Preparation and *X*-Ray Powder Diffraction Patterns of the Sodium Vanadates $NaVO_3$, $Na_4V_2O_7$, and Na_3VO_4

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The reactions of various sodium oxo-compounds with vanadium pentoxide and sodium metavanadate are described. Products of reaction are characterised by means of thermal gravimetric analysis, differential thermal analysis, and powder *X*-ray crystallography. Sodium metavanadate, $NaVO_3$, and sodium pyrovanadate, $Na_4V_2O_7$, are found to possess two temperature-dependent structural modifications, whilst four structural modifications of the ortho-vanadate, Na_3VO_4, are obtained depending on the method of preparation.

THE sodium oxide–vanadium pentoxide phase diagram [1,2] indicates the presence of two alkali-metal-rich vanadates, namely the pyrovanadate, $Na_4V_2O_7$, and the orthovanadate, Na_3VO_4. Together with the metavanadate, $NaVO_3$, these compounds represent the least well characterised compounds in the sodium oxide–vanadium pentoxide system. Although the alkali-metal vanadates were first prepared in 1831,[3] they have only in recent years been investigated in any detail.[4]

The general method used for the preparation of the sodium vanadates is the reaction of sodium carbonate with the pentoxide, V_2O_5. Equimolar proportions of these reactants yield the metavanadate, whilst proportions in the ratios 2 : 1 and 3 : 1 ($Na_2CO_3 : V_2O_5$) give the pyro- and ortho-vanadates.

Polymorphism has been reported for all the alkali-metal-rich sodium vanadates and the transition temperatures between the high- and low-temperature forms have been determined.[2,5,6] However, in the case of the pyrovanadate the *X*-ray powder diffraction patterns of both forms were not reported.

We describe here the reactions of various alkali-metal oxo-compounds with vanadium pentoxide for the range of compositions between $Na_2O : V_2O_5$ 1 : 1 and 4 : 1. Reactions were followed by differential thermal analysis (d.t.a.) and thermogravimetric analysis (t.g.a.) and the results of these will be described first. A separate series of solid-state reactions were carried out, and the products of these reactions together with those from the d.t.a. and t.g.a. experiments were examined by *X*-ray powder diffraction. The results of the *X*-ray diffraction study are reported later in the paper.

RESULTS AND DISCUSSION

D.t.a. and t.g.a. of the reactions between sodium carbonate and vanadium pentoxide in the molar ratios 1 : 1, 2 : 1, and 3 : 1 were carried out with an identical heating rate. The results (Table 1) are in good agreement in terms of both temperature and composition with those shown in the phase diagram of ref. 2.

TABLE 1

Differential thermal analysis of Na_2CO_3–V_2O_5 reaction mixtures

$Na_2CO_3 : V_2O_5$/mol	Temp./°C	Transition type	Assignment
1 : 1 (heating)	530	Sharp endo.[a]	Melting $Na_2O : V_2O_5$ 40 : 60 mol %
	570	Sharp exo.[b]	Solidification $NaVO_3$
	620	Sharp endo.	Melting $NaVO_3$
1 : 1 (cooling)	570	Sharp exo.	Solidification $NaVO_3$
	450	Broad, small exo.	Oxygen-loss
2 : 1 (heating)	530	Endo.	Melting $Na_2O : V_2O_5$ 40 : 60 mol %
	555	Endo.	Melting $Na_2O : V_2O_5$ 57 : 43 mol %
	570	Small endo.	Melting $Na_2O : V_2O_5$ 60 : 40 mol %
2 : 1 (cooling)	650	Sharp exo.	Solidification $Na_4V_2O_7$
	429	Sharp, small exo.	Phase transition $Na_4V_2O_7$
3 : 1 (heating)	535	Endo.	Melting $Na_2O : V_2O_5$ 41 : 59 mol %
	555	Endo.	Melting $Na_2O : V_2O_5$ 58 : 42 mol %
	615	Small endo.	Melting $Na_2O : V_2O_5$ 63 : 37 mol %
3 : 1 (cooling)	555	Small endo.	Na_3VO_4 (IV) Na_3VO_4 (III) phase transition

[a] Endo. = Endothermic. [b] Exo. = exothermic.

