TABLE XV

DERIVED THERMOCHEMICAL DATA AT 298.16°K.[a,b]

	2,3-Dithiabutane	3,4-Dithiahexane	4,5-Dithiaoctane
$\Delta Ec°$ (compound)	-662.76 ± 0.17	-973.15 ± 0.19	-1285.05 ± 0.17
$\Delta Hc°$ (compound)	-665.43 ± 0.17	-976.41 ± 0.19	-1288.90 ± 0.17
$\Delta Hc°$ (sulfur)	-143.65 ± 0.05	-143.45 ± 0.07	-143.54 ± 0.07
$\Delta Hf°$, liquid	-14.93 ± 0.20	-28.28 ± 0.24	-40.71 ± 0.24
$\Delta Sf°$, liquid	-55.33	-103.83	-152.60
$\Delta Ff°$, liquid	$+1.57$	$+2.68$	$+4.79$
$\log_{10} Kf$, liquid	-1.15	-1.96	-3.51
$\Delta Hv°$	9.18 ± 0.03[c]	10.86 ± 0.05[c]	12.94 ± 0.10[c]
$\Delta Hf°$, gas	-5.75 ± 0.20	-17.42 ± 0.25	-27.77 ± 0.26
$\Delta Sf°$, gas	-31.13	-77.66	-123.6
$\Delta Ff°$, gas	$+3.53$	$+5.73$	$+9.08$
$\log_{10} Kf$, gas	-2.59	-4.20	-6.66

[a] Reference state for sulfur is S(c, rhombic). [b] Units: ΔEc^0, ΔHc^0, ΔHf^0, ΔFf^0 and ΔHv^0, kcal. mole^{-1}; ΔSf^0, cal. deg.$^{-1}$ mole^{-1}. [c] Estimated accuracy uncertainty.

The only previous thermochemical data for alkane disulfides are the results of Franklin and Lumpkin,[26] who used a static bomb method less adapted to organic sulfur compounds. Their values of −16.4 and −32.5 kcal. mole^{-1} for the heat of formation of liquid 2,3-dithiabutane and 3,4-dithiahexane, respectively, may be compared with the values −14.93 and −28.28 kcal. mole^{-1} from Table XV.

BARTLESVILLE, OKLA.

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[26] J. L. Franklin and H. E. Lumpkin, THIS JOURNAL, **74**, 1023 (1952).

[CONTRIBUTION NO. 70 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES U. S. DEPARTMENT OF THE INTERIOR]

Characteristic Vibrational Frequencies of Organic Sulfur Compounds[1]

BY D. W. SCOTT AND J. P. MCCULLOUGH

RECEIVED JANUARY 27, 1958

Calorimetric and spectroscopic data were used previously to make complete vibrational assignments for 10 organic sulfur compounds that contain only the CH_3S, C_2H_5S, $(CH_3)_2CHS$ and $(CH_3)_3CS$ groups. These assignments were used in calculating values of thermodynamic properties reported in earlier papers. In this paper, regularities found in the spectra of the 10 compounds are discussed. Characteristic fundamental frequencies of one alkyl group attached to sulfur are affected little by the nature of a second attached group. Incomplete vibrational assignments, based on limited spectroscopic data, are given for five other sulfur compounds to illustrate the utility of this correlation of characteristic frequencies with molecular structure.

In the last 10 years, experimental thermodynamic studies of about 35 organic sulfur compounds have been made in this Laboratory as part of American Petroleum Institute Research Project 48A. Complete vibrational assignments were made for many of these compounds and were used in calculating thermodynamic functions at temperatures inaccessible to calorimetric measurements. Significant regularities noted in the fundamental vibrational frequencies of related sulfur compounds will be discussed in this paper.

