Adiabatic Calorimetry of Organic Salts Tetra-n-hexylammonium Perchlorate

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We have measured the heat capacity of a zone refined sample of tetra-n-hexylammonium perchlorate (99.94 % pure, by analysis of the fusion curve). Values of the transition temperatures, enthalpies and entropies are: fusion 379.18 K, 16 350 J mol⁻¹, 43.10 J K⁻¹ mol⁻¹; transition (1) 367.51, 2658, 7.24; transition (2) 355.91, 5839, 16.42; transition (3) 333.57, 22 990, 68.93. We interpret fusion and transition (3) as being due, respectively, to ionic melting (break down of the lattice) and "melting" of the hexyl groups. Transitions (1) and (2) are explained by re-orientation of the perchlorate anions.

The melting points of quaternary ammonium salts are usually rather low, when compared with most ionic materials. This property has led to their investigation as possible media for organic reactions,¹ especially those involving materials unstable at elevated temperatures. The low fusion temperatures, which are easily accessible, have also encouraged study of the physico-chemical properties of these materials,²⁻⁴ particularly from the viewpoint of their fusion mechanisms.⁵ For these purposes salts with very poorly nucleophilic anions (ClO₄⁻, BF₄⁻) and consequent chemical stability in the melt, are of greatest importance.

Tetra-n-hexylammonium perchlorate, $(C_6H_{13})_4NClO_4$, although not the lowest melting of these materials, also shows solid state polymorphism. One of us (J. E. G.) has observed three phase transitions by microscopic and differential thermal techniques,⁶ but was unable to investigate them fully. Since then, Janz and co-workers have included this material in a study of several quaternary ammonium salts, using dilatometry, differential scanning calorimetry, and other techniques in an attempt to understand the thermodynamics of the fusion process.³

A precise determination of the heat capacity of this material, together with the enthalpy and entropy increments associated with the transitions, would provide a basis for a better understanding of these processes. In addition, we were curious as to the comparison of the adiabatic equilibrium results with those obtained by differential scanning calorimetry. This latter technique is in widespread use, yet its limitations are not universally understood. Tetrahexylammonium perchlorate is particularly suitable for this investigation as it is very stable and may be zone refined easily. We were able to achieve relatively high purity (using zone refining and calorimetric techniques) which has not been done in previous work with molten quaternary ammonium salts.

EXPERIMENTAL

MATERIAL

The sample of tetra-n-hexylammonium perchlorate was prepared by the reaction of the iodide with perchloric acid in aqueous ethanol solution, followed by two re-precipitations in

J. T. S. ANDREWS AND J. E. GORDON

the presence of excess perchloric acid. The material was recrystallized once from ethanol+ water and twice from ethyl acetate+diethyl ether and then was dried thoroughly under vacuum. The product contained less than 10 p.p.m. of iodine (the analysis was performed by Galbraith Laboratories, Knoxville, Tenn.). The fine white crystals were zone refined in evacuated Pyrex tubes until all solid zones were singly crystalline (after about 100 passes). The sample was loaded into the calorimeter by fusion through a Pyrex frit under vacuum, and the calorimeter sealed (gold gasket/knife edge) under a small pressure of helium (to assist in the attainment of equilibrium).

CALORIMETRY

A silver calorimeter fitted with a screw closure and an adiabatic vacuum thermostat were employed in the heat capacity measurements. Both the calorimeter and the thermostat were very similar to apparatus described by Westrum,⁷ except that four channels of automatic control were employed (one for each of the top, middle, and bottom portions of the adiabatic shield, and one for the guard shield which surrounded the adiabatic shield), and that an automatic a.c. resistance bridge was used for the temperature measurements. A full description of the apparatus will be presented elsewhere. All measurements of mass, temperature,⁸ and electrical energy were refered to calibrations performed by the National Bureau of Standards. The results of measurements on a standard sample of synthetic sapphire ⁸ indicate an overall accuracy of about 0.1 %, while the experimental precision is somewhat better than this.