Sodium metavanadate was found to exhibit pronounced supercooling, and the weak transition at 450 °C may be attributable to an oxygen-loss effect similar to that observed in the preparation of the vanadium bronzes. The phase transition of sodium pyrovanadate at 429 °C was readily observed on cooling, but not so easily detected on subsequent heating. The t.g.a. curve for the reaction of 3 mol of sodium carbonate with 1 mol of the pentoxide showed that the formation of the pyrovanadate was relatively rapid but the further reaction of 1 mol of sodium carbonate to give the orthovanadate was much slower. No thermal effects were therefore observed for the slower reaction on the d.t.a.

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[1] G. Canneri, *Gazzetta*, 1928, **58**, 6.

[2] A. A. Fotiev and B. V. Slobodin, *Zhur. priklad. Khim.*, 1965, **38**, 801.

[3] J. J. Berzelius, *Pogg. Ann.*, 1831, **22**, 1.

[4] M. Lelong, *Rev. Chim. minérale*, 1966, **3**, 259.

[5] I. Lukacs and C. Strusievici, *Z. anorg. Chem.*, 1962, **315**, 323.

[6] G. Le Flem and R. Olazcuaga, *Bull. Soc. chim. France*, 1968, 2769.

and the traces for the 2 : 1 and 3 : 1 reactions were therefore identical. The reaction of sodium oxide and sodium metavanadate was also studied by d.t.a. Reaction took place at the much lower temperature of 265 °C giving a large exothermic peak. On cooling, a small reversible endothermic transition at 330 °C was observed.

TABLE 2

X-Ray diffraction pattern of (*a*) α-$Na_4V_2O_7$

d/Å	I/I_0	*d*/Å	I/I_0	*d*/Å	I/I_0	*d*/Å	I/I_0
6·56	15	2·714	5	2·025	30	1·650	1
4·796	30	2·683	45	1·989	1	1·635	1
4·599	2	2·656	100	1·985	1	1·629	1
4·353	3	2·622	15	1·814	2	1·622	10
3·995	50	2·578	3	1·794	3	1·613	20
3·786	15	2·532	12	1·784	12	1·537	3
3·626	5	2·481	6	1·774	3	1·530	2
3·548	35	2·281	10	1·767	1	1·514	1
3·302	55	2·259	10	1·758	1	1·503	5
3·008	2	2·222	6	1·743	5		
2·862	25	2·080	1	1·725	1		
2·739	1	2·067	1	1·667	2		

(*b*) β-$Na_4V_2O_7$

d/Å	I/I_0	*d*/Å	I/I_0	*d*/Å	I/I_0	*d*/Å	I/I_0
5·609	10	3·243	35	2·254	8	1·674	8
5·372	4	3·137	30	2·141	25	1·583	10
4·928	6	2·979	4	2·103	6	1·551	6
4·647	15	2·912	2	2·010	10	1·499	8
4·529	8	2·823	100	1·945	4	1·466	6
4·230	20	2·600	25	1·903	20	1·431	30
4·077	6	2·468	2	1·884	35		
3·842	8	2·398	4	1·841	6		
3·389	4	2·332	4	1·698	2		

X-*Ray Powder Diffraction Studies.—Sodium metavanadate.* The *X*-ray powder diffraction patterns of the products obtained from both the d.t.a. and t.g.a. experiments and from corresponding mixtures of sodium carbonate and the pentoxide heated in argon, oxygen, and air indicated the formation of the high-temperature form of the metavanadate, α-$NaVO_3$. The *X*-ray pattern was in excellent agreement with that given in ref. 5. The low-temperature form of sodium metavanadate may not be prepared by the reaction of sodium carbonate and the pentoxide, since for complete reaction, the mixture must be heated to form the eutectic composition at 530 °C. Reaction mixtures which were heated for long periods below this temperature did not reach equilibrium and *X*-ray diffraction patterns of these products showed them to contain unreacted pentoxide.

