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Note

THERMAL DECOMPOSITION KINETIC PARAMETERS OF SOME ORGANIC DECAVANADATES(II)

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Recently the thermal decomposition kinetics of some decavanadates of organic bases were investigated [1]. In this paper we present a study of the thermal stability and decomposition kinetic parameters of a new group of decavanadates of organic bases which were synthesized for the first time in our laboratory. The new compounds belong to the series of general formula $(BH)_3H_3V_{10}O_{28} \cdot x\ H_2O$ with $0.5 \leqslant x \leqslant 2.5$ and B represents pyridine (= J_1), 2,4-dimethylpyridine (= J_8), 3,4-dimethylpyridine (= J_{10}), 3,5-dimethylpyridine (= J_{11}) or 2,4,6-trimethylpyridine (= J_{12}). These compounds are listed in Table 1. For a better comparison with previous studies [1,2] the kinetic study was made in a dynamic regime and the theoretical analysis by means of Satava's method [3].

EXPERIMENTAL

The compounds were synthesized by means of a modification of the method described by Clare et al. [4]. A solution of vanadium pentoxide in sodium hydroxide was prepared, followed by acidification. For the chemical reaction to take place the solution was driven to a pH = 1.5 and excess of the organic bases was added at the same pH while stirring. All the compounds have a low solubility in water and dimethylsulphoxide and are almost insoluble in the usual organic solvents. Results from conventional chemical analysis appear in Table 1. The apparatus, experimental conditions, and spread in the processed data were the same as described in a previous paper [1].

RESULTS AND DISCUSSION

The registered decomposition curves are similar to those in ref. 1 except in the number of steps associated with each compound. The pathway is not simple and therefore only the whole process, as in ref. 1, can be described. The activation energy for each step was obtained from the plot of $\ln F(\alpha)$ vs. $1/T$ following Satava's method [3]. For every step a random nucleation mechanism was found as the rate-determining process $\{-\ln(1-\alpha)\}^{1/3} = KT$.

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TABLE 1

Chemical Analysis

Compound	V_2O_5		C		H		N	
	Theor	Exp.	Theor	Exp	Theor.	Exp.	Theor.	Exp.
J_1 $(C_5H_5NH)_3H_3V_{10}O_{28} \cdot 1/2\ H_2O$	75.17	75.21	14.89	14.85	1.83	1.93	3.47	3.65
J_8 $(C_7H_9NH)_3H_3V_{10}O_{28} \cdot 1\ H_2O$	69.80	70.04	19.36	20.00	2.71	2.69	3.23	3.45
J_{10} $(C_7H_9NH)_3H_3V_{10}O_{28} \cdot 1\ H_2O$	69.80	69.71	19.36	19.39	2.71	3.04	3.23	3.32
J_{11} $(C_7H_9NH)_3H_3V_{10}O_{28}$ 5/2 H_2O	68.38	68.26	18.97	19.70	2.88	3.03	3.16	3.44
J_{12} $(C_8H_{11}NH)_3H_3V_{10}O_{28} \cdot 1\ H_2O$	67.61	67.66	21.43	21.66	2.92	2.89	3.12	3.25

TABLE 2

E_a, T_1 and T_f for the decomposition steps of the compounds studied

Compound *	First step			Second step			Third step		
	T_1 (°C)	T_f (°C)	E_a (kJ mole^{-1})	T_1 (°C)	T_f (°C)	E_a (kJ mole^{-1})	T_1 (°C)	T_f (°C)	E_a (kJ mole^{-1})
J_1	151	221	27.98	236	346	16.88	391	437	135.25
J_8	161	246	44.34				413	496	111.55
J_{10}	124	236	22.57				374	537	44.29
J_{11}	148	198	72.52	203	281	2.19	408	471	160.31
J_{12}	159	247	25.03				431	501	94.17

* See Table 1 for details.

Table 2 shows the initial and final decomposition temperatures as well as the activation energy associated with each step. From the α vs. T curves we find the same behaviour as that previously described [1].

The IR spectra show that the base is protonated and therefore it must be bonded to the most basic oxygen of the decavanadate group. This point was confirmed by means of X-ray diffraction [5]. All the compounds show monoclinic structure at room temperature, with three N—H···O bonds. From ref. 5 we see that the distances between N and O are 2.63 Å and 2.73 Å. This physical situation could be consistent with the following interpretation. In the first two steps a part of the organic base is lost while in the last step the remaining organic base is lost and at the same time the transformation of the decavanadate structure in vanadium dioxide would take place. This could explain the high activation values for the last decomposition step.

On the other side, we find that compounds with methyl or ethyl groups in site 2 are more stable than the others. This point could be associated with the possibility of an additional C—H···O bond of the alkyl group in site 2.

As in ref. 1, no relation seems to exist between the pK_a of the base and the kinetic parameters. In order to find complementary information about these compounds a decomposition study by means of isothermal techniques is being continued in our laboratory.

REFERENCES

1 J.M. Arrieta, P. Gili and M.J. Tello, Thermochim. Acta, 44 (1981) 109 and references cited therein.

2 M.J. Tello, E.H. Bocanegra, P. Gili, L. Lorente and P. Roman, Thermochim. Acta, 12 (1975) 65.

3 V. Satava, Thermochim. Acta, 2 (1971) 423.

4 B.W. Clare, D.L. Kepert and D.W. Watss, J. Chem. Soc., Dalton Trans., (1973) 2481.

5 T. Debaerdemaeker, J.M. Amigo and J.M. Arrieta, to be published.