

EPR Study of the Radicals Formed during the Vacuum Thermal Decomposition of $(\text{NH}_4)_2\text{Mg}(\text{S}_2\text{O}_3)_2 \cdot 6\text{H}_2\text{O}$

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Received July 5, 1976

It has been previously shown¹⁻⁶ that the gaseous species produced during the thermolysis of some inorganic oxysalts could be retained at the support surface as molecular or ionic adsorbed species. Oxalates and thiosulfates turned out to be very good examples for studying the properties of radicals such as CO , CO^+ , CO_2^- , CO_4^- , O_3^{3-} (oxalates)¹⁻³ or SO_2^- , SO_3^- (thiosulfates and sulfites)^{4,5} and hence for investigating extensive decomposition mechanisms of the starting materials. On the other hand, carbon, oxygen and sulfur ions stabilized on the surface as radicals are supposed to play an important role in different catalytic processes.

The present approach consists in looking into the progressive decomposition *in vacuo* of a double thio-sulfate, $(\text{NH}_4)_2\text{Mg}(\text{S}_2\text{O}_3)_2 \cdot 6\text{H}_2\text{O}$ by the use of the combined TGA/EPR techniques.

Experimental

$(\text{NH}_4)_2\text{Mg}(\text{S}_2\text{O}_3)_2 \cdot 6\text{H}_2\text{O}$ has been prepared from $(\text{NH}_4)_2\text{S}_2\text{O}_3$ and $\text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ as described elsewhere.⁷

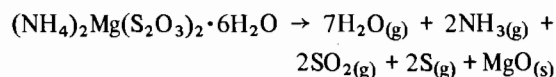
The course of decomposition was investigated by thermogravimetric analysis (TGA) in dynamic *vacuo* (5×10^{-3} torr) in the 25–830 °C temperature range, the thermograms being recorded on a TH-59 Adamel thermobalance. A heating rate of 150 °C h⁻¹ was used.

The EPR measurements were carried out using a X-band (9.56 GHz) Varian E-12 spectrometer, with a 100 kHz field modulation. The samples were heated *in vacuo* (10^{-4} torr) for every 25 degrees of temperature from room temperature up to 950 °C. After 30 min heating, the reaction was interrupted by cooling the tube and the spectra were then recorded *in vacuo* either at 77 or 300 °K. The g values were calculated by comparison with the g value of the DPPH radical ($g = 2.0036$).

Results and Discussion

We have previously shown⁷ that the vacuum thermal decomposition of $(\text{NH}_4)_2\text{Mg}(\text{S}_2\text{O}_3)_2 \cdot 6\text{H}_2\text{O}$ proceeds between 35 and 540 °C through several

complex steps, the solid residue at 540 °C being MgO. The whole reaction is to be written:



In the temperature range 185–850 °C, three different EPR signals, A, B and C, are observed.

The *signal A* is anisotropic (Fig. 1a and 1b) and appears between 185 and 850 °C; it shows a slight

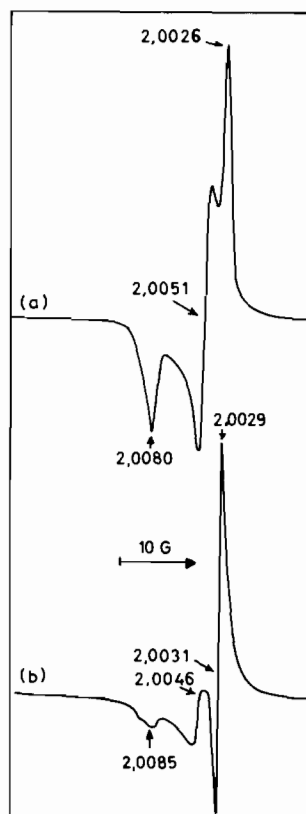


Figure 1. 25 °C EPR spectra of $(\text{NH}_4)_2\text{Mg}(\text{S}_2\text{O}_3)_2 \cdot 6\text{H}_2\text{O}$ activated a) at 275 °C, b) at 475 °C.

temperature dependence, the g values ranging from 2.0081 to 2.0085 for g_1 , from 2.0046 to 2.0051 for g_2 and from 2.0026 to 2.0029 for g_3 . The comparison of these g values with those of the SO_2^- radical adsorbed on various supports (Table I) indicates that the SO_2 evolved during the decomposition forms its anion radical on the solid residue.