RESULTS

The experimental heat capacity measurements are presented in table 1. These values are expressed on a molal basis (sample mass *in vacuo* 39.7329 g, $C_{24}H_{52}NClO_4 = 454.1373$ g mol⁻¹, density 0.913 g ml⁻¹³) taking the ice point as 273.15 K. The results have been corrected for "curvature", and for the (small) differences in addenda (helium, gold) to the calorimeter when run empty and with sample. These data are illustrated in fig. 1. No difficulties were encountered during the measurements, except that very long equilibration times were encountered in the transition regions. In fusion, for example, equilibrium was reached only two to three days after an energy addition. Equilibration times in crystal I were also long (about half a day).

The purity of the sample was determined by "fractional fusion" (table 2).⁸ The slope of a plot of the reciprocal of the fraction melted against the melting temperature gave a sample purity of 99.94 %.

Table 3 summarizes the enthalpy determinations for the transition regions. Transition enthalpies and entropies were obtained by integrating the difference between the experimental heat capacity curves and a "lattice" obtained by judicious extrapolation of the heat capacity observed above and below the transition temperatures.

The lowest temperature transition (3) differed from the others in that several weeks were required to obtain the equilibrium form after cooling through the transition (shown both by positive temperature drifts and by the spread of the transition energy values). This corresponds to the difficulty reported by Janz *et al.* for tetra-n-amyl-ammonium thiocyanate.² We encountered no difficulty with the other transitions reported here, but it should be remembered that our cooling rates were less than those used by Janz. The transition enthalpy reported for transition (3), accordingly, is that observed after the sample had remained below the transition for several weeks. The other values in table 3 reflect lesser equilibration times.

DISCUSSION

The fusion thermodynamics of several quaternary ammonium salts (including tetrahexylammonium perchlorate) have been reported by Janz and his associates.³

ADIABATIC CALORIMETRY OF ORGANIC SALTS

These workers used differential scanning calorimetry and assigned uncertainties of ± 0.5 K to the reported transition temperatures and ± 3 % to the transition enthalpies. Table 4 reproduces their reported values together with those found by adiabatic calorimetry in this research. The two sets of values are not entirely consistent and those temperatures found in the equilibrium measurements are lower. We suggest that this discrepancy is to be expected because of the sluggish transitions which we observed in this material. Apparently the elevated scanning calorimetric temperatures are the result of overheating. Differences in sample purity may also account for these discrepancies.

TRANSITION (3) AND FUSION

Janz et al.² have suggested that the melting of quaternary ammonium salts may be considered as two processes which are essentially separate. They are positional melting, or break up of the crystal lattice which should be comparable to the melting of the alkali halides, and configurational melting of the alkyl chains attached to the ammonium ion which should be comparable to the melting of the n-paraffins. Further, these authors suggest that the entropy change for this configurational melting should be calculable as $R \ln \Omega$, where Ω is the number of configurations available to

TABLE	1.—Experimental	HEAT	CAPACITY	DETERMINATIONS	OF	TETRA-n-HEXYLAMMONIUM
PERCHLORATE ^{<i>a,b.</i>}						

