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THERMOGRAVIMETRIC STUDY OF SOME DICHROMATES AND MOLYBDATES OF ORGANIC BASES

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ABSTRACT

A comparative study is made of the thermal and kinetic stabilities of the thermal decomposition of dichromates and molybdates of organic bases with formulae $(BH)_2Cr_2O_7$ and $(BH)_4Mo_8O_{26}$, respectively. The compounds show several steps of decomposition controlled by a random nucleation mechanism.

INTRODUCTION

In previous works [1—6] the kinetics of the thermal decomposition of some molybdates of organic bases have been investigated, relations being obtained between the pK_a of the bases, the initial temperatures of decomposition and the activation energies obtained by dynamic methods. A connection was also found between the initial decomposition temperatures and the symmetry of steric effects of the organic bases.

Continuing a systematic investigation of oxoanions of organic bases, the kinetics of the thermal decomposition of organic based dichromates $\{(BH)_2Cr_2O_7\}$ and molybdates of the same bases $\{(BH)_4Mo_8O_{26}\}$ studied by thermogravimetry are reported here. The bases are: 2-methylquinoline (C-1 for the dichromate and M-1 for the molybdate); 4-methylquinoline (C-2 for the dichromate and M-2 for the molybdate); 6-methylquinoline (C-3 for the dichromate and M-3 for the molybdate); and 8-methylquinoline (C-4 for the dichromate and M-4 for the molybdate). The kinetic study has been carried out in a dynamic regime following the theoretical model of Šatavá [13].

EXPERIMENTAL

The compounds were prepared for the first time in our laboratory, the X-ray and IR characterization being described in refs. 3 and 7. The molybdates proved to have a low solubility in water, being soluble only in acids and concentrated inorganic bases, with very low solubility in the usual organic solvents. The dichromates, on the contrary, are soluble in cold water, slightly soluble in ethanol and acetone and only very slightly in ether and benzene. They are sensitive to sunlight and humidity. With aqueous solutions as starting material, crystals were obtained in both the molybdates and dichromates.

By IR spectroscopic methods and V—UV, evidence is obtained for the existence of the protonated base in all the compounds as also for the $Cr_2O_7^{2-}$ anion. The determination of the structure by X-ray in a monocrystal of a compound similar to the molybdates under study shows that it is an octomolybdate $(BH)_4Mo_8O_{26}$ [8] and not a tetramolybdate as described in ref. 3, since the studies were carried out on polycrystalline samples and were represented by the simplest formulae.

Both the equipment and the experimental conditions have been described refs. 9 and 10. Several runs were made on each sample with good reproducibility.

RESULTS AND DISCUSSION

The stability interval was obtained for each compound studied from thermogravimetric curves (Table 1). Decomposition of the dichromates begins in the 355—362 K interval and occurs in a violent way, so the work had to be carried out at a heating rate of 1.25°C min^{-1}. However, the molybdates present a higher interval in the initial temperature of decomposition, 417—474 K, and are less energetic than the dichromates. All the dichromates present three steps in the thermal decomposition, except compound C-3 which shows five.

In accordance with the weight loss, the following decomposition equations may be given for compounds C-1 and C-2

1st step: $(BH)_2Cr_2O_7 \rightarrow B + H_2O + B \cdot 2\,CrO_3$

2nd step: $B \cdot 2\,CrO_3 \rightarrow 2\,CrO_2 + B + O_2$

3rd step: $2\,CrO_2 \rightarrow Cr_2O_3 + 1/2\,O_2$

Compounds C-3 and C-4 follow the same behaviour pattern for the first step but differ thereafter. However, the global process is identical for all

$$(BH)_2Cr_2O_7 \rightarrow Cr_2O_3 + H_2O + 2\,B + 3/2\,O_2$$

The Cr_2O_3 is confirmed by X-ray, allowing the quantitative determination of the chrome content of the compounds to be established with great precision.