TABLE 3

Stoicheiometric reaction (Na : V 3 : 1)

Expt. no.	Reaction	Ratio	Atmosphere	Temp./°C	Time/h	Modification *
(1)	$Na_2CO_3 + V_2O_5$	3 : 1	Air	700	†	(IV) + (III)
(2)	$Na_2CO_3 + V_2O_5$	3 : 1	Ar	700	†	(IV) + (III)
(3)	$Na_2CO_3 + V_2O_5$	3 : 1	O_2	700	†	(IV) + (III)
(4)	$Na_2CO_3 + V_2O_5$	3 : 1	Ar	600	72	(II) + (IV)
(5)	$NaOH + V_2O_5$	6 : 1	N_2	600	24	(IV) + (III) + (I)
(6)	$Na_2O + V_2O_5$	3 : 1	Ar	600	24	(III) + (IV)
(7)	$Na_2O_2 + V_2O_5$	3 : 1	Air	600	$\frac{1}{2}$	(IV) + (III) + (I)
(8)	$Na_2O + NaVO_3$	1 : 1	Ar	315	96	(I) + (IV) + (III)
(9)	$Na_2O + NaVO_3$	1 : 1	Ar	375	4	(I) + (IV)
(10)	$Na_2O + NaVO_3$	1 : 1	Ar	600	24	(III) + (IV)

* Modification of Na_3VO_4 produced, in order of bulk. † T.g.a. experiments; in these the reaction mixtures were heated to 700 °C at 14° min^{-1}, maintained at that temperature for 4 h, and then cooled to 200 °C at 14° min^{-1}.

The low-temperature form was prepared by the addition of a stoicheiometric quantity of sodium hydroxide in solution to a boiling solution of ammonium metavanadate. Evaporation to dryness of the solution on a water bath gave orange plate-like crystals which, when ground, gave a cream coloured powder. The *X*-ray diffraction pattern of the powder showed it to be the low-temperature form of sodium metavanadate β-$NaVO_3$.[5] No structure change was evident for the thermal effect observed at 450 °C by d.t.a., but some line-broadening was observed at this temperature. The sample changed from white to grey during the thermal cycle, and exhibited a small weight gain (*ca.* 0·35%) and restoration of the white colouration when re-heated in oxygen at 400 °C.

Sodium pyrovanadate, $Na_4V_2O_7$. *X*-Ray powder diffraction patterns of the pyrovanadate showed that the phase transition at 429 °C is not completely reversible, both high- and low-temperature forms being present. Attempts to obtain a pure sample of the high-temperature form by quenching molten pyrovanadate were unsuccessful. The *X*-ray diffraction pattern of the high-temperature form (β-$Na_4V_2O_7$) was obtained by use of a high-temperature *X*-ray diffraction camera, the sample being maintained at 600 °C for 24 h before exposure of the film. By use of the data for the high-temperature phase the pattern of the low-temperature phase was established by removal of the lines due to the former from the pattern for a mixture of both phases. The *X*-ray diffraction patterns of both forms are given in Table 2.

Sodium orthovanadate, Na_3VO_4. This compound was prepared by the reaction of either vanadium pentoxide with sodium carbonate, sodium hydroxide, sodium peroxide, or sodium oxide, or of sodium metavanadate and sodium oxide (Table 3). The *X*-ray diffraction patterns of the products from these reactions were not, however, identical. Close examination of the patterns revealed the existence of some four different phases. Chemical analyses (Table 4) gave values in good agreement with those calculated for the stoicheiometry Na_3VO_4, and this was also confirmed by t.g.a. of the sodium carbonate–vanadium pentoxide reactions. The analytical results indicate that the four phases observed by use of *X*-ray diffraction are therefore phase modifications of the compounds Na_3VO_4. To assist in the recognition of these phases they have been numbered in the Tables with Roman numerals in parentheses, *e.g.* Na_3VO_4 (IV) and will be referred thus in the text.

TABLE 4

Chemical analyses

Preparation	%Na	%V	%O (difference)
$3Na_2CO_3 + V_2O_5$ (700°, air)	37·6	27·7	34·7
$3Na_2O + V_2O_5$ (600°, air)	37·3	27·7	35·0
$Na_2O + NaVO_3$ (315°, Ar)	37·3	27·6	35·1
$3Na_2CO_3 + V_2O_5$ (650°, O_2)	37·6	27·6	34·8
Na_3VO_4 (calc.)	37·5	27·7	34·8

