapropyl)cyclopentane..	25.76	1.21	100.00	2.32	.55	.30
(1-Thiahexyl)cyclopentane...............	35.07	30.54	1.53	31.12	1.52	.73
(1-Thiaheptyl)cyclopentane..............	38.55	41.28	5.50	3.00	24.95	.70
CYCLOHEXYL SULFIDES						
(1-Thiaethyl)cyclohexane................	17.22	3.99	0.62	2.61	2.07	0.32
(1-Thiapropyl)cyclohexane...............	37.34	3.52	1.15	2.84	1.85	.37
(1-Thiabutyl)cyclohexane................	22.58	26.01	.70	3.02	1.71	.26
(2-Methyl-1-thiapropyl)cyclohexane.......	20.39	56.61	1.09	3.98	2.18	.41
(1-Thiapentyl)cyclohexane...............	46.63	6.63	19.85	2.37	1.55	.24
(2-Methyl-1-thiabutyl)cyclohexane........	70.52	4.25	48.52	3.68	1.93	.37
(2,2-Dimethyl-1-thiapropyl)cyclohexane...	30.81	1.68	100.00	1.86	.80	.14
(1-Thiahexyl)cyclohexane................	44.52	26.29	1.37	17.38	1.64	.35
(4-Methyl-1-thiapentyl)cyclohexane.......	37.45	40.35	4.82	24.88	1.96	.37
(1-Thiaheptyl)cyclohexane...............	42.85	32.66	3.98	2.11	13.76	.30

[1] n=1 (m/e 15) not scanned.

Although indirectly related to alkyl chain length, the m/e 35 peak shows an interesting correlation where an ethyl group is attached to the sulfur. Intensities of 9 to 10 percent of the base peak for m/e 35 are recorded in the spectra of (1-thiapropyl)cyclopentane and (1-thiapropyl)cyclohexane. The peak must be characteristic of the influence of the ethyl group in the two compounds, since m/e 35 intensities in the spectra of other alkylcycloalkyl sulfides studied are not nearly as strong (s-butyl groupings are closest in intensity with about 2 percent). The ion involved is the H_3S^+ (3) (an analog of H_3O^+).

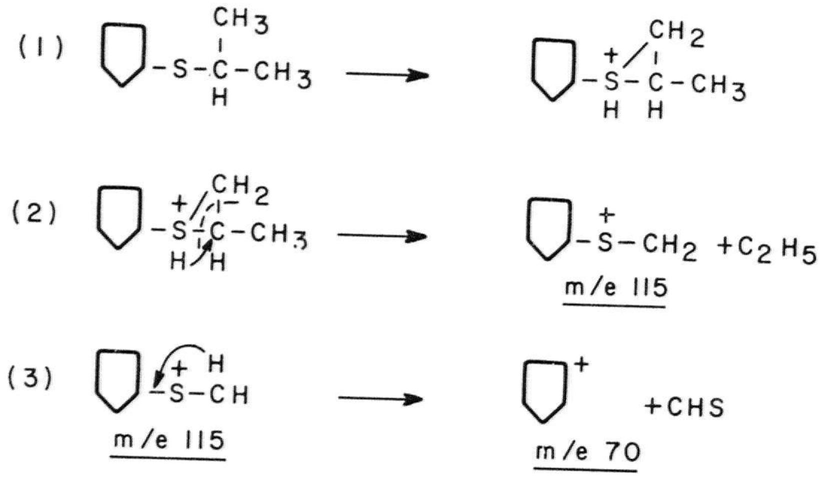
Butyl groups have a characteristic metastable ion which helps identify the 4-carbon chain. The ion registers at m/e 29.5 and probably results from the process $57 \xrightarrow{16^\circ} 41$. Intensity of this metastable ion is largest for the t-butyl group. All of the compounds containing butyl groups (total of seven) show this ion in their spectra.

As denoted in tables 1 to 3, a metastable ion exists at m/e 42.6 in the spectra of those cyclic sulfides that have either propyl, pentyl, or hexyl alkyl chains. Considering the variety of compounds involved in the production of this metastable ion, it is evident that more than one fragmentation process is occurring.

The metastable ion may result from the transition $71 \xrightarrow{16^\circ} 55$ for the three cyclic sulfides that have C_5S side chains. This transition involves cleavage of the chain at the bond α to the sulfur atom. The same transition is also applicable to a lesser extent to the two cyclic sulfides with C_6 alkyl chains, except that cleavage occurs at the bond β to the sulfur atom.

A second transition to consider is $158 \xrightarrow{76^\circ} 82$. This process applies to the two cyclohexyl derivatives that have C_3 groups attached to the sulfur. The fragmentation process would involve the formation of the base peak by cleavage of the bond α to the ring.

