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Note

KINETIC PARAMETERS FOR THE THERMAL DECOMPOSITION REACTIONS OF CrO_3 IN AIR

Y. LAUREIRO, M. GAITAN, A. JEREZ, C. PICO and M.L. VEIGA *

Departamento de Química Inorgánica I, Facultad de Ciencias Químicas,
Universidad Complutense, 28040-Madrid (Spain)

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INTRODUCTION

Chromium oxides constitute a family of compounds with interesting magnetic and catalytic properties, which can be obtained, under various conditions [1–3], by the thermal decomposition of the highest oxide, CrO_3. However the conclusions drawn from the literature of this field cannot easily be compared because of the variations in experimental conditions. There has been no systematic study of the kinetics of the interconversion process, although some kinetic data can be found in the literature [4,5].

The aim of this Note is to establish the thermal behaviour of CrO_3 in air, and to determine the mechanisms and kinetic parameters of the involved processes of decomposition, for which we have considered the methods proposed by Jerez et al. [6], and by Achar et al. [7].

EXPERIMENTAL

The starting material was analytical grade CrO_3, supplied by Merck (FDR).

Thermal runs were performed in air at a heating rate of $4^\circ C\ min^{-1}$, using sample sizes of about 10 mg, in a Mettler TA3000 system equipped with a TG50 microbalance.

Thermal decomposition products were identified by powder X-ray diffraction in a Siemens Kristalloflex D500 diffractometer, using Cu $K\alpha$ radiation.

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* Author to whom all correspondence should be addressed.

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RESULTS AND DISCUSSIONS

Figure 1 shows TG and DTG curves for CrO_3. The three processes observed can be interpreted as

1) $6CrO_3 \xrightarrow[-O_2]{250-360\,°C} 2Cr_3O_8$: experimental weight loss, 5.4%;
calculated, 5.3%.

2) $2Cr_3O_8 \xrightarrow[-1/2O_2]{360-435\,°C} 3Cr_2O_5$: experimental weight loss, 2.6%;
calculated, 2.7%.

3) $3Cr_2O_5 \xrightarrow[-3O_2]{435-495\,°C} 3Cr_2O_3$: experimental weight loss, 16.2%;
calculated, 16.0%.

in which the weight loss percentages are with reference to the initial CrO_3.

The decomposition products Cr_3O_8, Cr_2O_5 and Cr_2O_3 were isolated as poorly crystallized solid phases, which, nevertheless, yielded readable X-ray diffraction patterns, listed in Table 1. For each compound the *d*-spacings are unambiguously concordant with those previously cited in the literature [8], (A.S.T.M. powder diffraction cards numbers 36-1330 for Cr_3O_8, 36-1329 for Cr_2O_5 and 6-504 for Cr_2O_3,and references quoted thereon).

Kinetic analyses were performed according to the method proposed by Jerez et al. [6], and the method of Achar et al. [7]. Results are presented in Tables 1–3, in which the analysed mechanisms are referred to with the

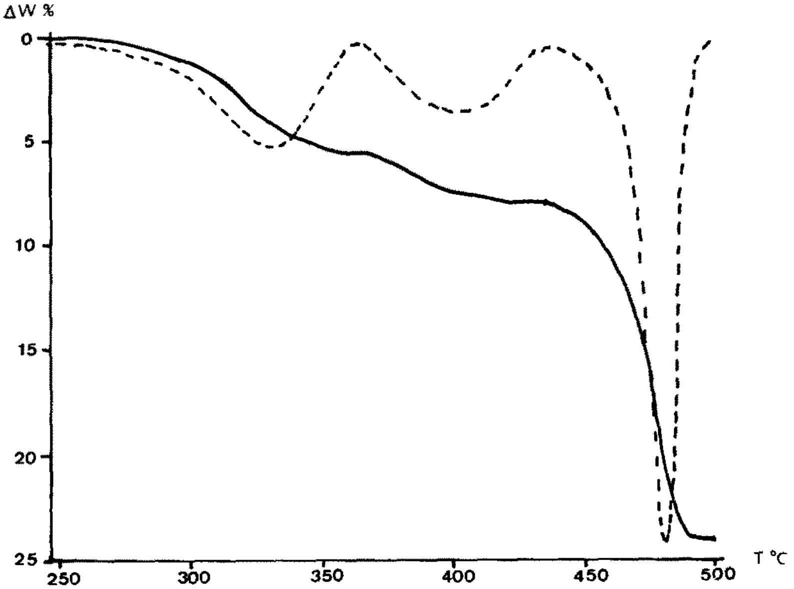

Fig. 1. Thermogravimetric curves for CrO_3 in air: ———, TG; — — —, DTG.