T/K	Ср/ J mol ⁻¹ К ⁻¹	T/K	$C_{p}/$ J mol ⁻¹ K ⁻¹	T/K	С _Р / J mol ⁻¹ К ⁻¹	T/K	$C_p/$ J mol ⁻¹ K ⁻¹
s	eries I	se	ries III	355.91	8.892E5	ΔE	I run C
306.98	777.0	357.68	1031	356.22	3374	ΔE	I _f B
314.08	802.5	359.24	972.3	357.34	1028	380.66	987.0
323.87	855.7	360.97	976.4	358.99	967.1		niaa V/I
331.11	1716	362.83	984.3	360.67	971.0	se	ries vi
335.48	2795	364.68	994.2			369.23	904.1
341.44	928.7	366.51	1015	S	eries V	370.16	896.4
349.69	964.4	367.51	1.397E4	300.52	752.6	371.08	888.8
355.75	2427	368.56	954.7	304.35	766.6	sei	ies VII
361.74	977.3	370.49	906.0	308.28	781.9	ΔE	le C
369.01	1317	372.44	907.1	312.31	798.5		
375.61	1244	374.39	915.8	316.29	816.0	ser	ies VIII
379.07	7.527E4	376.32	944.4	320.21	835.4	ΔE	l run D
382.17	1454	377.79	1074	324.14	856.2	ΔE	I ₃ A
		L	$\Delta H_{\rm f}$ A	328.07	879.5	ΔE	I run E
S	eries II	380.12	1082	331.79	1372	ΔE	l ₂ B
374.40	924.2			333.57	5.931E5	ΔE	l run F
377.07	1057	se	eries IV	333.58	2.974E5	ΔE	I ₁ B
378.67	4643	339.87	917.9	333.69	3.478E4	ΔE	I run G
379.05	3.549E4	341.52	925.7	335.54	1378	ΔE	$I_{\rm f} D$
379.12	8.674E4	343.30	934.7	338.28	916.0	382.22	988.9
379.15	1.592E5	345.21	952.2	340.23	919.8	se	ries IX
379.17	1.506E5	347.11	954.9	Δ	H run A	٨F	I. B
379.31	6916	349.01	962.4	354.68	996.1	ΛF	
380.47	986.2	350.88	973.6	ΔI	H ₂ A	$\overline{\Lambda F}$	Î. Ĉ
382.52	989.1	352.75	986.3	360.44	972.4		
384.58	992.5	354.50	1002	Δ	4 run B	se	ries X
386.62	995.5	355.61	3592	ΔI	<i>H</i> ₁ A	ΔH	I ₃ C

^a A, B, C, etc. are the identification of the enthalpy determinations; ^b temperature scale, I.P.T.S., 1948. ⁸

J. T. S. ANDREWS AND J. E. GORDON

the chains through gauche-trans kinking (a "kink-block" process).⁹ For tetra-namyl- and tetra-n-hexyl-ammonium ions, respectively, these authors calculated the configurational entropy changes to be about 71 and 96 J K⁻¹ mol⁻¹. The experimental results for tetra-n-amylammonium thiocyanate agreed well with this prediction.

It seems likely, however, that the two processes are intermixed for tetrahexylammonium perchlorate. The melting entropy, $43.10 \text{ J K}^{-1} \text{ mol}^{-1}$, is considerably greater than that found for alkali halides (for example, $25 \text{ J K}^{-1} \text{ mol}^{-1}$ for KBr),¹⁰ whilst the entropy of transition (3) (68.93 J K⁻¹ mol⁻¹) is less than that predicted by the "kink-block" model, 96 J K⁻¹ mol⁻¹. The sum of the experimental entropies for fusion and transition (3) (112.03 J K⁻¹ mol⁻¹) is, however, close to the sum of



Fig. 1.—Heat capacity of tetra-n-hexylammonium perchlorate. A, 333.57; B, 355.91; C, 367.51; D, 379.18.

TABLE 2.—FRACTIONAI	. MELTING OF TET	RA-n-HEXYLAMMONIUM	PERCHLORATE "
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T/K	$C_p/J \text{ mol}^{-1} \text{ K}^{-1}$	$\Delta T/K$	$\Sigma \Delta H/J \text{ mol}^{-1}$	1 <i>\f</i>	$T_{\rm final}/{ m K}$
378.67	4643	0.670	2 920	5.59	379.01
379.05	3.549E4	0.095	6 206	2.63	379.10
379.12	8.674E4	0.039	9 567	1.71	379.14
379.15	1.592E5	0.021	12 954	1.26	379.16
37 9 .17	1.506E5	0.011	14 603	1.12	379.17
	triple poi	nt of sampl	e	1.00	379.177
	triple poi	naterial	0.00	379.219	
	mole frac	tion of imp	urity	0.0006	