Still another process to consider is $115 \xrightarrow{45^\circ} 70$. For the compounds (1-thiabutyl) and (1-thiaheptyl)cyclopentane the fragmentation steps could result from cleavage of the bond β to the sulfur with subsequent loss of CHS. (2-Methyl-1-thiapropyl)cyclopentane may produce the m/e 42.6 ion through a cyclic transition (3) as follows:



For the compound (1-thiaheptyl)cyclohexane, cleavage could occur at the bond β to the ring, followed by possible loss of CHS (the carbon atom removed from the ring).

Ring Size

Ring size can be determined from the intensity of the $C_nH_{2n-2}^+$ (m/e 54, 68, etc.) series. Cyclopentyl compounds show ions in excess of 20 percent relative intensity at m/e 68, whereas cyclohexyl compounds have m/e 82 (in most cases the base peak) intensities greater than 50 percent relative to the base peak. The largest value in the series represents ring size. Dicyclics apparently follow the same pattern. If a cyclopentyl-cyclohexyl combination is present, both the m/e 68 and m/e 82 ions are intense with the m/e 82 (cyclohexyl ion) showing the greater intensity. The base peak for the mixed ring compound is apparently formed from fragmentation of both rings. Table 7 contains data for these correlations with underlined values indicating correlative support.

TABLE 7. - Relative intensities of ions for n in formula $C_nH_{2n-2}^+$

	Relative intensities					
	n=3	n=4	n=5 (m/e 68)	n=6 (m/e 82)	n=7	n=8
CYCLOPENTYL SULFIDES						
(1-Thiaethyl)cyclopentane.............	6.95	0.84	100.00	0.09	0.03	-
(1-Thiapropyl)cyclopentane............	5.88	.74	100.00	.15	.04	-
(1-Thiabutyl)cyclopentane.............	4.95	.88	99.80	.73	-	-
(2-Methyl-1-thiapropyl)cyclopentane...	7.71	.78	77.42	.09	.13	-
(1-Thiapentyl)cyclopentane............	6.44	1.76	98.98	.95	.08	-
(2-Methyl-1-thiabutyl)cyclopentane....	5.72	1.12	34.44	.09	.36	-
(3-Methyl-1-thiabutyl)cyclopentane....	6.69	1.33	61.71	1.89	.05	-
(2,2-Dimethyl-1-thiapropyl) cyclopentane.........................	3.98	.61	27.13	.08	.02	-
(1-Thiahexyl)cyclopentane.............	6.10	1.22	77.80	.91	.08	0.04
(1-Thiaheptyl)cyclopentane............	5.50	2.02	69.49	1.90	.08	.03
CYCLOHEXYL SULFIDES						
(1-Thiaethyl)cyclohexane..............	3.96	37.25	5.15	100.00	0.04	0.04
(1-Thiapropyl)cyclohexane.............	3.22	35.73	5.66	100.00	.04	.04
(1-Thiabutyl)cyclohexane..............	3.78	30.52	5.19	100.00	.21	-
(2-Methyl-1-thiapropyl)cyclohexane....	5.23	32.90	5.82	100.00	.04	.11
(1-Thiapentyl)cyclohexane.............	3.00	23.90	4.49	100.00	.27	.04
(2-Methyl-1-thiabutyl)cyclohexane.....	4.07	23.56	3.90	60.52	.06	.48
(2,2-Dimethyl-1-thiapropyl)cyclohexane	2.55	7.31	1.16	58.34	.04	.03
(1-Thiahexyl)cyclohexane..............	3.57	22.04	5.11	100.00	.34	.04
(4-Methyl-1-thiapentyl)cyclohexane....	4.13	22.64	4.90	100.00	.62	.06
(1-Thiaheptyl)cyclohexane.............	3.01	18.94	4.12	100.00	.35	.04
DICYCLIC SULFIDES						
Dicyclopentylthiamethane..............	5.39	0.78	51.03	0.16	0.07	0.03
Cyclopentylcyclohexylthiamethane......	5.40	16.13	24.30	65.46	.09	.06

To some degree, the $C_nH_{2n-1}S^+$ (m/e 87, 101, etc.) and $C_nH_{2n}S^+$ (m/e 88, 102, etc.) ions are useful in indicating ring size but not as effectively as $C_nH_{2n-2}^+$. For alkylcyclopentyl sulfides, m/e 101 >m/e 115, and m/e 102 >m/e 116, and conversely, for alkylcyclohexyl sulfides, m/e 115 >m/e 101, and m/e 116 >m/e 102. Three anomalies occur in this correlation:

1. In the spectrum of (1-thiaethyl)cyclopentane, m/e 116 is more intense than m/e 102, probably the result of m/e 116 being the parent peak (<u>16</u>).

2. The spectrum of (3-methyl-1-thiabutyl)cyclopentane shows m/e 115 >m/e 101, a result of branching in the chain.

3. The (1-thiahexyl)cyclohexane spectrum has an m/e 102 ion larger than the m/e 116 ion.

This probably results from contribution of the chain (including the sulfur atom) to the m/e 101, 102, and 103 group of ions. Dicyclics conform to the correlation provided the assumption is made that the C_5 ring dominates fragmentation where both C_5 and C_6 rings are involved.