The *signal B* (Fig. 1b) which is isotropic ($g_{\text{iso}} = 2.0031$) arises between 300 and 775 °C. Its intensity is rather weak. This signal is assigned to a SO_3^- radical by comparison of its shape and g value with those of the SO_3^- radicals occurring in various environments (Table I). The formation of SO_3^- is

TABLE I. g Values for the SO_2^- and SO_3^- Radicals.

	g Values			Ref.
	g_1	g_2	g_3	
SO_2^-/MgO (A)	2.0097	2.0052	2.0028	10
SO_2^-/MgO (B)	2.0078	2.0033	2.0014	10
$\text{SO}_2^-/\text{V}_2\text{O}_5$ -silica	2.008	2.006	2.002	11
$\text{SO}_2^-/\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ X-irradiated	2.0095	2.0070	2.0047	12
$\text{SO}_2^-/\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ γ -irradiated	2.0102	2.0057	2.0024	13
$\text{SO}_2^-/\text{CdS}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ thermolysis	2.0096	2.0062	2.0023	4
$\text{SO}_2^-/\text{BaS}_2\text{O}_3 \cdot \text{H}_2\text{O}$ thermolysis	2.0115	2.0055	2.0029	4
$\text{SO}_2^-/\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ thermolysis	2.0089	2.0041	2.0022	5
$\text{SO}_2^-/\text{CdSO}_3 \cdot 2\text{H}_2\text{O}$ thermolysis	2.0082	2.0037	2.0022	5
$\text{SO}_2^-/(\text{NH}_4)_2\text{Mg}(\text{S}_2\text{O}_3)_2 \cdot 6\text{H}_2\text{O}$ thermolysis	2.0080 \rightarrow 2.0085	2.0046 \rightarrow 2.0051	2.0026 \rightarrow 2.0029	This work
	g_{iso}			
SO_3^-/MgO	2.0034			8
$\text{SO}_3^-/\text{K}_2\text{H}_2(\text{SO}_3)_2$	2.0036			14
$\text{SO}_3^-/\text{taurine}$	2.0035			15
$\text{SO}_3^-/\text{CdS}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ thermolysis	2.0034			4
$\text{SO}_3^-/(\text{NH}_4)_2\text{Mg}(\text{S}_2\text{O}_3)_2 \cdot 6\text{H}_2\text{O}$ thermolysis	2.0031			This work

believed to occur *via* the sulfite ions, the latter being retained on the surface of MgO as SO_3^- radicals, either by straightforward decomposition of $\text{S}_2\text{O}_3^{2-}$ entities into SO_3^- and sulfur, or by reaction of gaseous or adsorbed sulfur dioxide and residual oxygen retained at the surface of the solid residue; a possible mechanism of SO_3^- formation could involve an intermediate complex.^{4,8} The second hypothesis is supported by the relative intensity changes of the signals A and B as a function of temperature (Fig. 2). It can be seen that SO_3^- is formed right when the amount of SO_2^- is decreasing.

The *signal C*, of weak intensity, is observed between 520 and 700 °C. It could be seen that only one g value could be determined (2.046), the other components of this highly anisotropic signal being probably obscured by the other two intense peaks (signals A and B). The g value of the signal C is similar to the one observed by Lunsford *et al.*⁹ in the case of a S_3^- radical adsorbed on MgO; this species was characterised by the following g values: $g_1 = g_2 = 2.043$; $g_3 = 2.004$. Stable S_3^- species were supposed to result from the reaction of the elemental sulfur

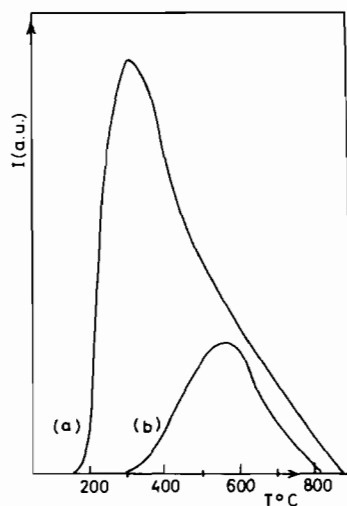


Figure 2. Temperature dependence of the intensities (arbitrary units) a) of the SO_2^- EPR signal, b) of the SO_3^- EPR signal.

with the MgO surface at 400 °C.⁹ We have actually shown⁷ that alkali and magnesium thiosulfates under-

go thermal decomposition *in vacuo* by releasing elemental sulfur in the temperature range 350–600 °C; the sulfur is able to react with the solid residue, *i.e.* MgO in the case of $(\text{NH}_4)_2\text{Mg}(\text{S}_2\text{O}_3)_2 \cdot 6\text{H}_2\text{O}$, and to form S_3^- radical. Further studies are being carried out to support these assumptions.

Conclusion

Our contribution shows that EPR could be a quite powerful technique to complete thermogravimetry data when paramagnetic species are produced during the course of the decomposition.

Although the TGA curve reveals that the thermal decomposition of $(\text{NH}_4)_2\text{Mg}(\text{S}_2\text{O}_3)_2 \cdot 6\text{H}_2\text{O}$ is complete at 540 °C, the solid residue being MgO, EPR data show that various sulfur adsorbed radicals can be retained stable at the MgO surface at far higher temperatures (850 °C for SO_2^-). As superficial and hence catalytic properties of oxydes such as MgO are strongly influenced by the presence of adsorbed radicals, the choice of an oxysalt as precursor for preparing catalytic active oxydes will be of the most critical importance.

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