TABLE 1

Observed *d*-spacings (in Å) for the products of thermal decomposition of CrO_3

Cr_3O_8	Cr_2O_5	Cr_2O_3
11.9	8.50	3.65
6.20	6.28	2.64
5.87	5.99	2.49
4.92	5.01	2.25
4.48	3.26	2.19
3.80	3.10	2.00
3.70	3.02	1.82
3.34	2.79	1.66
3.20	2.17	
3.09		
2.95		
2.80		
2.65		
2.60		
2.12		
2.00		
1.92		

TABLE 2

Results of the kinetic analysis for process 1

Mechanism	Method of Jerez et al.			Method of Achar et al.		
	r	E^*/R (K)	i	r	$\ln A/\beta$	E^*/R (K)
D1	−0.995	37947	1.282	−0.842	18.895	13864
D2	−0.995	38663	0.923	−0.953	31.021	21280
D3	−0.995	38579	0.740	−0.976	30.855	24612
D4	−0.995	38579	0.406	−0.994	45.977	30833
F1	−0.994	20241	0.0117	−0.999	30.192	20004
R2	−0.994	20241	0.512	−0.948	13.416	10672
R3	−0.994	20241	0.345	−0.984	18.371	13782
	$A = 1.95 \times 10^{14}$ s^{-1}			$E^* = 166$ kJ mol^{-1}		

TABLE 3

Results of the kinetic analysis for process 2

Mechanism	Method of Jerez et al.			Method of Achar et al.		
	r	E^*/R (K)	i	r	$\ln A/\beta$	E^*/R (K)
D1	−0.992	44739	1.043	−0.940	27.059	20866
D2	−0.992	45800	0.673	−0.986	41.219	30589
D3	−0.992	45677	0.491	−0.993	45.963	34690
D4	−0.992	45677	0.158	−0.999	57.799	42454
F1	−0.989	19907	−0.243	−0.999	35.309	25810
R2	−0.989	19907	0.257	−0.984	16.860	14164
R3	−0.989	19907	0.0907	−0.996	22.373	19846
	$A = 7.81 \times 10^{10}$ s^{-1}			$E^* = 165$ kJ mol^{-1}		

TABLE 4

Results of the kinetic analysis for process 3

Mechanism	Method of Jerez et al.			Method of Achar et al.		
	r	E^*/R (K)	i	r	$\ln A/\beta$	E^*/R (K)
D1	−0.991	62004	1.431	−0.998	56.330	45770
D2	−0.991	62306	0.990	−0.999	62.917	51082
D3	−0.991	62272	0.817	−0.999	64.061	53016
D4	−0.991	62272	0.484	−0.998	69.246	56802
F1	−0.987	30319	−0.019	−0.999	36.901	30543
R2	−0.987	30319	0.481	−0.998	28.430	24865
R3	−0.987	30319	0.315	−0.998	30.617	26757
	$A = 1.59 \times 10^{17}$ s^{-1}			$E^* = 254$ kJ mol^{-1}		

classification symbols of Sharp et al. [9]. As can easily be seen, the slopes (E^*/R) obtained from both methods are concordant when the intercept of the straight line determined from the method of Jerez et al. is closest to zero. From these values of slopes and intercepts obtained from the method of Achar et al. for the established mechanism, activation energy and preexponential factor values were calculated and are also listed in Tables 2–4. As can be seen, the best fit is obtained for the mechanisms F1 (decomposition of CrO_3 to Cr_3O_8), R3 (decomposition of Cr_3O_8 to Cr_2O_5) and F1 (decomposition of Cr_2O_5 to Cr_2O_3).

We can observe that the obtained value of E^* for the decomposition reaction of Cr_2O_5, 254 kJ mol^{-1} is very close to that reported by Kubota [4], 258 kJ mol^{-1}, which was calculated by an isothermal method.

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