a data from fusion series II

source	no. of runs	<i>T</i> ./K	TalK	$H_{T_2} - H_{T_1}$	$H_{381} - H_{371}/$
fusion	not of runs	- 1/AC	12/10	5 1101 -	5 1101 -
IUSIOII	3	372 22	385 10	20 601	26 140 a
1	9	373.00	303.19	20 001	20140°
ш	5	373.00	381.08	24 070	25 401 *
v	3	371.41	381.60	25 457	25 572
vii	1	371.41	381.02	25 091	25 501
VIII	2	371.30	381.10	25 001	25 577
* * * * *	-	571,52	501.19	2J 470	25 573 LAB
				lattice	23 374 <u>+</u> 4 °
				ΛH_{c}	16 349
				Шı	10.549
transition (1)					
					$H_{371} - H_{361} / J \text{ mol}^{-1}$
Ι	2	357.72	372.26	16 422	12 090 a
III	6	361.90	371.47	11 693	12 145 a
V	2	361.37	371.41	12 220	12 211
VIII	2	359.44	371.30	14 006	12 205
IX	1	366.47	371.10	6 859	12 198
				average	$12205+8^{b}$
				lattice	9 547
				ΔH_1	2 658
transition (2)					
transition (2)					$H_{361} - H_{349}$
т	2	252 75	265.76	17.570	J moi 1
	2	353.75	305.70	1/5/2	1/516
IV V	2	351.82	359.84	13 392	17 262 4
VIII	3	354.18	361.37	12 819	17 524
	1	355.10	359.43	9 993	17 515
IA	1	352.17	339.30	12 982	17 520
				average	$1/519\pm4^{\circ}$
				lattice	11 680
				ΔH_2	5 839
transition (3)					
					$H_{339} - H_{325}$ J mol ⁻¹
I	3	328.44	337.26	30 612	35 20 5 c
v	7	326.12	339.26	34 196	34 931 c
VIII	1	327.56	339.36	33 425	35 324
IX	1	323.03	338.30	36 169	35 130 c
Х	1	323.02	338.33	36 139	35 060 c
XI	1	325.36	340.47	36 205	35 165 c
				value	35 324
				lattice	12 332
				ΔH_3	22 992

TABLE 3.—ENTHALPY INCREMENTS OF FUSION AND TRANSITION OF TETRA-n-HEXYLAMMONIUM PERCHLORATE

^a Excluded from the average as drift correction uncertain; ^b precision index is twice the standard deviation of the mean; ^c excluded because of non-equilibrium behaviour.

that predicted by the two models $(121 \text{ J K}^{-1} \text{ mol}^{-1})$. We suggest that the configurational entropy is acquired in two steps : the greater portion in transition (3) (68.93 J K⁻¹ mol⁻¹), and most of the remainder in fusion. The alkyl chains are probably extended and overlapping in the low temperature phase,¹¹ and some configurations of the kinked chains may be unobtainable until the lattice breaks up; the difference between the observed entropy sum for fusion and transition (3) and that predicted by the models may be due to the maintenance of some structure in the melt immediately above fusion.

TABLE 4.—TRANSITION PARAMETERS FOR TETRA-n-HEXYLAMMONIUM PERCHLORATE ^a

		this work	ref. (3)
fusion	$T_{\rm f}/{ m K}$	379.18	383
	$\Delta H_{\rm f}/{\rm J}~{\rm mol}^{-1}$	16 350	18 000
	$\Delta S_{\rm f}/{ m J}~{ m mol}^{-1}~{ m K}^{-1}$	43.10	48
transition (1)	T_1/K	367.51	369
	ΔH_1 /J mol ⁻¹	2 658	2 500
	ΔS_1 /J mol ⁻¹ K ⁻¹	7.24	6.3
transition (2)	T_2/K	355.91	358
	$\Delta H_2/J \text{ mol}^{-1}$	5 839	5 900
	$\Delta S_2/J \text{ mol}^{-1} \text{ K}^{-1}$	16.42	16
transition (3)	T_3/K	333.57	335
	$\Delta H_3/J \text{ mol}^{-1}$	22 990	23 000
	ΔS_3 /J mol ⁻¹ K ⁻¹	68.93	69

"Temperature uncertainty ± 0.01 K (this work), ± 0.5 K (ref. (3)). Enthalpy uncertainty ± 0.1 % (this work), ± 3 % (ref. (3)).