Vibrational assignments have been reported from this Laboratory for these several ten compounds: methanethiol,[2] 2-thiapropane,[3] 2,3-dithiabutane,[4] 2-thiabutane,[2,5] 3-methyl-2-thiabutane,[6] ethanethiol,[7] 3-thiapentane,[8] 3,4-dithiahexane,[9] 2-propanethiol[10] and 2-methyl-2-propanethiol.[11] The assignments for these compounds form the basis for the present discussion. Details of the assignments and reference to earlier work can be found in the articles cited. All of the assignments were based on good Raman and infrared spectroscopic

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[1] This investigation was part of American Petroleum Institute Research Project 48A on the "Production, Isolation and Purification of Sulfur Compounds and Measurement of Their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

[2] D. W. Scott, H. L. Finke, J. P. McCullough, M. E. Gross, K. D. Williamson, Guy Waddington and H. M. Huffman, THIS JOURNAL, **73**, 261 (1951).

[3] J. P. McCullough, W. N. Hubbard, F. R. Frow, I. A. Hossenlopp and Guy Waddington, *ibid.*, **79**, 561 (1957).

[4] D. W. Scott, H. L. Finke, M. E. Gross, G. B. Guthrie and H. M. Huffman, *ibid.*, **72**, 2424 (1950).

[5] D. W. Scott, J. P. McCullough and Guy Waddington, to be published.

[6] J. P. McCullough, H. L. Finke, J. F. Messerly, R. E. Pennington, I. A. Hossenlopp and Guy Waddington, THIS JOURNAL, **77**, 6119 (1955).

[7] J. P. McCullough, D. W. Scott, H. L. Finke, M. E. Gross, K. D. Williamson, R. E. Pennington, Guy Waddington and H. M. Huffman, *ibid.*, **74**, 2801 (1952).

[8] D. W. Scott, H. L. Finke, W. N. Hubbard, J. P. McCullough, G. D. Oliver, M. E. Gross, C. Katz, K. D. Williamson, Guy Waddington and H. M. Huffman, *ibid.*, **74**, 4656 (1952).

[9] D. W. Scott, H. L. Finke, J. P. McCullough, M. E. Gross, R. E. Pennington and Guy Waddington, *ibid.*, **74**, 2478 (1952).

[10] J. P. McCullough, H. L. Finke, D. W. Scott, M. E. Gross, J. F. Messerly, R. E. Pennington and Guy Waddington, *ibid.*, **76**, 4796 (1954).

[11] J. P. McCullough, D. W. Scott, H. L. Finke, W. N. Hubbard, M. E. Gross, C. Katz, R. E. Pennington, J. F. Messerly and Guy Waddington, *ibid.*, **75**, 1818 (1953).

Table I: Vibrational Assignments, in Cm.$^{-1}$[a]

