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# THERMAL DECOMPOSITION KINETIC PARAMETERS OF SOME ORGANIC DECAVANADATES(I)

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Within the general field related to the polyanions of organic bases special interest has arisen in the decavanadates since Evans [1] established the correct formulation of the decavanadate ion. Until now most work has dealt with the inorganic decavanadates [1—5] and of those with organic bases only the quinoline and isoquinoline decavanadates [6] have been synthesized.

As a next step in our program of studying the polyanions of organic bases and taking into account the interesting results relating to molybdates [7,8], we present in this paper a study of the thermal stability and kinetic parameters related to the thermal decomposition for a group of decavanadates of organic bases $[(BH_3)_3H_3V_{10}O_{28} \cdot xH_2O$ with $0.5 \leqslant x \leqslant 2$ and B = 2-methylpyridine (= $J_2$), 3-methylpyridine (= $J_3$), 4-methylpyridine (= $J_4$), 2-ethylpyridine (= $J_5$) or 3-ethylpyridine (= $J_6$)] which were synthesized for the first time in our laboratory [9] and which are enumerated in Table 1. The kinetic study was made in a dynamic regime and the theoretical analyses were similar to those described in a previous paper [7]. Therefore all the symbols used here are the same as in ref. 10.

## EXPERIMENTAL

The synthesis and characterization (IR, UV, NMR and X-ray diffraction) are described in ref. 9. All the compounds have a low solubility in water and dimethyl sulphoxide and are almost insoluble in the usual organic solvents. Results of conventional chemical analysis appear in Table 1. Vanadio was analyzed as $V_2O_5$ before the thermal decomposition of each compound at 550°C for 2 h in an air atmosphere. This point was confirmed by means of X-ray diffraction. The apparatus, experimental conditions and spread in the processed data have been described in refs. 8 and 11.

## RESULTS AND DISCUSSION

From Table 2 we can observe that all compounds studied exhibit a three-step decomposition pattern leading to a residual weight equal to that expected for $VO_2$ when the process is carried out in an atmosphere of nitrogen. This point was confirmed by means of X-ray diffraction. In order to obtain complementary information, the $\alpha$ vs. $t$ curves were plotted for each

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TABLE 1

Chemical analysis

| Compound | | $V_2O_5$ | | C | | H | | N | |
|---|---|---|---|---|---|---|---|---|---|
| | | Theor. | Exp. | Theor. | Exp. | Theor. | Exp. | Theor. | Exp. |
| $J_2$ | $(C_6H_7NH)_3\ H_3V_{10}O_{28} \cdot 1/2\ H_2O$ | 72.64 | 72.57 | 17.25 | 17.52 | 2.25 | 2.36 | 3.35 | 3.42 |
| $J_3$ | $(C_6H_7NH)_3\ H_3V_{10}O_{28} \cdot 3/2\ H_2O$ | 71.61 | 71.57 | 17.03 | 17.53 | 2.28 | 2.36 | 3.31 | 3.52 |
| $J_4$ | $(C_6H_7NH)_3\ H_3V_{10}O_{28} \cdot 2\ H_2O$ | 71.11 | 71.30 | 16.91 | 17.46 | 2.44 | 2.42 | 3.29 | 3.57 |
| $J_5$ | $(C_6H_7NH)_3\ H_3V_{10}O_{28} \cdot 1/2\ H_2O$ | 70.28 | 70.44 | 19.49 | 19.38 | 2.65 | 2.78 | 3.25 | 3.50 |
| $J_6$ | $(C_6H_7NH)_3\ H_3V_{10}O_{28} \cdot 1\ H_2O$ | 69.80 | 69.57 | 19.36 | 19.73 | 2.71 | 2.69 | 3.23 | 3.57 |