TRANSITIONS (1) AND (2)

We believe that the entropy increments for these two transitions are adequately explained in terms of the rotational disorder of the perchlorate ions. Guthrie and McCullough ¹² have shown that the transition entropies of plastic crystals (in which the molecules rotate in a restricted manner in the solid state) accord well with those calculated by considering possible orientations of the molecules in the different phases. Furthermore, Newns and Staveley ¹³ have demonstrated that transitions in ionic materials involving polyatomic ions may similarly be explained in many cases.

Guthrie and McCullough suggest that possible orientations will match symmetry elements of both molecule (or ion) and crystal lattice. If the perchlorate ion is considered as a tetrahedron in a cubic environment (the high temperature phase of ammonium perchlorate is cubic)¹⁴ there are four sets of such orientations. These are illustrated in fig. 2, and the corresponding symmetry elements are listed in table 5. They may be designated T_d (two distinguishable orientations), D_{2d} (6), C_{3v} (8), and C_{2v} (12). The entropy due to the orientational configuration of the ion is $R \ln N$ (where N is the number of distinguishable orientations available to the ion), and the change of orientational entropy on passing from one phase to another is $R \ln N_2/N_1$. If the major contribution to the entropy of transition comes from the orientational changes, then transitional entropies may be calculated for various combinations of the sets of orientations, and the results compared with the experimental values. The work of Newns and Staveley suggests that this procedure is of value, and that entropy contributions due to volume increments may be ignored.

Two transition schemes are suggested by the experimental results, and they are summarized in table 6. Both schemes correctly predict the entropy of transition (2),

ADIABATIC CALORIMETRY OF ORGANIC SALTS

but are rather low in their predictions of the entropy of transition (1). Scheme 2, however, is more nearly correct for transition (1) and the sum of the entropies of transitions (1) and (2) (\mathbf{R} ln 17.3) is much closer to that predicted by scheme 2 (\mathbf{R} ln 16) than that predicted by scheme 1 (\mathbf{R} ln 14.5). Scheme 1 utilises all the sets of orientations, while scheme 2 arbitrarily excludes the 12 C_{2v} orientations. Furthermore, scheme 2 requires that only one of the two possible T_d orientations be used in phase III, so that this phase is ordered in scheme 2, but disordered according to scheme 1.

We feel that the choice between these two schemes may not be made on the basis of the thermodynamic data alone. Both schemes lead to reasonably accurate predictions for the entropies of transitions 1 and 2, particularly since the effect of volume increments has not been considered (although we expect this to be small).¹³ It is conceivable that the C_{2v} orientations might be excluded in this material, due to steric



FIG. 2.-Sets of distinguishable orientations of a tetrahedron in a cubic environment.

TABLE 5.—SYMMETRY ELEMENTS FOR A TETRAHEDRON IN A CUBIC LAT	SYMMETRY ELEMENTS FOR A TETRAHEDRON IN A CUBIC	LATTICE
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set	coincidir tetrahedron	ng symmetry elements cubic lattice	distinguishable orientations
T _d	(4) 3-fold axis(3) 2-fold axis(6) mirror plane	(4) 3-fold axis(3) 4-fold axis(6) diagonal mirror plane	2
D _{2d}	(1) 2-fold axis(2) 2-fold axis(6) mirror plane	 (1) 4-fold axis (2) 2-fold axis (2) vertical mirror plane (4) diagonal mirror plane 	6
C_{3v}	(1) 3-fold axis(3) mirror plane	(1) 3-fold axis(3) diagonal mirror plane	8
C _{2v}	(1) 2-fold axis(2) mirror plane	 (1) 2-fold axis (1) horizontal mirror plane (1) vertical mirror plane 	12

