

616. *The Thermal Decomposition of Some 12-Heteropolytungstates and their Ether-addition Compounds.*

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The thermal decompositions are studied of 12-tungstozincic(II), 12-tungstoferric(III), 12-tungstocobaltic(II), 12-tungstoboric, 12-tungstosilicic, 12-tungstophosphoric acids, their potassium salts, and their ether-addition compounds. The energies of activation for each stage in the dehydrations are calculated and related to the structures of the anions.

12-HETEROPOLYTUNGSTATES are known to exist in different hydrated forms. When freshly recrystallised from water, they generally contain around twenty nine water molecules for each molecule of the acid, but, on exposure to air, some of this water of hydration is lost. Keggin,¹ for his structural determinations, obtained the 5-hydrate by dehydrating 12-tungstophosphoric acid over phosphorus pentoxide. Signer and Cross² prepared the 5-hydrates of the corresponding 12-tungstosilicic, 12-tungstoboric, and metatungstic acids, and showed their structures to be similar to that of 12-tungstophosphoric acid. Other work³ has shown that 12-tungstozincic acid had the same type of complex anion with, however, a larger central ion than the 12-tungstophosphoric acid. The present work investigates the different hydrates, the thermal stabilities of the anhydrous acids prepared both from aqueous solution and from the ether-addition compound, and relates these stabilities to the properties of the central ion in the heteropoly-acid.

EXPERIMENTAL

The heteropoly-acids were all prepared by heating the corresponding ether-addition compounds with water at 80° for 1 hr., the acids being recrystallised from water immediately before use. The potassium salts were prepared by precipitation with saturated potassium chloride solution and recrystallised from water. The thermal-decomposition measurements were done with a Stanton thermogravimetric balance at a chart speed of 6 in./hr. The purity of the specimens was checked by analysis, and the following results were obtained: 12-tungstozincic acid (Found: ZnO, 2.4; WO₃, 82.4; H₂O, 15.3. Calc. for ZnO,12WO₃,29H₂O: ZnO, 2.4; WO₃, 82.2; H₂O, 15.5%), 12-tungstoferric acid (Found: Fe₂O₃, 2.4; WO₃, 83.0; H₂O, 14.5. Calc. for $\frac{1}{2}$ Fe₂O₃,12WO₃,27H₂O: Fe₂O₃, 2.4; WO₃, 83.1; H₂O, 14.5%), 12-tungstocobaltic

¹ Keggin, *Proc. Roy. Soc.*, 1934, A, **144**, 75.

² Signer and Cross, *Helv. Chim. Acta*, 1934, **17**, 1074.

³ Brown and Mair, *J.*, 1958, 2597.

acid (Found: CoO, 2.4; WO₃, 82.0; H₂O, 15.6. Calc. for CoO,12WO₃,29H₂O: CoO, 2.3; WO₃, 82.4; H₂O, 15.5%), 12-tungstosilicic acid (Found: SiO₂, 1.8; WO₃, 82.9; H₂O, 15.4. Calc. for SiO₂,12WO₃,29H₂O: SiO₂, 1.8; WO₃, 83.7; H₂O, 15.5%), 12-tungstoboric acid (Found: B₂O₃, 1.0; WO₃, 84.6; H₂O, 14.5. Calc. for $\frac{1}{2}$ B₂O₃,12WO₃,27H₂O: B₂O₃, 1.1; WO₃, 84.2; H₂O, 14.7%), and 12-tungstophosphoric acid (Found: PO₄, 2.7; WO₃, 82.1; H₂O, 15.5. Calc. for PO₄,12WO₃,29H₂O: PO₄, 2.8; WO₃, 81.9; H₂O, 15.4%).

RESULTS

The thermal analysis of 12-tungstozincic acid showed three distinct regions where loss of weight occurred and also a region of constant weight corresponding to the anhydrous

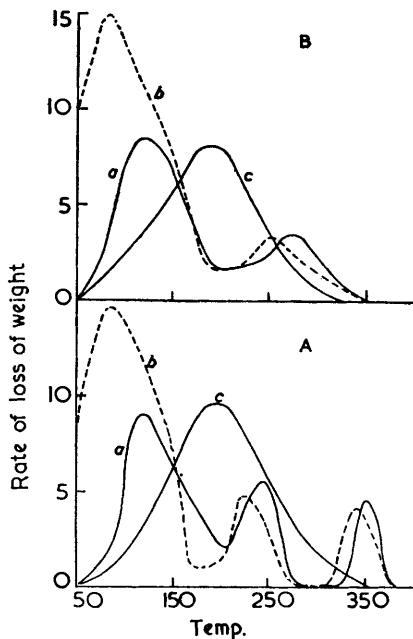


FIG. 1. Thermal analyses.

