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

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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).

sented by a differential peak, will in all cases be indicative of a phase change. In the event that no latent heat accompanies a phase change, the method of DTA will often fail to reveal a change of state providing that the experiments are performed under pseudo equilibrium conditions, and depending on the nature of the transformation. Pseudo equilibrium is more nearly approximated the closer the rate of temperature variation as a function of time approaches zero. Thus, one should rely not on rapidly varying temperatures to produce large apparent heat effects, as is almost universally done, but rather on amplification of differential signals generated at low values of dT/dt as compared to τ, the time constant of the furnace. Consequently, if one finds the limiting temperature value of a thermal anomaly by performing experiments at high gains and different rates of temperature variation, the closest approximation to equilibrium conditions in an essentially non-equilibrium experiment will be achieved. Furthermore the use of high sensitivities and small variations of temperature/unit time will completely obviate the difficulties experienced by many investigators insofar as slope of the differential curve is concerned.

If a phase transformation is suspended, or if the specimens are highly strained, DTA may either fail to reveal the phase change because the heat effect is not spontaneous, or indicate an erroneous transformation temperature because the heat effect is spontaneous at the wrong temperature. In any event the method remains a powerful tool, because except in the case of higher order or suspended transformations not even X-ray analysis can provide as much qualitative and quantitative information. As concerns higher order or suspended transformations, even X-ray techniques often can prove unsuccessful.

In the present investigation, adjunct X-ray analysis could not be obtained because of the great reactivity of the materials with transparent sample containers. Consequently, until such time as X-ray studies can be made, the DTA results reported are indicative only of the minimum number of changes of state.

Figure 1a shows a typical cooling thermogram for Li_2CO_3. Although the traces were recorded on a 10″ scale with a sensitivity of 10 μv./inch, in an effort to conserve space only the pertinent portions of the graph are reproduced. The freezing point of Li_2CO_3 was found to be 720 ± 1° on the basis of six cooling experiments performed at rates varying from 0.1 to 1°/minute in a CO_2 atmosphere. This is in sharp contrast to the value of 618° reported in the Handbook of Chemistry and Physics, but in good agreement with other published values.[5] Without CO_2, freezing points as low as 714° were observed, depending upon the length of time the sample was molten prior to freezing. Since seeding did not change the results, and since, within the limits of detectability, melting point experiments gave identical results, there was no evidence of any tendency for the melts to supercool. One transition was observed in Li_2CO_3, at 410 ± 3°.

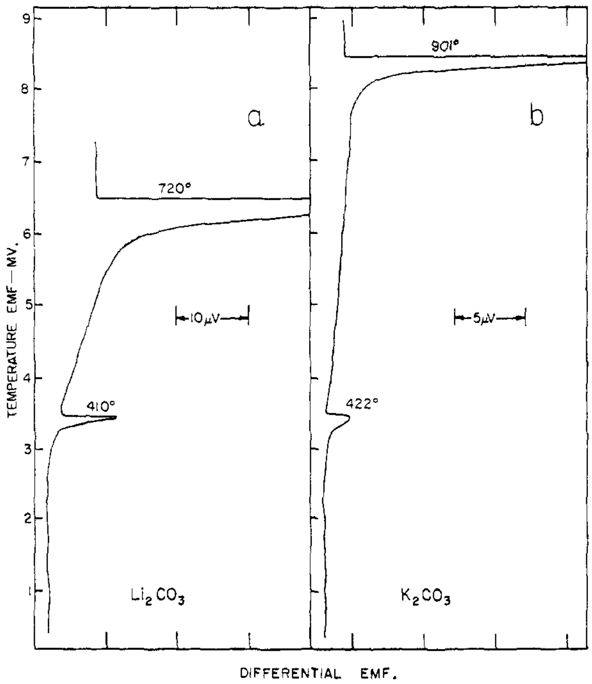

Fig. 1.—DTA traces of Li_2CO_3 and K_2CO_3.

In the absence of CO_2 an additional heat effect appeared at 350°, its order of magnitude being approximately one fourth that of the 410° peak. As the 410° transition was not affected by the 350° heat effect, the latter can be attributed to either a phase transformation in Li_2O, or more probably to the eutectic solidification in the high carbonate region of the system Li_2O–Li_2CO_3.