Group	Descriptive mode	$CH_3{-}SH$[2]	CH_3SCH_3[3]	$CH_3S{-}SCH_3$[4]	$CH_3S{-}C_2H_5$[2,5]	$CH_3S{-}CH(CH_3)_2$[5]	$C_2H_5{-}SH$[7]	$C_2H_5S{-}C_2H_5$[8]	$C_2H_5S{-}SC_2H_5$[8]	$(CH_3)_2{-}CHSH$[10]	$(CH_3)_3{-}CSH$[11]	$CH_3S{-}C(CH_3)_3$[b]	$C_2H_5S{-}CH(CH_3)_2$[c]	$C_2H_5S{-}C(CH_3)_3$[d]	$(CH_3)_2{-}CHS{-}CH{-}(CH_3)_2$[e]	$(CH_3)_2{-}CHS{-}SCH{-}(CH_3)_2$[f]
CH_3S-	CH_3 rock.	976	906 972	954(4)	956	954						953				
	CH_3 rock.	1074	[1000] 1028		1062	1058						..				
	CH_3 sym. bend.	1335	1309 1334	1305(2)	1323	1315						1316				
C_2H_5S-	CH_3 rock.				1042		1049	1047(2)	1029(2)				1043	1020		
	CH_3 rock.				1098		1097	1074(2)	1050(2)				1073	1053		
	CH_3 sym. bend.				1378		1385	1380(2)	1374(2)				1382	1390		
	CH_2 rock.				757		745	738(2)	759(2)				760	786		
	CH_2 wag.				1264		1269	1254(2)	1254(2)				1240	1260		
	CH_2 twist.				1311		1309	1310(2)	1309(2)				1308	..		
	C–C stretch.				973		978	974(2)	967(2)				973	976		
$(CH_3)_2CHS-$	CH_3 rock.					925				929			927		924(2)	920(2)
	CH_3 rock.					(1058)				1063			1058		1060(2)	1047(2)
	CH_3 rock.					1110				1131			1113		1110(2)	1107(2)
	CH_3 rock.					1154				1161			1157		1152(2)	1154(2)
	CH_3 sym. bend.					1364				1368			1363		1365(2)	1360(2)
	CH_3 sym. bend.					1386				1386			(1382)		1380(2)	.....
	CH wag.					1244				1257			1262		1235(2)	1234(2)
	CH wag.					(1315)				1334			(1308)		1312(2)	1307(2)
	C–C stretch.					882				893			882		883(2)	869(2)
	C–C stretch.					1200				1084			1027		1042(2)	(1047)(2)
$(CH_3)_3CS-$	CH_3 rock.										932(2)	935(2)		930(2)		
	CH_3 rock.										965	(953)		(976)		
	CH_3 rock.										1033(2)	1028(2)		(1020)(2)		
	CH_3 rock.										1165	1161		1162		
	CH_3 sym. bend.										1367(2)	1362(2)		1365(2)		
	CH_3 sym. bend.										1391	1389		(1390)		
	C–C stretch.										820	816		816		
	C–C stretch.										1218(2)	1181		1205(2)		
	C–C stretch.											1206				
Skeletal–	C–S–S bend.			239					180							.....
	C–S–S bend.			272					198							.....
	C–S–C bend.		282		216	215		187				..	..	.....	.....	.....
	C–C–S bend.				355	[270]	332	305	323	310	295(2)	..	..	.....	.....	.....
	C–C–S bend.					336		381	360	336		..	..	.....	.....	.....
	C–C–C bend.					427				414	368	..	..	.....	.....	.....
	C–C–C bend.										395(2)		..	.....	.....	.....
	C–S–H bend.	803					870			858	867					
	S–S stretch.			509					507							.....
	C–S stretch.	708	691	689(2)	653	638	660	693(2)	642(2)	624	587	..	678	696	.....	.....
	C–S stretch		741		727	724						723	695	750	.....	.....

[a] Frequencies above 1400 cm.$^{-1}$ have been omitted. Frequencies enclosed in brackets [ ] were estimated; see references indicated by the superscript on the compound formula. Frequencies enclosed in parentheses ( ) have been used more than once. Frequencies followed by (2) are unresolved pairs. Dotted lines indicate an expected but presumably unobserved frequency. [b] Assignment based on data tabulated in the "Catalog of Infrared Spectral Data," American Petroleum Institute Research Project 44, serial no. 1523. [c] *Ibid.*, serial no. 1200. [d] *Ibid.*, serial no. 1464. [e] *Ibid.*, serial no. 1465. [f] *Ibid.*, serial no. 1122.

data and were confirmed by close agreement between calculated and experimental values of both entropy ($S°$) and heat capacity ($C_p°$) in every instance except methanethiol. An accurate value of $S°$ for methanethiol[12] supports the assignment for this substance.

The vibrational assignments for the 10 sulfur compounds listed in the previous paragraph are given in the first 10 columns of Table I. In a few instances these assignments are slight revisions, based on recent spectroscopic work, of those given previously. For substances that have rotational isomers, the assignment for a single isomer is given. Only frequencies below 1400 cm.$^{-1}$ are listed in the table.

In the last five columns of Table I are incomplete vibrational assignments for other sulfur compounds having only CH_3S, C_2H_5S, $(CH_3)_2CHS$ and $(CH_3)_3CS$ groups. For these five compounds only infrared spectra have been reported. The limited assignments are included to support the correlations based on the complete assignments and to illustrate the usefulness of these correlations.

