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THRESHOLD LIMITS AND KINETICS OF THE NON-ISOTHERMAL DECOMPOSITION OF AMMONIUM NITRATE CATALYSED BY CHROMIUM IONS

STELIOS SKARIBAS, TIBERIUS C. VAIMAKIS and PHILIP J. POMONIS *

Department of Chemistry, University of Ioannina, Ioannina 45332 (Greece)

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ABSTRACT

Ammonium nitrate (AN) samples, containing varying amounts of Cr^{3+} cations were prepared and their mode of thermal decomposition was analysed under non-isothermal conditions in a thermogravimetric balance. Pure AN decomposes endothermically, but addition of Cr^{3+} in amounts larger than one mole of Cr^{3+} per 3000 moles of AN acts catalytically, changing the decomposition to an exothermic mode. At concentrations lower than this, the diffusion limitations prevent the condensation of Cr^{3+} species into $Cr_2O_7^{2-}$ which are the catalytically active species. The rates of decomposition, described by a typical Coats–Redfern kinetic equation, show two stages. Satisfactory results were obtained using a modified Coats–Redfern equation and by taking into account the continuous increment of chromium catalyst in the melt. The second stage of the decomposition shows an increased activation energy compared with the first. This is probably caused by a change in the rate-determining step of the reaction path, which is most likely the decomposition of dichromates.

INTRODUCTION

The thermal decomposition of ammonium nitrate (AN) has attracted the interest of many workers over the last thirty years [1–21]. The probable reason for this interest can be attributed to the fact that AN is an explosive compound; it is also produced in very large quantities as a common fertiliser. Therefore, particular care must be taken in order to avoid potentially disastrous conditions.

A particular feature of this reaction is that it is catalysed by chloride [5,6,14] and chromium compounds [7,8,12]. The mechanism by which those species act catalytically towards the decomposition is believed to be a chain one. Chromium compounds in particular show a greater catalytic action than other cations [12]. Although the detailed decomposition mechanism is

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* Author to whom correspondence should be addressed.

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rather complex, several incontrovertible conclusions have been reached. Among them is that the active species in the decomposition are the dichromates [8,12,22] which undergo continuous catalytic cycles in the acidic melt via Lux-type acid–base displacement, acidified to $HCrO_4^-$ and condensed again to $Cr_2O_7^{2-}$ whereas at the same time NO_3^- ions are deoxygenised to NO_2^+

$$Cr_2O_7^{2-} + NO_3^- \rightarrow 2CrO_4^{2-} + NO_2^+ \tag{1}$$

$$CrO_4^{2-} + H^+ \rightarrow HCrO_4^- \tag{2}$$

$$2HCrO_4^- \rightarrow Cr_2O_7^{2-} + H_2O \tag{3}$$

Then the NO_2^+ species undergo a number of reactions with NH_3 and/or NH_2^-, forming intermediate nitramides or nitrosamines which are then decomposed to nitrogen or nitrous oxide and water [12,18].

There are several questions arising from the above reactions. Firstly, if chromium was initially added to the mixture as Cr^{3+} ions, then, at low concentrations, formation of $Cr_2O_7^{2-}$ may be difficult because of diffusion limitations. The same limitations also apply to reaction (3). The threshold at which these limitations are overcome, thus leading to catalysed explosion, should be determined. In previous works, the amount of chromium initially used was constant at around 0.1–0.3 wt.% [8,12]. A second question relates to the rate-determining step (r.d.s.) of the decomposition which may be different at the initial and final stages of reaction. This may result from the changing concentrations of both ammonium nitrate and chromium species as the degree of decomposition tends to unity.

In this paper, we attempt to explore these questions by studying the thermal decomposition of AN samples containing different amounts of chromium. The study was carried out in a thermobalance under non-isothermal conditions. In such cases, the Coats–Redfern equation is often used to describe the process [23]. This equation is used in a modified form in order to describe our results.

EXPERIMENTAL

The specimens used in the thermogravimetric experiments (Table 1) contained molar ratios AN: Cr of 150000 : 1, 30000 : 1, 15000 : 1, 5000 : 1, 1500 : 1 and 150 : 1, designated ANCr-*n*, where *n* equals 1–7, corresponding to the seven specimens.

