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Note

THERMOGRAVIMETRIC STUDIES OF SILICA-GEL SUPPORTED CHROMIC ACID REAGENT

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Silica-gel supported chromic acid reagents are useful for many organic reactions in a solid matrix [1,2]. Chromium(VI) has been found to oxidize primary and secondary alcohols in the form of tetraoxochromic acid which forms a rapid equilibrium mixture with a chromium(VI)–alcohol complex mixture [3]. The rate determining step is considered to be a two-electron transfer yielding chromium(IV).

The present work is devoted to the study of the silica-gel supported chromic acid reagent by thermogravimetric method so as to evaluate the thermal stability of the reagent and the nature of thermochemical processes in air up to 1073 K. The optical density vs. wavelength plots of both the original reagent and its preheated form were obtained by spectrophotometric studies of their solutions in mild sulphuric acid.

EXPERIMENTAL

The silica-gel supported chromic acid reagent was supplied by S. Dev and co-workers of Multi-chem Research Centre, Nandesari, and contained 0.1263 g of $Na_2Cr_2O_7 \cdot 2\,H_2O$ per gramme of the reagent equivalent to 0.424 mole. This sample was used for recording the TG data on a balance supplied by the FCIL, Sindri, at a heating rate of 10°C min^{-1} up to 1073 K in air. A portion of the sample was also heated in a nickel crucible over a burner in air for several hours. The original yellow-brown free-flowing material changed into a heterogeneous mixture of a yellow and green residue. Solutions of the original and the preheated reagent in dilute sulphuric acid were used to record the optical density on a Beckman BG-grating spectrophotometer. The λ_{max} for both the solutions were found to be 440 μm corresponding to Cr_2O_7(II). Figures 1, 2 and 3 exhibit the TG plot and plots for $g(\alpha)$ vs. time and $\log_e[g(\alpha)/T^2]$ vs. $1000/T$ for $n = 1$, 2 and 3, respectively. The rate constants and energy of activation of the three distinct thermal events were evaluated from these plots [4] and are reproduced in Table 1.

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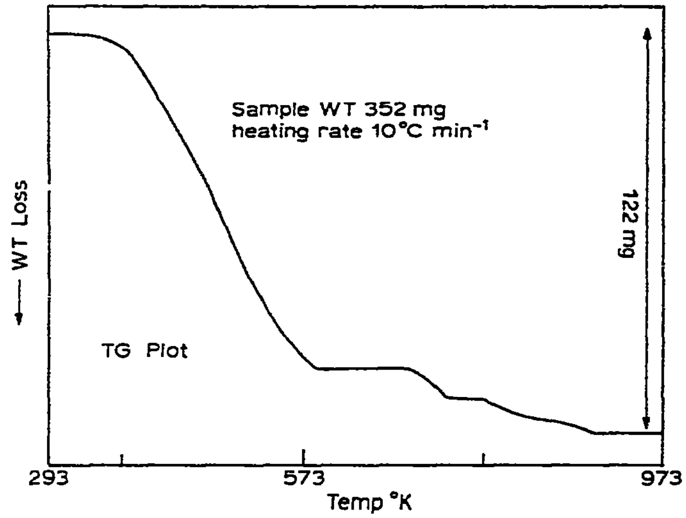

Fig. 1. TG plot for silica-gel supported chromic acid reagent from 293 to 973 K.

RESULTS AND DISCUSSION

Dried silica-gel retains water tenaciously. The chromic acid reagent supported on silica-gel, as its preparation suggests, is expected to contain much water even after drying under reduced pressure. The reagent, from its method of preparation, can also be assumed to contain $HCrO_4$(I) and $CrO_3 \cdot O \cdot SO_3$(II) ions as active constituents for oxidation reactions. The first major weight-loss step (29.3%) in the TG plot from 353 to 593 K can be attributed to the decomposition of these products