Characteristic Group Frequencies.—Inspection of Table I shows significant regularities in the spectra of related compounds. Frequencies characteristic of the CH_3S, C_2H_5S, $(CH_3)_2CHS$ and $(CH_3)_3CS$ groups are readily apparent and will be discussed in the following. Common descriptive terms will be used for the several modes of molecular vibration. The *skeletal bending* modes are angle-bending vibrations for chains of three heavy atoms. The *skeletal stretching* modes are stretching vibrations of bonds between two heavy atoms. The two *methyl rocking* modes of an X–CH_3 group (X = C or S) are X–C–H bending vibrations in which the CH_3 group as a whole rocks in mutually perpendicular directions. The three *methyl bending* modes of a CH_3 group are H–C–H bending vibrations; one is symmetrical with respect to the CH_3 group and two are unsymmetrical. The *CH_2 rocking, wagging* and *twisting* modes of a CH_2 group are X–C–H bending vibrations. In the rocking and wagging modes, the CH_2 group as a whole rocks in its own plane and wags perpendicular to its plane, respectively. In the twisting mode, the CH_2 group undergoes torsional oscillation about the bisector of the H–C–H angle. The one *CH_2 bending* mode of the CH_2 group is simply an H–C–H bending vibration. The two *C–H wagging* modes of a CH group are X–C–H bending vibrations in which the hydrogen atom wags in two mutually perpendicular directions. The *C–H stretching* modes will not be considered.

The various modes of vibration described in the preceding paragraph are only approximate descriptions of the complicated modes of actual molecular vibrations. Interactions of one simple mode with others may have such pronounced effects that it is difficult to separate, for example, CH_3 or CH_2 rocking modes from C–C or C–S stretching modes. Nevertheless, if the possibility of strong coupling between simple modes is kept in mind, the designations used here provide a convenient system of classification for complex but often unsymmetrical molecules.

The hydrogen deformation frequencies will be discussed first.

CH_3S Group.—As shown in Table I and summarized in Table II, the two methyl rocking modes of this group have frequencies of about 960 and 1060 cm.$^{-1}$. Both frequencies are observed as strong infrared bands and appear in the Raman spectrum, if at all, as lines of weak or medium intensity. The largest deviations from these selected values are in 2-thiapropane and 2,3-dithiabutane, both of which are somewhat atypical. In the spectrum of 2-thiapropane, the two pairs of CH_3 rocking frequencies are split because there are 2 interacting CH_3 groups in the molecule. The four CH_3 rocking frequencies of 2,3-dithiabutane are not split enough to be resolved in the spectra, presumably because the long S–S bond isolates the CH_3 groups, even to the extent of eliminating the splitting found in methanethiol.

TABLE II

SELECTED CHARACTERISTIC FREQUENCIES IN CM.$^{-1}$

Descriptive mode	CH_3S	C_2H_5S	$(CH_3)_2$-CHS	$(CH_3)_3CS$[a]
CH_3 rock.	960	1040	925	935(2)
CH_3 rock.	1060	1075	1060	960
CH_3 rock.			1110	1030(2)
CH_3 rock.			1155	1160
CH_3 sym. bend.	1320	1385	1365	1365(2)
CH_3 sym. bend.			1380	1390
CH_2 rock.		750		
CH_2 wag.		1260		
CH_2 twist.		1310		
CH wag.			1245	
CH wag.			1320	
C–C stretch.		975	880	820
C–C stretch.			1100	1200(2)

[a] Numbers in parentheses indicate accidental degeneracy.

As Sheppard has shown,[13] the symmetrical CH_3 bending frequency of a CH_3 group attached to sulfur is observed consistently at about 1320 cm.$^{-1}$ (Tables I and II). The unsymmetrical CH_3 bending frequencies appear as unresolved bands near 1450 cm.$^{-1}$.

C_2H_5S Group.—Reference to the tables shows that the two CH_3 rocking frequencies of the C_2H_5S group, at about 1040 and 1075 cm.$^{-1}$, are nearly constant and are quite distinct from those of the CH_3S group. Both frequencies are observed in the Raman spectrum but may be missing in the infrared. Again in accord with Sheppard's observations,[13] the symmetrical CH_3 bending frequency when the CH_3 group is attached to a carbon atom is observed at about 1385 cm.$^{-1}$, usually as a strong infrared band and weak Raman line.