The calculated amounts of $Cr(NO_3)_3 \cdot 9H_2O$ (Merck p.a.) and NH_4NO_3 (Ferak p.a.) were dissolved in 100 ml of distilled water. 1 M NH_3 (Ferak) solution was added drop-wise to pH 9.2 with continuous stirring. The gel thus obtained was dried at 105 °C for 24 h and the resulting solid was ground in an agate mortar. The amount of NH_4NO_3 in the samples was

TABLE 1

Composition of samples prepared, activation energies, E, logarithms of pre-expomential factors, log A, orders of reaction, n, correlation coefficients r for the fitting of results with the corresponding equation, and the range of per cent weight loss (α) used for calculation. The equation used for the calculations is indicated in each case. All the results are for the first stage of decomposition, except when indicated. For details see text

Sample code number	Composition		Equation (7)						Equation (22)	
			E (kJ mol^{-1})	log A	n	Corr. coeff. (r)	Range of α	E (kJ/mol^{-1}) 2nd stage	E (kJ mol^{-1})	Corr. coeff. (r)
1	NH_4NO_3	pure	100.4	8.74	1.3	0.9981	0–0.87	564.9	100.4	0.9981
2	$NH_4NO_3:Cr^{3+}$	150000:1	86.6	7.18	0.3	0.9970	0–0.80	579.2	119.2	0.9919
3	$NH_4NO_3:Cr^{3+}$	30000:1	89.4	7.95	0.2	0.9986	0–0.87	1516.2(?)	130.6	0.9930
4	$NH_4NO_3:Cr^{3+}$	15000:1	100.0	8.48	0.6	0.9937	0–0.83	(?)	112.56	0.9934
5	$NH_4NO_3:Cr^{3+}$	5000:1	102.7	9.74	1.9	0.9998	0–0.79	820.3	114.9	0.9946
6	$NH_4NO_3:Cr^{3+}$	1500:1	94.3	8.70	0.5	0.9960	0–0.85	492.1	103.1	0.9953
7	$NH_4NO_3:Cr^{3+}$	150:1	179.0	18.84	1.0	0.9996	0–0.76	2218.4(?)	184.4	0.9957

taken to be equal to that from the nitrate anions added initially, the excess ammonia being evaporated during drying.

The thermal analysis of the obtained solids took place in a Chyo-TRDA-3-H thermal balance with simultaneous recording of temperature (T), thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) data. All the analyses used α-Al_2O_3 as a blank and a heating rate of 1° C min^{-1} with a nitrogen flow of 15 lh^{-1}.

RESULTS

Figure 1 illustrates the DTA curves for all the samples ANCr-1–7. In Fig. 2, the TG, DTG and DTA curves are shown for three typical samples, namely ANCr-1, -5 and -7.

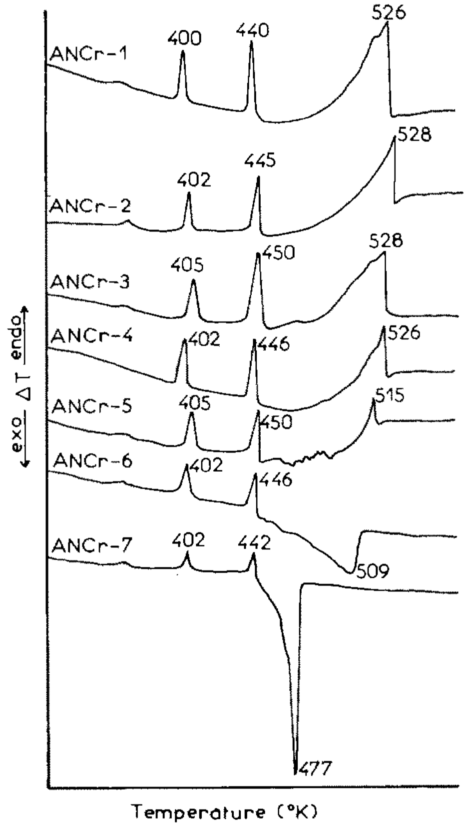

Fig. 1. DTA curves of the species ANCr-1–7. Rate of heating 1° C min^{-1}: ANCr-1 (94.0 mg), pure NH_4NO_3; ANCr-2 (94.5 mg), NH_4NO_3 : Cr = 150 000; ANCr-3 (96.4 mg), NH_4NO_3 : Cr = 30000; ANCr-4 (85.2 mg), NH_4NO_3 : Cr = 15000; ANCr-5 (98.2 mg), NH_4NO_3 : Cr = 5000; ANCr-6 (89.9 mg), NH_4NO_3 : Cr = 1500; and ANCr-7 (86.9 mg), NH_4NO_3 : Cr = 150.