Preparations at 700 °C by use of sodium carbonate gave products which were identical irrespective of the atmosphere used. The products were however faintly coloured and feebly paramagnetic [the products of experiments (1)—(3) gave values for the room-temperature magnetic moment μ_{eff} of 0·612, 0·625, and 0·603 B.M.]. The colour and paramagnetism of the samples suggests some reduction of the vanadium had taken place possibly by oxygen loss. A decrease in temperature of the reaction [experiment (4)] gave a less paramagnetic product Na_3VO_4 (II) as the major constituent. The reaction of sodium oxide with sodium metavanadate at either 315 or 375 °C [experiments (8) and (9)] gave a white product, which in both cases consisted largely of the phase Na_3VO_4 (I). Although reaction takes place at the lower temperature, it is also very exothermic and the subsequent rise in temperature gives rise to the formation of the more reduced phases Na_3VO_4 (IV) and Na_3VO_4 (III) in small quantities. If the reaction mixture is heated to 600 °C [experiment (10)] the phase Na_3VO_4 (I) is no longer produced, the products being Na_3VO_4 (II) and Na_3VO_4 (IV).

Mixed-phase regions. An *X*-ray study of the compounds formed in the regions between $Na_4V_2O_7$ and Na_3VO_4 (Table 5) showed that the pyrovanadate was always present in both the high- and low-temperature modifications with an excess of the latter over the former. The orthovanadate was always present as the modification Na_3VO_4 (IV) together with, at the higher Na : V ratios, the modification Na_3VO_4 (III). Thermogravimetric analyses gave the observed loss of CO_2 to be in good agreement with that calculated for the formation of mixtures of the pyro- and ortho-vanadates. Reactions were also carried out (Table 6) between vanadium pentoxide and both sodium carbonate and sodium oxide in which the Na : V ratio was >3 : 1. All the products contained unreacted carbonate or oxide; for the sake of clarity, these have been omitted from the Table.

TABLE 5

The region $Na_4V_2O_7$ to Na_3VO_4

Expt. no.	Ratio $Na_2CO_3 : V_2O_5$	Atmosphere	Products
(1)	2·0 : 1	Air	$Na_4V_2O_7$ †
(2)	2·2 : 1	Air	$Na_4V_2O_7 + Na_3VO_4$ (IV)
(3)	2·4 : 1	Air	$Na_4V_2O_7 + Na_3VO_4$ (IV)
(4)	2·6 : 1	Air	Na_3VO_4 (IV) + $Na_4V_2O_7 + Na_3VO_4$ (III)
(5)	2·8 : 1	Air	
(6)	2·6 : 1	Ar	
(7)	2·8 : 1	Ar	
(8)	2·6 : 1	O_2	
(9)	2·8 : 1	O_2	
(10)	4 : 1 *	N_2	$Na_4V_2O_7$
(11)	5 : 1 *	N_2	Na_3VO_4 (IV) + $Na_4V_2O_7$

* NaOH : V_2O_5 at 600 °C for 24 h; experiments (1)—(9) were t.g.a. at 700 °C. † $Na_4V_2O_7$ refers to a mixture of both high- and low-temperature forms.

TABLE 6

The alkali-metal-rich region, Na : V >3 : 1

Expt. no.	Ratio	Atmosphere	Temp. / °C	Time/ h	Modification of Na_3VO_4
(1)	3·2 : 1	Air	700	*	(IV) + (III)
(2)	3·4 : 1	Air	700	*	(IV)
(3)	3·2 : 1	Ar	700	*	(IV) + (III)
(4)	3·4 : 1	Ar	700	*	(IV)
(5)	3·2 : 1	O_2	700	*	(IV) + (III)
(6)	3·4 : 1	O_2	700	*	(IV) + (III)
(7)	3·25 : 1	Air	600	2	(IV) + (III)
(8)	3·5 : 1	Air	650	1	(IV)
(9)	4·0 : 1	Air	650	1	(IV)
(10)	3·1 : 1	Ar	600	24	(III) + (IV) + (I)
(11)	3·2 : 1	Ar	600	24	(II) + (IV)
(12)	3·3 : 1	Ar	600	24	(III) + (IV)
(13)	3·4 : 1	Ar	600	24	(II) + (IV)
(14)	3·5 : 1	Ar	600	24	(III) + (IV) + (I)
(15)	7·0 : 1	N_2	600	24	(IV) + (III) + (I) + NaOH

* All t.g.a.

Reactants: expt. (1)—(9) $Na_2CO_3 + V_2O_5$; expt. (10)—(14) $Na_2O + V_2O_5$; expt. (15) NaOH + V_2O_5.