The CH_2 rocking and wagging frequencies are located at about 750 and 1260 cm.$^{-1}$, respectively. Both frequencies normally are observed with relatively high intensity in the Raman and infrared spectra.

The location of the CH_2 twisting frequency is uncertain. In Tables I and II, this frequency is shown near 1310 cm.$^{-1}$; it is observed almost al-

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[12] H. Russel, D. W. Osborne and D. M. Yost, THIS JOURNAL, **64**, 165 (1942).

[13] N. Sheppard, *Trans. Faraday Soc.*, **51**, 1465 (1955).

ways as a relatively weak band or line. Hayashi, Shimanouchi and Mizushima[14] have interpreted the frequency at 1311 cm.$^{-1}$ in 2-thiabutane as the overtone of the C–S stretching frequency, 2 × 653 = 1306 cm.$^{-1}$. In some other cases considered in Table I, the frequency near 1310 cm.$^{-1}$ also can be explained as the overtone of a C–S stretching frequency. However, the consistency with which frequencies near 1310 cm.$^{-1}$ are observed and the fact that the C–S stretching overtone does *not* appear in the spectra of methanethiol and 2-thiapropane support the belief that the frequencies near 1310 cm.$^{-1}$ are fundamentals. Unfortunately, the thermodynamic properties are not sensitive enough to frequencies in this region to lend much support to the present assignment of CH_2 twisting frequencies. However, the calorimetric data used for verifying assignments in Table I are accurate enough to suggest that the CH_2 twisting frequency is not as low as the value (about 1110 cm.$^{-1}$) suggested by Hayashi, *et al.*, for 2-thiabutane on the basis of normal coördinate calculations.[14]

The CH_2 bending frequency appears near 1450 cm.$^{-1}$ and often is not resolved from the unsymmetrical CH_3 bending frequency. If they are resolved, the CH_2 bending frequency usually is lower than the unsymmetrical CH_3 bending frequency.

$(CH_3)_2CHS$ Group.—This group has four CH_3 rocking modes with frequencies at about 925, 1060, 1110 and 1155 cm.$^{-1}$. All of these frequencies usually appear with relatively high intensity in the infrared spectrum, although that near 1110 cm.$^{-1}$ may be missing or weak. The strong infrared band at 925 cm.$^{-1}$ may not have a counterpart in the Raman spectrum.

The two symmetrical CH_3 bending frequencies of the $(CH_3)_2CHS$ group appear at about 1365 and 1380 cm.$^{-1}$. The former is observed only as a strong infrared band; the latter appears as a strong infrared band with a weak counterpart in the Raman spectrum.

The two CH wagging frequencies are near 1245 and 1320 cm.$^{-1}$ and appear with moderate intensity in both spectra.

$(CH_3)_3CS$ Group.—This group should exhibit six CH_3 rocking frequencies, but only four are found in the spectra of the one substance containing this group for which complete spectroscopic and calorimetric data are available, 2-methyl-2-propanethiol. However, incomplete spectral data for other compounds having the $(CH_3)_3CS$ group support the conclusion that two of the CH_3 rocking modes are not resolved from two of the other four. The CH_3 rocking frequencies chosen as characteristic of the $(CH_3)_3CS$ group are 935(2), 960, 1030(2) and 1160 cm.$^{-1}$. The frequencies at 935 and 1030 were doubled to give best agreement with the calorimetric data and to be consistent with the assignment of Pitzer and Kilpatrick for the related molecule, isobutane,[15] which has a pair of degenerate methyl rocking modes. The assignment of the value 960 cm.$^{-1}$ to a methyl rocking vibration is uncertain.[11] There are not enough spectral data for the $(CH_3)_3CS$ group to draw conclusions about the activity and intensity of characteristic frequencies.