In 1940 Makarov and Shulgina,[1] on the basis of DTA studies, reported that K_2CO_3 exists in four polymorphic forms with transitions at approximately 250, 430 and 625°. The DTA traces obtained in the present investigation indicate the existence of only one phase transformation, at 422 ± 2°, Fig. 1b. If, however, the experiments were performed under atmospheric conditions, additional transformations appeared at 253 and 367°, Fig. 3. Never has any sign of a transition been observed in the vicinity of 600°. Since, as has been demonstrated,[2] the data reported for Na_2CO_3[1] are also in error, it would appear that the previous investigators were studying materials which were contaminated with oxides. Consequently, the solid system K_2CO_3–Na_2CO_3 as constructed by them must be completely in error, because all of the postulated phase regions depend on the interactions between four K_2CO_3 and four Na_2CO_3 phases. It is of interest that when partially decomposed K_2CO_3 is permitted to pick up moisture from the air, the transitions at 253 and 367° disappear, indicating a conversion of K_2O to KOH. If we assume that the 367° transition is the carbonate rich eutectic in the system K_2O–K_2CO_3, then it is probable that the 253° heat effect corresponds to a phase change in K_2O. It should be noted that the 422° transition in K_2CO_3 is unaffected by the oxide impurity. In order to obtain some preliminary information about the system K_2CO_3–Na_2CO_3, mixtures of K_2CO_3 and Na_2CO_3 were melted in gold–

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(5) E. Levin, H. F. McMurdie and F. P. Hall, "Phase Diagrams for Ceramists," The American Ceramics Society, Inc., 1956, Figs. 723–4.

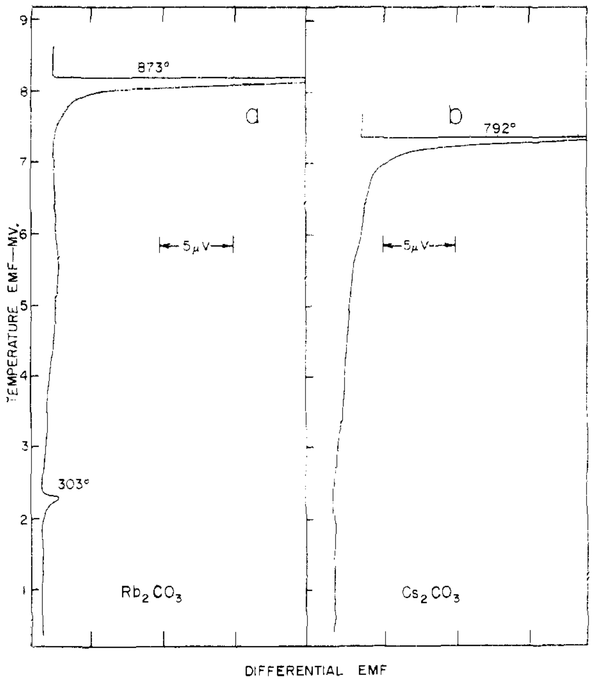

Fig. 2.—DTA traces of Rb_2CO_3 and Cs_2CO_3.

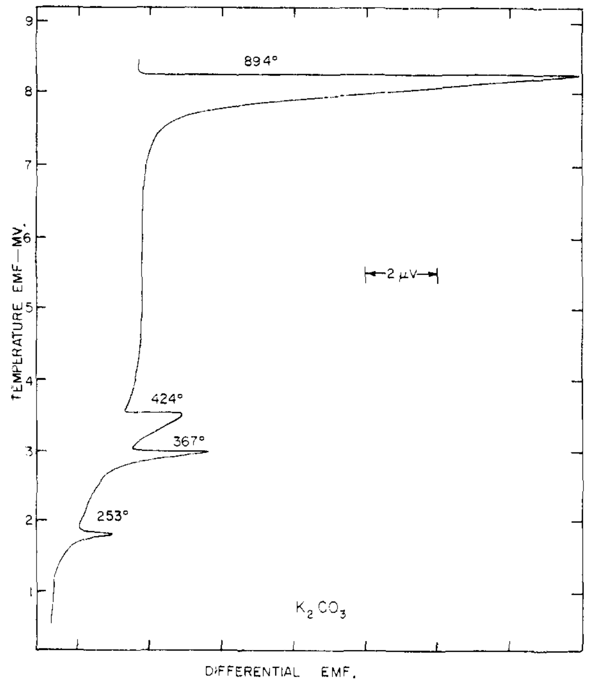

Fig. 3.—DTA trace of K_2CO_3 in absence of a CO_2 atmosphere.