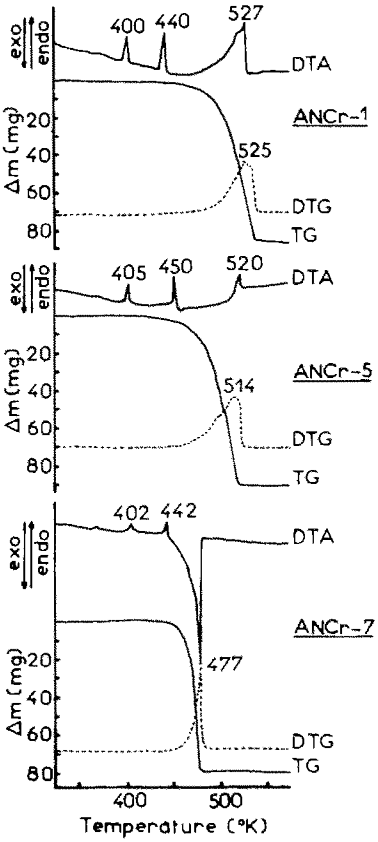

Fig. 2. DTA, TG and DTG curves for the species ANCr-1, -5 and -7.

DISCUSSION

Pure ammonium nitrate is known to decompose according to the following routes

$$NH_4NO_3 \xrightarrow{T=150\,^\circ C} NH_3 + HNO_3 \quad \Delta H = +176 \text{ kJ mol}^{-1} \tag{4}$$

$$NH_4NO_3 \xrightarrow{T=200\text{–}270\,^\circ C} N_2O + 2H_2O \quad \Delta H = +38 \text{ kJ mol}^{-1} \tag{5}$$

$$NH_4NO_3 \xrightarrow{T=400\text{–}500\,^\circ C} N_2 + 2H_2O + \tfrac{1}{2}O_2 \quad \Delta H = -120 \text{ kJ mol}^{-1} \tag{6}$$

It is further believed that decomposition occurs with release of ammonia and melting of the solid [17,24], the resulting nitrate anion being the last to break down. In the present case, pure AN begins to loose weight at around 440 °C (Figs. 1 and 2), immediately after a sharp endothermic peak due to its melting. This weight loss, which is gradual, is accompanied by an endothermic effect, most probably due to reaction (4), which ceases abruptly at $T_{max} = 526\,^\circ C$, at which point all the NH_4NO_3 has decomposed.

Addition of Cr^{3+} to the pure AN results in the endothermic decomposition becoming exothermic (Fig. 1), i.e. reaction (6) becomes dominant. This happens gradually with the Cr^{3+} doping, but the critical concentration at which the total thermal effect is almost zero seems to be between samples ANCr-5 and -6 at a ratio of NH_4NO_3 moles : Cr moles of 3000 : 1. At concentrations higher than this, chromium can act as an effective catalyst accelerating the decomposition to explosive rates (see sample 7 in Fig. 1). At lower concentrations, the effect is minimal under the experimental conditions described above.

To describe the experimental curves, and at the same time to calculate the activation energies of the reaction, we started, as often happens in similar cases, with the well-known Coats–Redfern equation [23]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(1-\alpha)^n \tag{7}$$

where α is the percent weight lost at time t, n the reaction order and k a constant usually considered to show an Arrhenius-type dependence on temperature, $k = A\exp(-E/AT)$. Equation (7), after integration and taking logarithms, becomes

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\frac{AR}{bE}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.303RT} \tag{8}$$

for $n \neq 1$, whereas, for $n = 1$, the left side reduces to $\log[-\log(1-\alpha)/T^2]$ where b, the heating rate, is 1°C min^{-1}.