The three symmetrical CH_3 bending frequencies of the $(CH_3)_3CS$ group are not all resolved. A CH_3 bending frequency near 1365 cm.$^{-1}$ is definitely characteristic of this group. Another frequency near 1390 cm.$^{-1}$ also seems to be characteristic, but it is not necessarily a fundamental.[11]

Characteristic Skeletal Vibrations.—The skeletal bending frequencies are, of course, more characteristic of the entire molecule than of its constituent groups. Nevertheless, some generalities can be pointed out that are reasonable in view of the atomic masses involved in the vibrations. The C–S–S bending frequencies are the lowest fundamentals in the spectra of the sulfur compounds under consideration, exclusive of rarely observed torsional frequencies. In Table I, the C–S–S bending frequencies are in the region 180 to 272 cm.$^{-1}$. The C–S–C bending frequencies are found only slightly higher in the spectra, 187 to 282 cm.$^{-1}$, and the C–C–S bending frequencies are still higher, 270 to 381 cm.$^{-1}$. Higher still are the C–C–C bending frequencies, in the region 368 to 427 cm.$^{-1}$. Although not a skeletal bending frequency as previously defined, the C–S–H bending frequency is included for convenience with the true skeletal frequencies in Table I. This frequency is a prominent feature of the spectra of thiols in the region 800 to 870 cm.$^{-1}$.

The skeletal stretching modes may be divided into three types—the S–S, C–S and C–C stretching modes. The S–S stretching frequencies in disulfides appear at about 500 cm.$^{-1}$. The C–S stretching frequency is almost always a prominent spectral feature of organic sulfur compounds. A single C–S stretching frequency is characteristic of thiols; this frequency shifts from 708 to 587 cm.$^{-1}$ as the size of the alkyl group increases from methyl to *t*-butyl. The symmetrical disulfides show an unresolved pair of C–S stretching frequencies in the range 640 to 700 cm.$^{-1}$. The sulfides exhibit two C–S stretching frequencies—one in the range 640 to 695 cm.$^{-1}$ and the other in the range 695 to 750 cm.$^{-1}$

The C_2H_5S group has one C–C stretching frequency near 975 cm.$^{-1}$.

The $(CH_3)_2CHS$ group has two C–C stretching modes. A frequency near 880 cm.$^{-1}$ is characteristic of both the Raman and infrared spectra of compounds containing this group and is assigned as a C–C stretching frequency. The assignment of the other C–C stretching frequency is much less certain, but a value near 1100 cm.$^{-1}$ is likely.

The $(CH_3)_3CS$ group has three C–C stretching modes, but two of these are doubly degenerate in isobutane[15] and possibly are not resolved in *less* symmetrical sulfur compounds, just as they are not resolved in 2-methyl-2-propanethiol.[11] A strong Raman line and moderately intense infrared band near 820 cm.$^{-1}$ is selected as the non-degenerate C–C stretching frequency. The degenerate or slightly split frequency is observed near 1200 cm.$^{-1}$.

If the substance has rotational isomers of com-

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(14) M. Hayashi, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **26**, 608 (1957).

(15) K. S. Pitzer and J. E. Kilpatrick, *Chem. Revs.*, **39**, 435 (1946).

parable energy, lower skeletal frequencies of more than one isomer appear in the spectra.

Conclusions

This correlation of the vibrational spectra of 15 organic sulfur compounds shows that characteristic frequencies appear with excellent consistency within relatively narrow regions of the spectra. The variation in characteristic frequency from molecule to molecule is less than in related hydrocarbons because of the isolating effect of the heavy sulfur atom and the greater length of C–S bonds as compared to C–C bonds. In effect, the vibrational modes of one group attached to a sulfur atom are affected only slightly by the nature of the second attached group, whether the latter be H or $(CH_3)_3C$.

The present assignment of particular characteristic frequencies to specific molecular motions may be disputed. With a few exceptions, however, the characteristic fundamental frequencies are located reliably, regardless of the vibrational mode to which they are assigned.

The principal uncertainties in the correlation are the locations of (1) the CH_2 twisting frequency of the C_2H_5S group, (2) the higher of the two C–C stretching frequencies of the $(CH_3)_2CHS$ group and (3) the CH_3 rocking frequency of the $(CH_3)_3CS$ group that corresponds to the a_2 rocking mode of isobutane[15] (assigned near 960 cm.$^{-1}$ in Tables I and II). Additional spectroscopic studies, particularly of appropriate deuterated species, are needed to resolve these uncertainties.