- A (a) 12-Tungstozincic acid, (b) the ether-addition compound of 12-tungstozincic acid, and (c) potassium 12-tungstozincate.
 B (a) 12-Tungstophosphoric acid, (b) the ether-addition compound of 12-tungstophosphoric acid, and (c) potassium 12-tungstophosphate.

acid. These are shown in Fig. 1A as three peaks at 120°, 240°, and 350°. The numbers of water molecules lost were 21, 5, and 3, respectively. The first two stages were reversible and the third was not. This third stage appeared to be due to the decomposition of the anionic oxide lattice since an acid solution of material which had been heated above 350° showed the presence of free zinc ions whereas a solution of the material which had been heated to 250° showed only the existence of the complex anion. Similar results were obtained with 12-tungstoferric acid and 12-tungstocobaltic acid. The results are shown in Table I.

With 12-tungstosilicic, 12-tungstophosphoric, and 12-tungstoboric acids, however, different results were obtained. With the chart of the thermal balance running at 6 in./hr.,

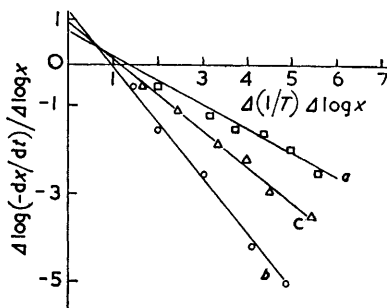


FIG. 2. Specimen graphs for the calculation of energies of activation: (a) E_2 for 12-tungstoferric acid, (b) E_3 for 12-tungstoferric acid, and (c) E_2 for 12-tungstophosphoric acid.

no region of constant weight corresponding to the existence of the anhydrous acid was observed and only two stages where loss of weight occurred were obtained. The results for tungstophosphoric acid are shown in Fig. 1B. Only by carefully controlling the rise in temperature in steps and allowing the crucible to come to constant weight could an approximate value for the decomposition temperature be obtained. However, no accurate values could be obtained as the loss of the five remaining water molecules appeared to be accompanied by decomposition of the complex anion. The temperatures at which maximum rate of loss of water occurred, the number of water molecules involved, and the energies of activation for each stage are shown in Table 1. The energies of

TABLE 1.

Acid	Temp. of max. rate of water loss			No. of molecules of water lost			E_1^*	E_2^*	E_3^*
	120°	240°	350°	21	5	3			
12-Tungstozincic	120°	240°	350°	21	5	3	6	21	56
12-Tungstoferric	120	240	390	19.5	5	2.5	7	23	60
12-Tungstocobaltic	120	240	350	21	5	3	7	21	58
12-Tungstophosphoric...	120	270	—	22.5	6.5	—	6	36	—
12-Tungstoboric	120	270	—	19.5	7.5	—	6	36	—
12-Tungstosilicic	120	270	—	22	7	—	7	38	—

* In kcal./mole.

activation were calculated by the method described by Freeman and Carrol⁴ for a system involving a solid decomposing into a solid and a gas. This involved plotting $\Delta(1/T)/\Delta \log x$ against $\Delta \log(-dx/dt)/\Delta \log x$ where T was the absolute temperature and x was the number of molecules of water at temperature T . This plot gave a straight line with slope $-E/2.3R$ where E was the energy of activation and R the gas constant, and intercept of $+X$ where X was the order of the reaction. In each case evaluated, free acid, potassium salt, and ether-addition compound, water, and ether were lost in accordance with a first-order reaction. Specimen graphs are shown in Fig. 2. The energies of activation are only accurate to within ± 2 kcal./mole.

The potassium salts of these six heteropoly-acids were prepared and examined on the thermal balance. In each case the maximum rate of water loss (Fig. 1) occurred around 180—200°. Only one stage in the dehydration was observed. The salts appeared to retain their crystalline structure after all the water of hydration had been removed. Again the energies of activation were calculated and the results are shown in Table 2.

TABLE 2.

K salt of	Temp. of max. rate of water loss		No. of molecules of water lost	E^*
	180—200°	180—200		
12-Tungstozincic	180—200°	180—200	18	8
12-Tungstoferric	180—200	180—200	20	8
12-Tungstocobaltic	180—200	180—200	18	9
12-Tungstophosphoric	180—200	180—200	16	10
12-Tungstoboric	180—200	180—200	14	9
12-Tungstosilicic	180—200	180—200	14	9

* kcal./mole.

The ether-addition compounds were then examined on the thermogravimetric balance. Again with the 12-tungstozincic, 12-tungstoferric, and 12-tungstocobaltic acid, three regions of loss of weight were observed, the first around 80—100°, the second around 240°, and the third at a higher temperature. The first loss of weight from the ether-addition compound of 12-tungstozincic acid was due to ether, and the second and third to water (Fig. 1A); these compositions were confirmed by testing the gases evolved when separate samples were heated to the specific temperatures. The ether-addition compounds of the other three acids showed only two regions of weight loss, the first due to loss of ether and

⁴ Freeman and Carrol, *J. Phys. Chem.*, 1958, **62**, 394.