$CrO_3 \cdot B$ addition compounds are well known [11,12], as is the ferromagnetic and metallic conductor CrO_2. The chrome passes from an initial state (VI) to a final state (III). As for the molybdates, compounds M-1 and M-4 present three decomposition steps while M-2 and M-3 show only two. In accordance with weight losses, the following model of decomposition may be given for compounds M-1 and M-4

1st step: $(BH)_4Mo_8O_{26} \rightarrow 8\,MoO_3 \cdot 5/2B + 3/2\,B + 2\,H_2O$

2nd step: $8\,MoO_3 \cdot 5/2\,B \rightarrow 8\,MoO_3 \cdot B + 3/2\,B$

3rd step: $8\,MoO_3 \cdot B \rightarrow 8\,MoO_3 + B$

TABLE 1

Initial and final temperatures of decomposition and activation energy for each decomposition step of the compounds studied

Compound	1st step			2nd step			3rd step			4th step			5th step		
	T_i(K)	T_f(K)	E_a kJ (mole^{-1})	T_i	T_f	E_a	T_i	T_f	E_a	T_i	T_f	E_a	T_i	T_f	E_a
C-1	362	408	30.13	523	649	21.97	649	688	59.00						
C-2	361	382	43.86	570	632	35.43	672	704	97.35						
C-3	355	374	35.61	374	395	35.43	408	430	37.54	600	670	32.64	670	797	14.25
C-4	362	414	16.08	586	656	32.06	656	744	20.98						
M-1	474	545	21.50	557	641	17.48	641	758	19.66						
M-2	473	557	12.92	557	689	8.01									
M-3	417	561	4.22	605	688	23.24									
M-4	446	497	29.76	497	567	8.69	596	755	11.60						

For compounds M-3 and M-2, we have
1st step: $(BH)_4Mo_8O_{26} \rightarrow 8\ MoO_3 \cdot 4/5\ B + 16/5\ B + 2\ H_2O$
2nd step: $8\ MoO_3 \cdot 4/5\ B \rightarrow 8\ MoO_3 + 4/5\ B$
According to the experimental results the global process is

$$(BH)_4Mo_8O_{26} \rightarrow 8\ MoO_3 + 4\ B + 2\ H_2O$$

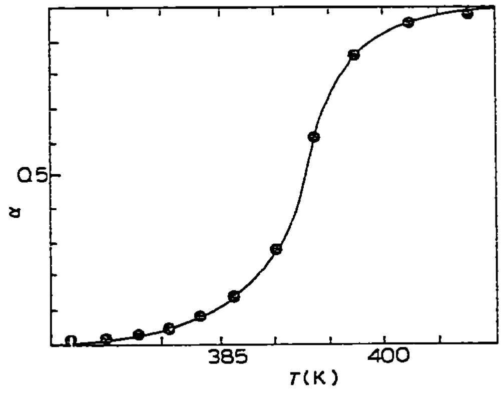
Addition compounds of general formula MoO_3nB as described previously [3—5] are also presented here, but there is no reduction in the Mo(VI) in the final product, which is not the case of the dichromates. The MoO_3 was confirmed by means of X-ray diffraction.

Selected α vs. T. curves for the dichromates are presented in Figs. 1 and 2. The curves obtained show a reaction with an initial acceleratory period followed by a deceleratory one. In some cases such as the second step of compound C-3, for example, the behaviour is more complex.

The α vs. T curves are shown for the molybdates in Figs. 3 and 4. The shape of the curves in the first step is the same for all the compounds , being of the type previously described for the dichromates. Compounds M-1 and M-4 present curves in the second step of decomposition, in which there scarcely exists an acceleratory period. Finally, in the last step the α vs. T curves again become similar to those of the first step.

Figures 5 and 6 show a Šatavá analysis for the first steps of the decomposition for both the dichromates and the molybdates. Similar plottings were observed for all other compounds and for all decomposition steps examined.