The modification Na_3VO_4 (IV) was produced in all reactions involving sodium carbonate and is apparently stabilised by the higher alkali-metal content in non-oxidising atmospheres. Room-temperature magnetic measurements on this modification showed it to be the most paramagnetic of the forms of the orthovanadate (μ_{eff} 0·811 B.M.).

The reaction of sodium oxide with vanadium pentoxide was very exothermic and it seems probable that the less oxygen-deficient phases are produced in the reaction but undergo oxygen loss due to the rapid rise in temperature on reaction.

X-Ray powder diffraction data. Interplanar spacings and relative intensities for the four modifications of the compound Na_3VO_4 are given in Table 7. Only the phase Na_3VO_4 (IV) could be satisfactorily indexed having a cubic structure based on the zinc sulphide lattice. Changes in the lattice parameter were observed from different preparations, varying from 7·60 to 7·69 Å suggesting a fairly wide stoicheiometry range. This compound is isostructural with the γ-form of sodium arsenate Na_3AsO_4[7] (a = 7·669 Å) and contains four formula units per unit cell. This phase has been reported recently,[8] and may now be best referred to as γ-Na_3VO_4 in view of its structural relationship with γ-Na_3AsO_4 and γ-Na_3PO_4. In the same paper,[8] a phase

[7] M. Palazzi and F. Remy, *Bull. Soc. chim. France*, 1971, 2795.

[8] G. Le Flem, R. Olazcuaga, J. P. Parant, J. M. Réau, and C. Foussier, *Compt. rend.*, 1971, *C*, **273**, 1358.

TABLE 7

X-Ray diffraction patterns of modifications of Na_3VO_4

(*a*) Na_3VO_4 (I)

d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
6·15	10	3·363	25	2·259	40	1·859	20
5·574	10	3·154	20	2·067	10	1·824	15
4·695	50	2·885	10	2·040	30	1·672	5
3·849	20	2·645	100	1·981	30	1·621	10
3·591	15	2·362	20	1·961	5		

(*b*) Na_3VO_4 (II)

d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
6·11	18	3·54	10	2·567	10	1·991	10
4·81	2	3·46	1	2·485	15	1·947	5
4·61	22	3·377	2	2·364	1	1·938	10
4·34	40	3·045	100	2·307	12	1·763	35
4·18	12	2·956	2	2·189	6	1·577	18
4·09	20	2·828	2	2·159	14	1·536	3
4·00	12	2·760	70	2·129	3	1·489	12
3·83	8	2·672	80	2·092	3	1·473	6
3·63	5	2·604	10	2·047	30		

(*c*) Na_3VO_4 (III)

d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
4·33	40	3·069	5	2·401	10	1·826	1
4·19	50	2·945	15	2·395	10	1·783	10
3·99	40	2·788	50	2·332	1	1·684	5
3·64	15	2·706	10	2·156	50	1·643	2
3·55	20	2·564	2	2·127	2		
3·45	2	2·546	100	2·019	2		
3·170	1	2·478	60	1·989	3		

(*d*) Na_3VO_4 (IV)

d/Å	h	k	l	I/I_0	d/Å	h	k	l	I/I_0
4·40	1	1	1	90	1·914	4	0	0	25
3·80	2	0	0	45	1·757	3	3	1	8
2·702	2	2	0	100	1·705	4	2	0	2
2·304	3	1	1	15	1·564	4	2	2	18
2·199	2	2	2	6	1·467	3	3	3	8

a = 7·60 Å, D (17·7 °C) = 2·722 at 17·7 °C, Z = 4 (Found 3·91).

β-Na_3VO_4 was prepared, being isostructural with the orthorhombic form of Na_3AsO_4. This phase is almost identical to Na_3VO_4 (II) but does not contain some of the weak lines observed in the diffraction pattern of the latter compound. The phase Na_3VO_4 (II) was observed in an earlier paper[6] which described the formation of a low-temperature phase α-Na_3VO_4, by the reaction of sodium carbonate and vanadium pentoxide at 600 °C in argon. The X-ray powder diffraction pattern of α-Na_3VO_4 may be interpreted as being a mixture of Na_3VO_4 (II) and the cubic form γ-Na_3VO_4.