Equation (8) can now be plotted in the form $\log\{[1-(1-\alpha)^{1-n}]/T^2(1-n)\}$ versus $1/T$ in order to find the activation energy of the process. This has been done using a computer program similar to that described by Dhar [25] to determine the optimum value of n resulting in the best correlation coefficient r. In all cases, such plots showed a clear change of slope (Fig. 3), which indicates that a second decomposition mechanism takes over in the final stages.

Therefore it was decided that the activation energies should be calculated by this procedure using the data from the first stage, because the decomposition mechanism of the second stage is, apparently, altered, a fact presumed from the different activation energies. The first stage results, namely the activation energies, E, the log of the pre-exponential factor, log A, and the optimum reaction orders, n, were calculated in this way and are shown in Table 1.

These results suggest that pure AN, or its mixtures with small amounts of Cr^{3+}, decomposes endothermically passing over a first-stage energy barrier of around 80–100 kJ mol^{-1}, whereas at the second stage of decomposition, an activation energy 5–10 times higher appears. Addition of increased amounts of chromium leads to a decomposition route over an activation barrier of around 180 kJ mol^{-1} (sample AN-7). To be more precise,

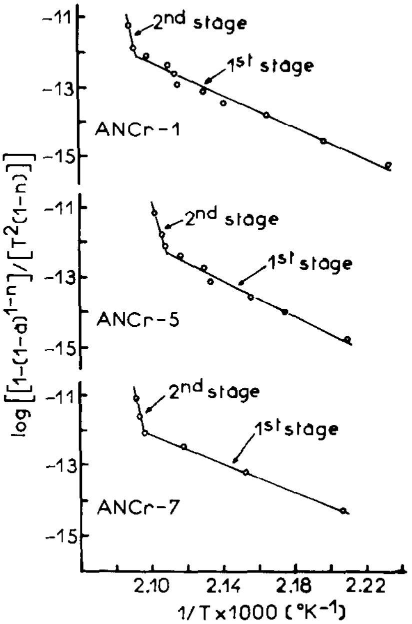

Fig. 3. Typical plots drawn according to the integrated Coats–Redfern equation (eqn. (8)) for the calculation of activation energies of decomposition of species ANCr-1, -5 and -7.

increasing Cr^{3+} causes the bending of the curves shown in Fig. 3 to occur at smaller values of percent decomposition, α. At the same time a compensation effect (not shown graphically) is observed between E and log A, described by the equation $E = 30.7 + 7.8 \log A$, with a correlation coefficient $r = 0.9994$. There are numerous discussions concerning the meaning of these observations [26–29], the proposed explanation often being that they are caused by a parallel increment of entropic and enthalpic effects on the process.

However, the results obtained by this classical treatment have some shortcomings. Firstly, it is difficult to account for the fluctuating reaction orders appearing in Table 1. Secondly, this procedure does not take into account the continually increasing amount of chromium species in the melt. And thirdly, the late stages of the decomposition should obviously be controlled by a different r.d.s. compared with the earlier ones. This slow rate-controlling process has a larger activation energy, as is clear from the curves shown in Fig. 3.

In addressing these questions, we used a rate equation of the form

$$R = KC_{AN}C_{Cr}^2 = KC_{AN}(1-\alpha)C_{Cr}^2(1+v\alpha)^2 \qquad (9)$$

where C is the initial concentrations of AN or Cr, and v is the ratio of moles Cr^{3+} : moles NH_4NO_3. This equation takes into account the continually increasing concentration of chromium species during the progress of the decomposition. The square on the chromium term needs some explanation. Rosser et al. [8] have proposed that the concentration of chromium in the kinetic low is in a power greater than unity and that this is the reason for the explosiveness of the reaction. Some justification towards this end may also be achieved by a closer scrutiny of the detailed reaction mechanism.

According to previous suggestions [12,22], the dichromates, $Cr_2O_7^{2-}$, are mainly responsible for the catalytic action of the chromium. These bimetallic anions should be produced by condensation of simple perchromates CrO_4^{2-} which, in turn, must be the product of oxidation of the Cr^{3+} added initially in the mixture. According to Keenan et al. [12], as soon as $Cr_2O_7^{2-}$ ions are formed they produce NO_2^+ and are transformed to CrO_4^{2-}, which in the acidic environment of the melt yields $HCrO_4^-$. These then condense to $Cr_2O_7^{2-}$ ions which join in the chain reaction. The formed NO_2^+ reacts with NH_3 to form intermediate nitramides and/or with NH_2^- to yield intermediate nitrosamines, which are finally decomposed to the end products N_2, H_2O and O_2. A detailed sequence of this catalytic chain mechanism may be envisaged as follows.