J. T. S. ANDREWS AND J. E. GORDON

hindrance from the "melted" hexyl chains. We would expect that the disorder of phase III implied by scheme 1 should be resolved by a transition to an ordered phase at some lower temperature. We found no evidence for any such transition (by differential thermal analysis) down to liquid nitrogen temperatures, but this does not exclude the possibility that ordering might take place as part of the processes leading to transition (3) or at temperatures below the limit of our d.t.a. scan.

TABLE 6.—TRANSITION SCHEMES FOR TETRA-n-HEXYLAMMONIUM PERCHLORATE

phase	orientation sets	total number of orientations	entropy/J mol-	1 K-1
scheme 1				
III	T_d	2		
		transition (2)	R ln (16/2)	17.29
П	$T_d + D_{2d} + C_{3v}$	16		
	u _u _u	transition (1)	R ln (28/16)	4.65
Ι	$T_d + D_{2d} + C_{3v} + C_{2v}$	28		
scheme 2				
III	one of T_d (ordered)	1		
		transition (2)	R ln (8/1)	17.29
II	both $T_d + D_{2d}$	8		
	u - 2u	transition (1)	R ln (16/8)	5.76
Ι	$T_d + D_{2d} + C_{3v}$	16		
experiment				
		transition (2)	$R \ln 7.2$	16.42
		transition (1)	R ln 2.4	7.24

CONCLUSION

The general model proposed by Janz is reasonable. The melting of these materials may be compared, on the one hand, to the positional melting of ionic materials, and, on the other, to the configurational melting of the n-paraffins. However, we believe that the two processes are intermixed in this material due to the rather long hexyl chains. Transitions (1) and (2) may be accounted for by considering the orientational entropy of the perchlorate ion.

The equilibrium data obtained in this research agree quite well with those obtained by differential scanning calorimetry. The transition temperatures found here are somewhat lower than those from d.s.c. measurements, probably due to overheating of the sample in the d.s.c. work.

ADDENDUM

We are grateful to a referee for drawing our attention to an alternative interpretation of our results. He pointed out that the sum of the entropies of transitions (1), (2) and (3) (93 J K⁻¹ mol⁻¹) is close to that predicted by the kink-block model for the configurational melting of the hexyl groups on the cation (96 J K⁻¹ mol⁻¹), and he suggested that the break up of the lattice and the rotational disordering of the anion occur together in the fusion transition.

We think that 24 J K⁻¹ mol⁻¹ is a reasonable approximation to the entropy of the lattice break up, as the fusion entropies of potassium bromide and potassium perchlorate are very similar (25 and 23 J K⁻¹ mol⁻¹ respectively),¹⁰ and the presence of a transition ($\simeq R \ln 18$ at 572.7 K)¹⁵ in potassium perchlorate implies that the perchlorate ion is disordered in the solid phase of this material. The entropy of fusion of tetrahexylammonium perchlorate is 43.10 J K⁻¹ mol⁻¹ so that this alternative explanation assigns about 19 J K⁻¹ mol⁻¹ to the

ADIABATIC CALORIMETRY OF ORGANIC SALTS

entropy of the rotational disordering of the perchlorate ion in this material. This is about $R \ln 10$, less than the full entropy of restricted rotational disorder of a tetrahedron in a cubic lattice ($R \ln 28$), which implies either that full disorder is not attained in the liquid phase, or that the ion is partially disordered in the solid phase.

This entropy "deficit" is rather large, and we do not think that this alternative interpretation is likely. In addition, it fails to account for the observed entropies of transitions (1) and (2), which are in close agreement with those expected from the restricted rotation of the tetrahedral anion.

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