The phase Na_3VO_4 (III) closely resembles that of Na_3VO_4 (II) and is almost identical to the phase reported in ref. 4, if the diffraction lines due to γ-Na_3VO_4 are removed from the published X-ray diffraction pattern. The phase Na_3VO_4 (I) has not been reported previously.

Inter-relationship of the Phase Modifications of the Orthovanadate, Na_3VO_4.—The relationship between the various phases of Na_3VO_4 is obviously complex. Le Flem has observed[8] that β-Na_3VO_4 may be converted into γ-Na_3VO_4 by heating to 700 °C, and that annealing of γ-Na_3VO_4 for 1 week at 450 °C initiated a reversal to β-Na_3VO_4. We have shown that all other modifications may be converted into γ-Na_3VO_4 by prolonged heating to 700 °C in inert atmospheres. A high-temperature X-ray study showed that the formation of γ-Na_3VO_4 commenced at 340 °C from Na_3VO_4 (I), 450 °C from Na_3VO_4 (II), and 555 °C from Na_3VO_4 (III). We have not, however, studied the reversibility of these transitions.

Changes in the relative intensities of the diffraction lines of the γ-form of Na_3VO_4 took place on heating the compound in a high-temperature X-ray diffractometer. The temperature at which this transformation (which was reversible) occurred was dependent upon the initial lattice parameter of the compound, being at 430 °C for the compound with the cell constant a = 7·69 Å, and at 750 °C for a = 7·60 Å. The X-ray diffraction pattern of this high-temperature phase is given in Table 8. At temperatures >800 °C all forms of the orthovanadate lost sodium oxide giving the pyrovanadate $Na_4V_2O_7$.

TABLE 8

X-Ray powder diffraction pattern of the high-temperature form of Na_3VO_4 at 550 °C

d/Å	h	k	l	I/I_0	d/Å	h	k	l	I/I_0
4·52	1	1	1	100	1·953	4	0	0	10
3·93	2	0	0	20	1·787	3	3	1	2
2·763	2	2	0	65	1·737	4	2	0	1
2·350	3	1	1	4	1·590	4	2	2	8
2·249	2	2	2	1	1·501	3	3	3	4

That a large number of phases is reported for Na_3VO_4, suggests that these are not simply temperature modifications, but may be the result of oxygen-loss effects. The observed paramagnetism and colouration of all the phases, other than Na_3VO_4 (I), implies that some reduction has taken place, the most paramagnetic species being γ-Na_3VO_4. The effect is most pronounced in preparations which require melt conditions to attain complete reaction. Reactions involving sodium carbonate, sodium oxide, and sodium hydroxide with the pentoxide all showed signs of fusion. Only the reaction of sodium oxide and the metavanadate, $NaVO_3$, occurred without melting, and the product of this reaction, Na_3VO_4 (I), was the least-reduced phase observed.

EXPERIMENTAL

Reagents.—The preparation of sodium oxide has been described previously.[9] Sodium hydroxide, sodium carbonate, and vanadium pentoxide were of AnalaR grade and were dried to constant weight before use.

Chemical Analyses.—All samples were readily dissolved in water. Vanadium analyses were carried out by titration of V^{4+} in solution (obtained by sulphur dioxide reduction) with potassium permanganate. Sodium was determined by flame photometry.

Differential Thermal Analysis.—The apparatus used consisted of four chromel–alumel thermocouple junctions all set at the same vertical height and arranged symmetrically about the central axis of a tubular electrical furnace. Two of these junctions were connected so that their differential thermal e.m.f. was recorded on a single-pen chart recorder. On each of these two junctions was mounted a sample container, one containing the thermally inert reference material, alumina, and the other containing the sample.

[9] M. G. Barker and D. J. Wood, *J.C.S. Dalton*, 1972, 9.

The quantities of alumina and sample used were as near identical as possible. The remaining thermocouples were used to provide (*a*) a direct measurement of the temperature and (*b*) a normal thermal analysis on a sample contained in a holder identical to that used for the differential analysis. The furnace was programmed to give a linear heating or cooling rate.

All the sample holders used were identical, being machined out of stainless steel to exact specifications. Each holder was fitted with a replaceable platinum liner.

Thermogravimetric Analysis.—The apparatus used has been described previously.[9]

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