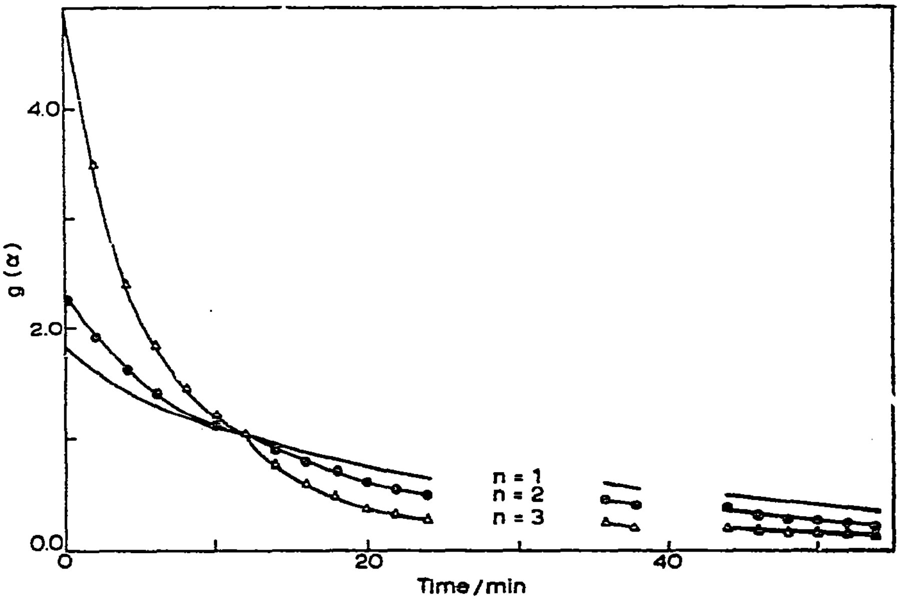

Fig. 2. Plots of $g(\alpha)$ vs. time for $n = 1$, 2 and 3 for silica-gel supported chromic acid.

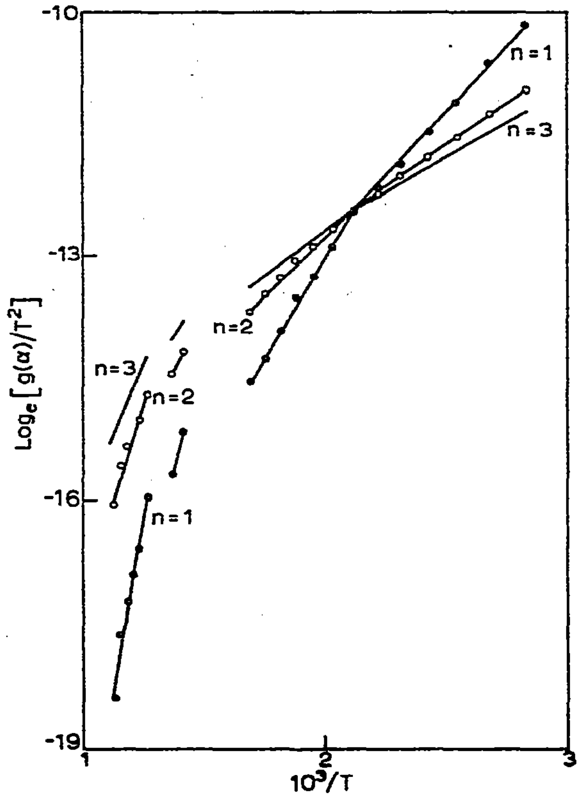

Fig. 3. Plots of $\ln[g(\alpha)/T^2]$ vs. $1000/T$ for $n=1$, 2 and 3 for silica-gel supported chromic acid.

with evolution of water and sulphuric anhydride leaving a residue of chromic(VI) oxide in the silica-gel support. However, the two-step weight losses from 353 to 473 K and from 473 to 593 K indicate that dehydration of $Na_2Cr_2O_7 \cdot 2\,H_2O$ occurs first (13.9% loss) followed by decomposition of tetraoxochromic acid from 473 K onwards (15.4% loss). These data compare well with the theoretical data for similar weight-loss events. The residue at 593 K remains stable up to 713 K and there are two further weight-loss steps beginning at 713 and 793 K, respectively. These steps

TABLE 1

TG data and kinetic parameters of thermal changes of silica-gel supported chromic acid

Wt. loss (%)	Temp. range for thermochemical reactions (K)	Rates of reaction ($\times 10^{-2}$ min^{-1})			Activation energy (kJ mole^{-1})		
		$n=1$	$n=2$	$n=3$	$n=1$	$n=2$	$n=3$
13.9	353–473	32.0	10.3	6.0	59.2	37.5	30.1
15.4	473–593	6.3	4.6	3.5	97.0	58.9	46.2
2.5	713–733	2.2	3.5	3.5	223.7	128.5	99.9
2.9	793–893	0.56	1.5	1.8	333.1	182.2	133.3

can be attributed to the partial decomposition of chromic(VI) oxide to chromic(III) oxide through the formation of a mixed residue of strongly paramagnetic Cr_6O_{15} and ferromagnetic Cr_5O_9. However, these two-step decomposition reactions at elevated temperatures take place at much higher temperatures as compared to the thermal behaviours of chromic(VI) oxide [5]. The earlier work mentions the formation of the intermediate products between 573 and 673 K and the final product Cr_2O_3 only beyond 773 K. In the present study these thermochemical changes not only occur at higher temperatures but the conversion of chromic(VI) oxide is also partial. The silica-gel support therefore, permits the formation of included CrO_3 complex in its pores as a result of heating to 593 K and makes the inclusion species quite stable towards further thermal change. After a partial transformation around 713 K a heterogeneous residue of CrO_3 and Cr_2O_3 remains beyond 893 K.

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