In addition to the above correlations, m/e 52 and m/e 53 may be useful in determining ring size. Both of these ions are larger in alkylcyclohexyl sulfides than in alkylcyclopentyl sulfides. Relative intensities for m/e 52 fall between 0.41 and 0.74 in cyclopentyl sulfides and between 0.86 and 2.71 in cyclohexyl sulfides. The m/e 53 ion relative intensities have a range of 3.27 to 9.01 for cyclopentyl sulfides and 9.46 to 14.40 for cyclohexyl sulfides. Tertiary butyl cyclohexyl sulfide does not conform for m/e 53. The dicyclic sulfides conform if the assumption is made that the C_6 ring effect is dominant where both C_5 and C_6 rings occur.

Alkylcyclohexyl sulfides have ions more intense at m/e 54 and 55 than alkylcyclopentyl sulfides. For m/e 54 ions, intensities greater than 7 percent represent cyclohexyl structures, whereas intensities less than 2.1 percent indicate the cyclopentyl structure. For m/e 55 ions, intensities more than 27 percent would be cyclohexyl, and those less than 26 percent would be cyclopentyl.

The base peak minus 2 ion may also be related to the number of carbons in the ring. In alkylcyclopentyl sulfide spectra, the base minus 2 peak is greater than 3 percent relative intensity. Alkylcyclohexyl sulfide spectra, however, show a base minus 2 peak of less than 3 percent relative intensity. An exception is t-butyl cyclohexyl sulfide in which m/e 57 (t-butyl group) is the base. The base minus 2 peak, therefore, falls in the C_nH_{2n-1} series, a series which happens to be very intense in alkylcyclohexyl sulfide spectra, as discussed above.

Metastable ions at m/e 24.4 and 52.8, which support the cyclopentyl structure, are present in all the cyclopentyl sulfides but do not appear in the cyclohexyl sulfides. The m/e 24.4 ion could result from a 69 $\xrightarrow{28^\circ}$ 41 transition whereas the 52.8 may come from a 101 $\xrightarrow{28^\circ}$ 73 transition.

Similarly, m/e 36.4 and 55.4 ions appear in cyclohexyl sulfides but not in cyclopentyl sulfides. There is one exception, the cyclopentyl sulfide containing a C_6 alkyl chain. These two ions then would be indicative of the C_6 ring and probably result from 83 $\xrightarrow{28^\circ}$ 55 transition (m/e 36.4) and 81 $\xrightarrow{14^\circ}$ 67 transition (m/e 55.4).

SUMMARY OF CORRELATIONS

Correlations observed for 20 alkylcycloalkyl sulfides and two dicycloalkyl sulfides follow.

Base Peaks

Alkylcyclohexyl Sulfides

Base peaks formed by α cleavage to ring in eight of 10 compounds. Base peaks determined by t-butyl and s-butyl alkyl chains in the other two compounds.

Alkylcyclopentyl Sulfides

Base peaks formed by fragmentation of ring plus contribution from the alkyl chain (for six compounds) provided alkyl chain length is 3 carbons or more. Two compounds had base peaks formed by cleavage α to the ring (alkyl chain lengths were less than 3 carbons). The remaining two compounds had base peaks determined by t-butyl and s-butyl groups.

Dicyclic Sulfides

Base peak is determined by cleavage α to ring where only cyclopentyl rings are involved. Where cyclopentyl and cyclohexyl rings are present in the same compound, both rings contribute to the base peak ion.

Determination of Ring Size

	C_5 ring	C_6 ring
1. $C_nH_{2n-2}^{+}$[1]	m/e 68 >82	m/e 82 >68
2. $C_nH_{2n-1}S^{+}$	m/e 101 >115	m/e 115 >101
3. $C_nH_{2n}S^{+}$	m/e 102 >116	m/e 116 >102
4. C_nH_{2n-1}	m/e 69 >83	m/e 83 >69
5. m/e 52	RI 0.41-0.74	0.86-2.71
6. m/e 53[1]	RI 3.27-9.01	9.46-14.40
7. Base -2 peak[1]	RI >3 pct	>3 pct
8. m/e 54[1]	RI >16 pct	>2.5 pct
9. m/e 55[1]	RI >50 pct	>26 pct
10. m/e 24.4, 52.8 (metastable)	Present	Absent
11. m/e 36.4, 55.4 (metastable)	Absent	Present

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[1] Anomalies are discussed in Ring Size section.

Determination of Chain Length

1. $C_nH_{2n+3}S^{+}$	Largest peak in the series gives the chain length (n).
2. $C_nH_{2n+1}^{+}$	Largest peak in the series gives the chain length (n).
3. $C_nH_{2n+1}S^{+}$	Largest peak in the series gives the chain length (n) for C_5 and longer chains.
4. $C_nH_{2n}^{+}$	Largest peak in the series gives the chain length (n) for C_5 and longer chains.
5. m/e 29.5 (metastable)	Determines butyl groups.
6. m/e 42.6 (metastable)	Determines propyl, pentyl, and hexyl groups.

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