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the second to loss of water (Fig. 1B). The temperatures of maximum rate of loss of weight, number of molecules lost, and the energies of activation are shown in Table 3.

TABLE 3.

Ether-addition compound of	Temp. of max. rate of loss			No. of molecules lost			E_1 *	E_2 *	E_3 *
				ether	water				
12-Tungstozincic	80°	220°	340°	20	5	3	7	23	55
12-Tungstoferric	80	230	380	21	5	2.5	7	22	57
12-Tungstocobaltic	80	220	340	20	5	3	7	22	56
12-Tungstophosphoric...	80	250	—	23	6.5	—	8	34	56
12-Tungstoboric	80	250	—	22	7.5	—	7	32	—
12-Tungstosilicic	80	250	—	21	7	—	7	33	—

DISCUSSION

The thermal analyses of the six heteropolytungstic acids confirm the existence of a stable pentahydrate particularly when zinc, iron, and cobalt are the central ions. With these three acids the dehydration of the pentahydrate can be identified over a distinct temperature range, and the activation energies measured. The values, 21, 23, and 21 kcal./mole, are significantly higher than those (around 6 kcal./mole) obtained for the first stage of the dehydration. The latter values suggest that the water of hydration is weakly bonded, probably through hydrogen bonding. X-Ray powder photographs^{1,5} show that the structures change from open to fairly closely packed ones from the 29- to the 5-hydrates, which would facilitate loss of water. For the potassium salts, however, the crystal form does not change greatly on dehydration. Hence the energy of activation should be slightly greater, as it was found to be. In both cases the water molecules of hydration are bound both to each other and to the heteropoly-anions. Thus, with progressive loss of water, the environment and hence the nature of the bonding of the water molecules would alter, which would probably account for the first-order kinetics.

Thermal analysis of the ether-addition compounds showed that five water molecules exist in the ether-addition compounds also. From a comparison of the activation energies, it appeared that they occupy a position in the lattice similar to that in the pentahydrate. X-Ray powder photographs confirmed that the pentahydrates were identical.

For the 12-tungstozincic, 12-tungstoferric, and 12-tungstocobaltic acids, the anhydrous acid could be isolated and the decomposition of the oxide lattice appeared as a third dehydration stage. The energies of activation for these reactions were much higher, *viz.*, 56, 60, and 58 kcal./mole from the 29-hydrates and 55, 57, 56 kcal./mole from the ether-addition compounds. With the other three heteropolytungstates, the dehydration of the pentahydrate and the decomposition of the oxide lattice were too close together to be separated and the energies of activation calculated were probably composite values for both of these reactions. Similar results were obtained, starting both from the 29-hydrates and from the ether addition compounds.

The ether molecules in the ether-addition compounds are lost fairly readily at room temperature. The calculated energies of activation were similar to those obtained for the first stage of the dehydration of the 29-hydrate. The ether molecules were probably hydrogen-bonded to the water molecules and the hydrogen ions associated with the heteropolyanions, giving rise to a liquid phase.

Of these six heteropolyanions it is apparent that the 12-tungstozincic, 12-tungstoferric, and 12-tungstocobaltic acids are much the most stable. Linnett⁶ pointed out that in 12-tungstoboric, 12-tungstophosphoric, and 12-tungstosilicic acids the bond distance between the central ion and the nearest oxygen ions, 1.7 Å, was considerably greater than the distance normally found. The reverse is probably true for the other three heteropolytungstates despite the dimensions of the complex anions and the unit cells of the crystals

⁵ Bradley and Illingworth, *Proc. Roy. Soc.*, 1936, A, 157, 113.

⁶ Linnett, *J.*, 1961, 3796.

appearing not to have altered.^{3,7} In Table 4, the decomposition temperatures are listed above the bond distances between the central ions and the four nearest oxygen atoms tetrahedrally distributed around them.

TABLE 4.

Central ion, R	Metatungstic acid	B	Si	P	Zn	Fe	Co
Approx. decomp. temp.	Unstable at room temp.	270°	270°	270°	350°	390°	350°
Normal R-O distance (Å)	—	1.50	1.61	1.54	1.95	2.08	2.08

The R-O bond distances are taken from "Interatomic Distances," Chemical Society Special Publication No. 11. The values for Fe-O and Co-O are for an octahedral environment. The others are for a tetrahedral environment which is the type that exists in a heteropolytungstate.¹

The thermal stability of a heteropolytungstate therefore seems to depend on the nature and size of the central ion; the larger central ions appear to impart greater stability to the lattice. The oxide lattice must, to some extent, contract or expand slightly to adapt itself to the size of the central ion. Without a stabilising central ion, as in metatungstic acid, the anion is unstable in aqueous solution and as solid.

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⁷ Brown and Mair, *J.*, 1962, 1512.