Thermal decomposition of AN, as with other ammonium salts, proceeds with the preliminary dissociation into its original components, ammonia and nitric acid, the reaction rate being determined by the dissociation of undissociated nitric acid molecules [17]

$$NH_4NO_3(l) \rightarrow NH_3(l) + HNO_3(l) \qquad (10)$$

As ammonia is considerably more volatile than nitric acid, an amount of it escapes in the gas phase

$$NH_3(l) \rightarrow NH_3(g) \qquad (11)$$

leaving the liquid phase much richer in HNO_3, which dissociates

$$HNO_3 \rightarrow H^+ + NO_3^- \qquad (12)$$

The excess of NO_3^- should oxidise Cr^{3+} to CrO_4^{2-}. This reaction is not easy to formulate and a number of different cases can be envisaged. Nevertheless, under somewhat similar conditions, the oxidation of Cr_2O_3 by BrO_3^- has been expressed by the reaction $5Cr_2O_3 + 6BrO_3^- + 7H_2O \rightarrow 10CrO_4^{2-} + 14H^+ + 3Br_2$. This takes place in an aquatic environment and the H^+ produced accelerates it. In a similar manner, NH_4NO_3, enriched in NO_3^- can react with Cr^{3+} as follows

$$10Cr^{3+} + 6NO_3^- + 11NH_4NO_3 \rightarrow 10CrO_4^{2+} + 44H^+ + 11N_2O + 3N_2 \qquad (13)$$

The thus formed CrO_4^{2-} ions are initially isolated and have to be paired with $Cr_2O_7^{2-}$ to form the catalytically active species [12,22]

$$2CrO_4^- \rightarrow Cr_2O_7^{2-} + \tfrac{1}{2}O_2 \qquad (14)$$

The $Cr_2O_7^{2-}$ ions enter the catalytic cycle in the melt via a Lux-type acid–base displacement, acidified to $HCrO_4^-$ and condensed again to $Cr_2O_7^{2-}$

$$Cr_2O_7^{2-} + NO_3^- \rightarrow 2CrO_4^{2-} + NO_2^+ \tag{15}$$

$$CrO_4^{2-} + H^+ \rightarrow HCrO_4^- \tag{16}$$

$$2HCrO_4^- \rightarrow Cr_2O_7^{2-} + H_2O \tag{17}$$

The cycle eventually stops when the nitrates are exhausted, probably via the reaction

$$Cr_2O_7^{2-} + 2H^+ \rightarrow Cr_2O_3 + H_2O + \tfrac{3}{2}O_2 \tag{18}$$

Meanwhile, the NO_2^+ species form intermediate nitramides or nitrosamines with NH_3 or NH_2^- which readily decompose

$$NO_2^+ + NH_3 \rightarrow [O_2NNH_3^+] \xrightarrow{\text{fast}} N_2O + H_2O + H^+ \tag{19}$$

$$NH_3 \rightarrow NH_2^- + H^+ \tag{20}$$

$$NO_2^+ + NH_2^- \rightarrow [H_2NNO_2] \xrightarrow{\text{fast}} N_2 + H_2O + \tfrac{1}{2}O_2 \tag{21}$$