BARTLESVILLE, OKLAHOMA

[CONTRIBUTION FROM THE WATSON LABORATORIES OF INTERNATIONAL BUSINESS MACHINES]

Reactions of the Group VB Pentoxides with Alkali Oxides and Carbonates. IX. A DTA Study of Alkali Metal Carbonates

BY ARNOLD REISMAN

RECEIVED JANUARY 14, 1958

The thermal behavior of alkali metal carbonates has been investigated by means of differential thermal analysis. In the absence of decomposition products, the freezing points of Li_2CO_3, Na_2CO_3, K_2CO_3, Rb_2CO_3 and Cs_2CO_3 were established at 720 ± 1°, 854 ± 1°, 901 ± 1°, 873 ± 1° and 792 ± 1°, respectively. Heat anomalies were observed in Li_2CO_3 at 410°, in K_2CO_3 at 422° and in Rb_2CO_3 at 303°. Unless the analyses were performed in a CO_2 atmosphere, additional heat effects occurred in Li_2CO_3 at 350° and in K_2CO_3 at 367 and 253°. The data obtained for K_2CO_3, in conjunction with other information, negate the published results for the solid system Na_2CO_3–K_2CO_3. The present studies provide a means for examining the binary systems alkali oxide–alkali carbonate.

Introduction

A number of papers have emanated from this Laboratory under the general heading, "Reactions of the Group VB Pentoxides with Alkali Oxides and Carbonates." It has been noted, during the course of these studies, that as little appeared to be known about the fusion and polymorphic behavior of alkali metal carbonates as about the more esoteric VB pentoxides.

Neither the Handbook of Chemistry and Physics nor the Smithsonian Tables provide much information about solid state transformations in the alkali compounds in question. Similarly, the published phase diagrams involving the carbonates, except in one instance,[1] give no pertinent information. In addition to the lack of transition data there appears to be some ambiguity as to the thermal stability of Rb_2CO_3 and Cs_2CO_3, and the melting point of Li_2CO_3. Studies of the alkali carbonates are complicated by their great reactivity, even at low temperatures, and the varying degrees of dissociation they undergo at elevated temperatures, both phenomena resulting in contamination of specimens. These factors make X-ray examination exceedingly difficult.

The above, coupled with the fact that a recent study of Na_2CO_3[2] indicated that the existing literature[1] is in error, made an examination of the alkali carbonates appear worthwhile.

Experimental Procedure

1. **DTA.**—The apparatus designed for high gain studies of phase transformations has been described previously.[2-4] It was used without modification except that an atmosphere of CO_2 was maintained, when required, during heating and cooling experiments. In most studies a sensitivity of 5 μv./inch was employed. The sensitivity was decreased to 10 μv./inch for experiments involving Li_2CO_3. Heating and cooling rates of 2°/minute or less were employed in all analyses.

2. **Reagents.**—All of the reagents were of the highest purity available, having minimum assays of 99.9%. Prior to the recording of their thermal behavior, the carbonates were dried to constant weight in a CO_2 atmosphere. All samples were then weighed and loaded into 1 cc. gold–20% palladium crucibles. Final weights were obtained after each experiment to ensure that the results were not representative of partially decomposed carbonates. It was found that under the conditions employed, *viz.*, a CO_2 atmosphere, short time periods of the specimens in the molten state, and minimal temperature elevation above their melting points, the weight losses never exceeded 0.5 mg. in a 0.5-g. sample. All samples were melted before cooling and heating curves were recorded, in order to increase the crystallinity of the compounds.

Discussion of Experimental Results

Before continuing, it is important to consider the applicability of the method employed. A thermal anomaly in a differential thermogram, as repre-

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(1) S. Makarov and M. P. Shulgina, *Bull. Acad. Sc. U.R.S.S.*, **5**, 691 (1940).

(2) A. Reisman, F. Holtzberg and E. Banks, THIS JOURNAL, **80**, 37 (1958).

(3) F. Holtzberg, A. Reisman, M. Berry and M. Berkenblit, *ibid.*, **79**, 2039 (1957).

(4) A. Reisman and F. Banks, *ibid.*, **80**, 1877 (1958).