20% palladium crucibles and quenched. The samples were ground and then annealed at 850° for 24 hours in the DTA apparatus. Cooling curve experiments showed only one phase transformation for both 97.5 and 95 mole % K_2CO_3 compositions, at 401 and 378°, respectively, which implies approximately a 9° decrease in the K_2CO_3 transition temperature per mole % Na_2CO_3. Furthermore, since no other transformation was observed, the indications are that at least one of the two Na_2CO_3 phase transformations is interrupted in the interior of the diagram. The freezing point of K_2CO_3 on the basis of twelve determinations was found to be 901 ± 1° with no tendency toward undercooling. In the absence of a CO_2 atmosphere, the freezing point was depressed to between 891 and 896°, depending on the length of time the material was molten, and consequently on the amount of oxide formed. These latter values approximate those normally accepted. The freezing point of Na_2CO_3 on the basis of three determinations was found to be 854 ± 1°.

The thermal behavior of Rb_2CO_3 is shown in Fig. 2a. The freezing point of this compound was established at 873 ± 1° on the basis of six determinations. This value is in marked disagreement with the recorded value of 837°. The constancy of weight of the samples precluded the possibility of decomposition, and a phase transformation was observed at 303 ± 2°. In the absence of CO_2 the freezing point was lowered to approximately 864°, but no new heat effects were observed, indicating that the interaction in the system Rb_2O–Rb_2CO_3 is of the solid solution variety. Furthermore, the results obtained in air do not corroborate the occurrence of a rapid decomposition. A cooling curve for Cs_2CO_3 is shown in Fig. 2b. The freezing point of this compound was found to be 792 ± 1° and no indication of a decomposition at 610° was observed in air, although the freezing point was depressed up to 15°. No additional heat effects were observed in Cs_2CO_3 in the temperature range surveyed, even at sensitivities of 1 μv./inch.

The relative heats of fusion for the carbonates are in order of decreasing molecular weights. Aside from Li_2CO_3, the latent heats of the other compounds are all within the same order of magnitude. The results of this investigation do not agree qualitatively with the published information concerning the dissociation pressures of the carbonates, since in the case of Li_2CO_3, Rb_2CO_3 and Cs_2CO_3 they appear to be less, and in the case of K_2CO_3 and Na_2CO_3 they appear to be more. As the dissociations are more in keeping with a non-reversible steady state, rather than a reversible equilibrium process, it is apparent that the values obtained will be critically dependent on the geometry of the equipment employed.

K_2CO_3, Rb_2CO_3 and Cs_2CO_3 show a decrease in freezing point with increasing molecular weight, and could conceivably be isomorphous with one another below their respective melting points. Li_2CO_3 and Na_2CO_3 do not however fall into place, which is to be expected for Li_2CO_3 but not for Na_2CO_3.

An interesting sidelight of this study is that it provides a means for investigating the systems alkali oxide–alkali carbonate, for the same alkali metal of course, without any particular experimental difficulty. The pure carbonates can be held at their melting points in a stream of air for varying lengths of time and then taken through cooling and subsequent heating cycles in a CO_2 atmosphere. The carbonate–oxide composition could then be ascertained readily at the conclusion of the experiment.

A re-evaluation of the system Na_2CO_3–K_2CO_3 is presently under way and will be reported at a later date.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Surface Tension of Synthetic High Polymer Solutions[1]

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The equilibrium value and the rate of approach to equilibrium of the surface tension of relatively dilute solutions of a number of fractions of polystyrene in tetralin and polyvinyl alcohol in water have been measured by means of a pendant drop apparatus. Certain modifications of the apparatus allow us to study polymer solution drops without visible changes for periods exceeding 24 hours. As the molecular weight of the polystyrene fractions decreases the surface tension increment changes sign, as expected from theory, due to an entropy effect. This suggests in turn that molecular weight estimates obtained from surface tension measurements are sensitive to the low molecular weight tail of the molecular weight distribution curve. Certain effects due to the configuration of the polymer at the interface are noted. Both the polystyrene and the polyvinyl alcohol solutions exhibit a dependence of the surface tension on the age of the solution drop surface. The magnitude of this relaxation time and some factors which affect it are discussed.