The above equations have been firmly established in the literature by different authors. Of greater probable importance is eqn. (14) which may be a rate-determining step for reasons related to the possibility of the initially isolated CrO_4^{2-} mono-chromate anions diffusing along a sufficiently long path to condense with a second, thus forming $Cr_2O_7^{2-}$. Similar diffusion limitations may also hold for reaction (17) but are probably of equal size. In other words, in the initial diluted samples, the chromium cations are separated by thousands of ångströms and although certainly oxidised to CrO_4^{2-}, cannot be catalytically active as it is difficult for them to pair to form $Cr_2O_7^{2-}$. This pairing gradually becomes dominant at around $NH_4NO_3 : Cr = 3000 : 1$ (see Fig. 1). At this concentration, there are 6000 ($NH_4^+ + NO_3^-$) ions to each Cr^{3+}, so assuming a mean diameter for the ions of about 8 Å, each Cr^{3+} (or CrO_4^{2-}) has to travel around 50000 Å or 5×10^{-4} cm to be paired. Assuming a diffusion coefficient of 10^{-5} cm^2 sec^{-1}, which is similar to the diffusivities of alumina species in cryolite melts [30], this distance is travelled, on average, in about one second by 32% of the particles. Any decrease in concentration results in longer diffusion times, thus prohibiting pairing before the homogeneous (non-catalytic) decomposition is totally completed. Pairing should start immediately after melting (endo-peak at 440–450 °C) and should proceed according to reaction (14). The pairing time, i.e. the time it takes a cation to diffuse one half of the distance between two initial CrO_4^{2-} sites, should be reflected in the time it takes for 100% decomposition after the melting point. In other words, the difference ($T_{\text{final decomposition}} - T_{\text{final melting}}$) should be inversely proportional to the concentration of CrO_4^{2-} ions produced by reaction (13), or to the initial concentration of Cr^{3+} ions, assuming reaction (13) is fast. This is indeed the case at can be seen from the results shown in Fig. 1.

We feel that the above discussion seems to justify the use of the square on the concentration of Cr species in eqn. (9), always assuming that steps (14) and/or (17) are rate limiting. Then eqn. (9) can be treated in the form

$$R = k(1 - a)(1 + v\alpha)^2 \tag{22}$$

in a manner similar to that carried out for eqn. (7). The activation energies obtained, for the first stage of the reaction, are shown in Table 1, together with the corresponding correlation coefficients. We observe that the new values of E are a few kJ higher than those determined by eqn. (7), but the mode in which they change in response to the addition of chromium is rather similar, clustering around 100 kJ mol^{-1}; only sample 7 shows a near doubling of this value.

This two-fold increase in activation energy values at higher concentrations of chromium, always for the first stage of decomposition, may indicate that the diffusion is the r.d.s. at low chromium concentrations, whereas the decomposition is the r.d.s. at high concentrations. Such phenomena are well known in chemical reactor engineering problems [31–33] where diffusion limitations lead to apparent activation energies a half of those observed when the chemical reaction is rate controlling. This point certainly merits further experimental scrutiny in this and other similar systems.

The correlation coefficients observed in the second method are slightly, but noticeably, worse than those for the first one (see Table 1). This disadvantage should be judged from the point of view of the steadiness of the reaction order in the second treatment as compared to its randomness in the first. It seems that this method may be useful in describing similar systems where one of the products is non-volatile and remains in the reacting system in continually increasing concentrations. Such systems, for example $Zn[Zn(C_2O_4)_2] \cdot 4H_2O$ which decomposes to ZnO, have been recently examined [34]. The extent to which the solid remaining acts catalytically or inhibitively, or even indifferently, toward the decomposition reaction, is certainly unknown. On the other hand, in other systems such as the decomposition of $PbNO_3$, the influence of CuO, MnO_2 and Al_2O_3 has been examined [35] using the Coats–Redfern method in the form of eqn. (7), i.e. without taking into account the continually increasing amount of catalyst or inhibitor present during the process. Again, the treatment of such experimental data according to an equation similar to eqn. (22) may be advisable.

A final discussion point is the second stage of decomposition (see Fig. 3) which has a slope 5–10 times larger than the first stage (see Table 1). This distinct difference certainly indicates a change in the r.d.s. It may be suggested that during this second stage, the concentration of CrO_4^{2-} is rather large so that the formation of $Cr_2O_7^{2-}$ presents no difficulty. In fact, it may be more difficult for the $Cr_2O_7^{2-}$ species to decompose to CrO_4^{2-}. It is well known that the higher chromium oxides can be decomposed with activation energies of around 200–250 kJ mol^{-1} [36,37]. It may be suggested that, in a somehow similar manner, the decomposition of $Cr_2O_7^{2-}$ to CrO_4^{2-} exhibits the high activation energies noticed above. This case is similar to that often observed in normal catalytic systems when one of the reactants is present in concentrations high enough to acts inhibitively by blocking the so-called active sites.

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