It is observed that the straight line criterion is better fulfilled by the equation corresponding to a random nucleation: $g(\alpha) = \{-\ln(1-\alpha)\}^{1/3}$. The rate-determining process must be related to the structure of the compounds. In the case of the dichromates, there are two CrO_4^{2-} ions of tetrahedral symmetry bonded by a vertex, while in the molybdates there are groups of 8 MoO_6 octahedra which join to form polymeric chains. Although the thermal



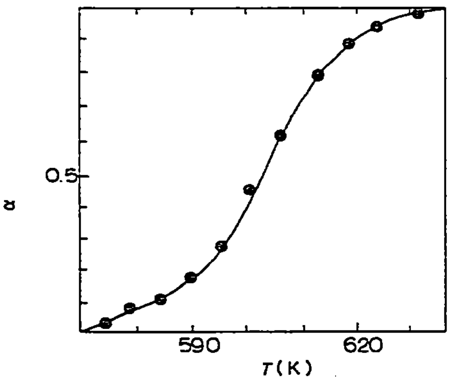
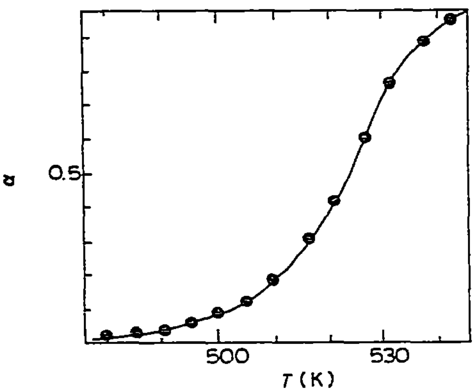


Fig. 1. Fraction of decomposed material (α) vs. temperature for the first step of compound C-1.

Fig. 2. Fraction of decomposed material (α) vs. temperature for the second step of compound C-2.



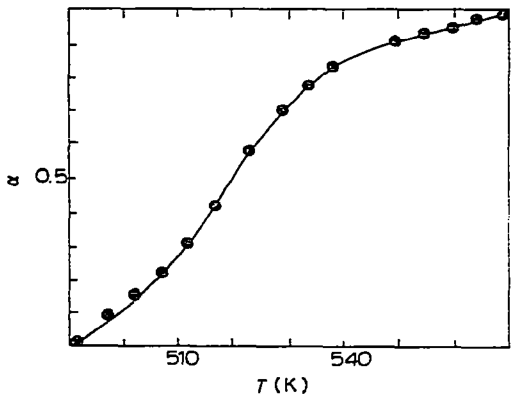


Fig. 3. Fraction of decomposed material (α) vs. temperature for the first step of compound M-1.

Fig. 4. Fraction of decomposed material (α) vs. temperature for the second step of compound M-4.

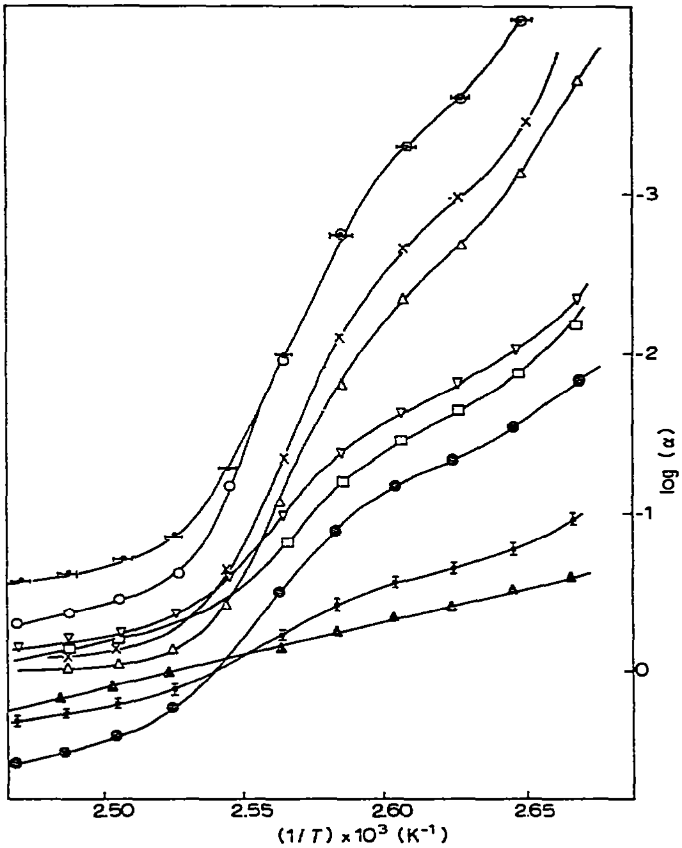


Fig. 5. Šatavá representations for the first step of compound C-1. △, D_1; ×, D_2; ⊙, D_3; ⊢⊣, D_4; ●, F_1; I, A_2; ▲, A_3; □, R_2; +, R_3 [13].