Introduction

Previous measurements[5–7] of the surface tension (S.T.) of solutions of synthetic macromolecules have been carried out on aqueous solutions of surface active high polymers whose monomers are themselves surface active.

A recently developed statistical mechanical theory[8] of the S.T. increment, $\Delta\gamma$ ($\Delta\gamma$ = S.T. of the solution − S.T. of the solvent), of a dilute solution of a linear high polymer leads us to expect that $\Delta\gamma$ could be positive as well as negative. For a sufficiently dilute solution $\Delta\gamma$ is given by the sum of a negative term describing the tendency of the polymer molecule to be adsorbed at the solution interface due to attractive forces between the interface and the polymer segments and a positive activity term. The latter results from the larger configurational entropy available to a chain present in the bulk of the solution over that present in the interface region. Thus[8]

$$\frac{\Delta\gamma}{c} = \left(\frac{kT}{A_0}\right)\left[\frac{\zeta\nu}{t} - K_{\text{ads}}\right] + O(c) \qquad (1)$$

where t is the degree of polymerization of the chain polymer, ν the average number of anchor segments per chain deposited in the interface, K_{ads} is in effect the surface adsorption isotherm equilibrium constant, A_0 is the ideal area occupied by a deposited anchor segment and ζ is a proportionality constant depending on the units of c if the latter is expressed in weight of polymer per unit volume of solution. In particular if the polymer chain is Gaussianly coiled, K_{ads} is proportional to a weakly increasing function of the molecular weight of the polymer, M, $f(M)$ (this increase is less than linear in M) and ν is proportional to $M^{1/2}$ so that at constant temperature

$$\frac{\Delta\gamma}{c} = AM^{-1/2} - Bf(M) + O(c) \qquad (2)$$

with A and B constants.

$\Delta\gamma$ is thus negative for a polymer–solvent system for which the term due to adsorption predominates. Such would be expected to be the case for a system consisting of a polymer with a highly lyophobic carbon backbone chain to which are regularly attached lyophilic functional groups particularly if the monomer segments are themselves surface active. This appears to be the case with the aqueous solutions of polyethylene glycols and the polyvinyl alcohol solutions studied by us. If on the other hand the attractive energetic interactions between the solution interface and the polymer segments are sufficiently weak, one expects that, although very high molecular weight fractions would possibly still be surface active (since adsorption is favored by large values of M under ideal conditions),[8] the entropy effect giving rise to the positive activity term would make $\Delta\gamma$ positive below a certain value of M.

In order to observe this effect we chose to investigate the S.T. of fractions of polystyrene (PSt.), a typical hydrocarbon polymer, in tetralin a "good" hydrocarbon, non-aqueous solvent. Tetralin was chosen as the solvent because it has a relatively low vapor pressure at 25° and because it is a relatively "good" (in the sense of polymer solution theory) solvent for PSt. thus decreasing the tendency of the PSt. molecules to be adsorbed at the interface.[8] Styrene monomer in tetralin is surface active. Tentatively this is thought by us to be due to the double bond present in the monomer but absent in the polymer.

For the sake of comparison, we measured also the S.T. of two fractions of polyvinyl alcohol (PVA) in water in the same concentration range as used for the PSt.–tetralin. PVA in water was expected to be moderately surface active. The hydrocarbon backbone of PVA is hydrophobic while the hydroxyl groups are hydrophilic; more-

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[1] Supported in part by the Office of Ordnance Research, U. S. Army.

[2] Presented in part at the 132nd meeting of the American Chemical Society, New York City, September, 1957.

[3] Bell Telephone Laboratories, Murray Hill, N. J.

[4] Based on the Master's Thesis of S. Al-Madfai, University of Southern California.

[5] A. Couper and D. D. Eley, *J. Polymer Sci.*, **3**, 345 (1948).

[6] A. Katchalsky and I. Miller, *J. Phys. Chem.*, **55**, 1182 (1951).

[7] C. Capitani and G. Righi, *Comp. rend.*, 27° Congr. intern. chim. ind. Bruxelles 1954, 3; *Industrie chim. belge*, **20**, Spec. No. 691, 695 (1955).

[8] H. L. Frisch and R. Simha, *J. Chem. Phys.*, **27**, 702 (1957).