TABLE 2

$E_a$, $T_i$ and $T_f$ for the three decomposition steps of the compounds studied

| Compound | First step | | | Second step | | | Third step | | |
|---|---|---|---|---|---|---|---|---|---|
| | $T_i$ (°C) | $T_f$ (°C) | $E_a$ (kJ mole$^{-1}$) | $T_i$ (°C) | $T_f$ (°C) | $E_a$ (kJ mole$^{-1}$) | $T_i$ (°C) | $T_f$ (°C) | $E_a$ kJ mole$^{-1}$) |
| $J_2$ | 171 | 246 | 36.92 | 256 | 371 | 14.97 | 376 | 459 | 100.36 |
| $J_3$ | 143 | 218 | 33.29 | 223 | 293 | 29.83 | 393 | 436 | 170.40 |
| $J_4$ | 112 | 192 | 22.32 | 197 | 292 | 11.90 | 362 | 492 | 60.49 |
| $J_5$ | 157 | 242 | 15.16 | 252 | 397 | 13.50 | 407 | 537 | 59.37 |
| $J_6$ | 123 | 243 | 23.07 | 248 | 353 | 18.29 | 368 | 517 | 48.82 |

step. From these plots we find that the first step of $J_2$, $J_3$, $J_4$ and $J_5$ compounds and the third step of $J_2$, $J_4$, $J_5$ and $J_6$ compounds correspond to a reaction with an initial large induction period followed by an acceleratory one up to $\alpha \simeq 0.5$. From this point a deceleratory period begins in which the reaction rate is lower. For the first step of $J_5$, second step of $J_2$ and third step of $J_3$ compounds we have the same physical situation but with a short induction period. For the other steps the initial induction period has disappeared and the initial acceleratory period shows a high reaction rate. In any case we find the more complicated reaction which appears in the molybdates given in Fig. 2a in ref. 7. The experimental results indicate that the pathway is not simple and therefore we cannot predict a clear pattern for each step and only the whole process can be written as follows

$$(BH)_3H_3V_{10}O_{28} \cdot x\ H_2O(s) = 10\ VO_2(s) + \text{gases}$$

within the accuracy of Satava's method from the plot of ln F($\alpha$) vs. $1/T$ the straight line criterium is fulfilled in the three steps for all the compound by the equation

$$(-\ln(1-\alpha))^{1/3} = KT$$

which gives a random nucleation mechanism as the rate-determining process. From the plot it is observed that the process becomes more complex in the successive steps. The activation energy values for each step are shown in Table 2. In order to see the possible relation between the kinetic parameters with the p$K_a$ values of the organic bases the p$K_a$ vs. $E_a$ and p$K_a$ vs. $T_i$ were plotted and, although different from the molybdates, no conclusive results were found on this point. It seems that in this case symmetry and steric effects are more important as well as the possible formation of hydrogen bonds between the substituent and the oxygen of the polyanion. The possible influence of the presence of water molecules in the first step of the decomposition must also be taken into account. In order to advance in this interpretation complete structural studies are being carried out in our laboratory.

## REFERENCES

1 H.T. Evans, Jr., Inorg. Chem., 5 (1966) 967.
2 A. Fock, Z. Kristallogr., 17 (1897) 1.
3 C. Radau, Ann. Chem. Liebing, 251 (1889) 114.
4 H.T. Evans, Jr., A.G. Swallow and W.H. Barnes, J. Am. Chem. Soc., 86 (1964) 4209.
5 A.G. Swallow, F.R. Ahmed and W.H. Barnes, Acta Crystallogr., 21 (1966) 397.
6 F. Corigliano and S. Di Pascuale, Inorg. Chim. Acta, 12 (1975) 99.
7 M.J. Tello, L. Lorente, P. Roman, P. Gili and C. Santiago, Thermochim. Acta, 21 (1977) 135.
8 M.J. Tello, E.H.Bocanegra, P. Gili, L. Lorente and P. Roman, Thermochim. Acta, 12 (1975) 65.
9 J.M. Arrieta, Doctoral Thesis, Bilbao, 1980.
10 V. Satava, Thermochim. Acta, 2 (1971) 423.
11 M.R. Alvarez, J.J. Icaza, E.H. Bocanegra and M.J. Tello, Thermochim. Acta, 12 (1975) 117.