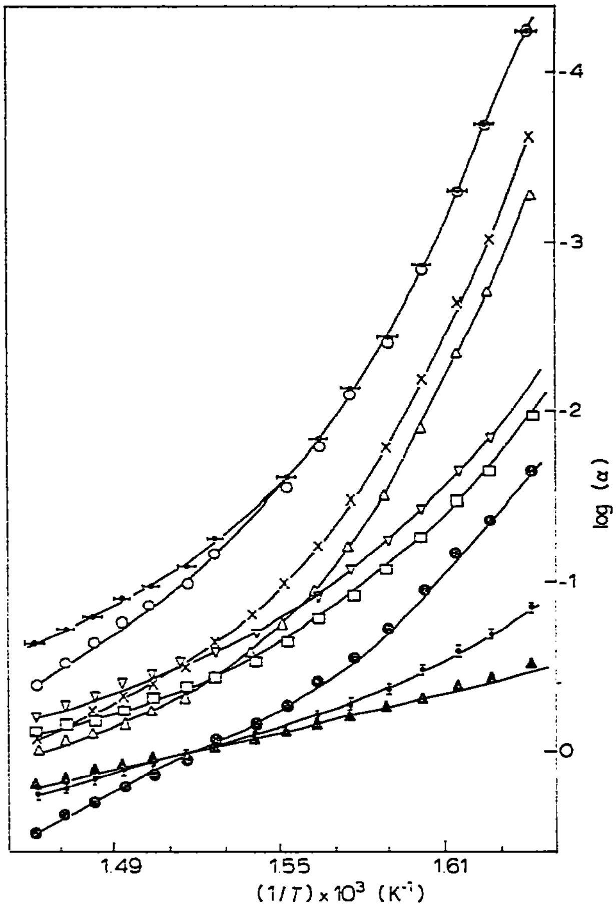


Fig. 6. Šatavá representations for the second step of compound M-3. The symbols have the same meaning as in Fig. 5.

decomposition kinetics of dichromates and molybdates follow the same random nucleation process, they present different behaviour patterns regarding the activation energy values. In general, the values of this parameter are greater in the dichromates than in the molybdates. Although the structure of the former is simpler, the decomposition brings about changes in the states of oxidation of the metal, which must imply greater activation energies. The structure of the $Cr_2O_7^{2-}$ ion is also very different from that of the Cr_2O_3. Contrarily, the molybdates present no changes in the states of oxidation and no changes exist in the coordination of the metal when passing from $(BH)_4Mo_8O_{26}$ to the MoO_3.

The values of the initial temperatures of decomposition of the dichromates indicate that the order of stability is: $C_3 < C_2 < C_1 \simeq C_4$. According to the position of the methyl group in the molecule of quinoline, steric effects should be produced and the incorporation of the methyl group in position 6 with regard to the nitrogen of the quinoline is what brings about the lesser thermal stability for the dichromate.

In the case of the molybdates, the order followed with regard to thermal stability is: $M_3 < M_4 < M_2 \simeq M_1$. It is also observed here that the 6-methylquinoline compound is the least stable. However, the order of stability is modified with regard to the dichromates. In studies carried out on tetramolybdates of methylated, ethylated and aminated derivatives of pyridine at positions 2, 3 and 4 [1—5] it is observed that the position of the alkyl group or the amine group produces a stablization upon emigration of the said group from position 2 to 4. These compounds have different bases from those studied in the present work and a symmetry observed in them is not to be found in the bases under study here. Relations have not been observed between the pK_a activation energy and initial temperatures of decomposition as in ref. 5.

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