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EXAMINATION OF THE DECOMPOSITION OF $AgNO_3$ BY MEANS OF SIMULTANEOUS EGA AND TG METHOD UNDER CONVENTIONAL AND QUASI ISOTHERMAL CIRCUMSTANCES

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INTRODUCTION

It is a general view that the decomposition of $AgNO_3$ is a simple one-step process [1-6]. The examination of this process by simultaneous TG and TGT combined with the quasi isothermal measuring technique proved that this compound may decompose also gradually.

EXPERIMENTAL

To the examination a Q-Derivatograph (Hungarian Optical Works, Budapest) was used which is suitable to simultaneous TG and TGT examinations as well under conventional as under quasi isothermal quasi isobaric conditions [7,8,9,10]. This latter technique differs from the conventional one only in respect of the heating control. With the help of this viz. the transformation process can be regulated in that way that it should take place extremely slowly (transformation rate: 0.3 mg min^{-1}/100 mg total weight change) and at a strictly constant rate (curves 1-4 in Fig.1.). The rate of the dynamic heating (curves 5,6 Fig.1) was $5^{o}min^{-1}$. To the examination an open sample holder was used. The weight of the samples was about 300 mg (Fig.1). As carrier gas O_2 was applied.

The TGT (thermo-gas-titrimetric) technique can be placed among the methods of EGA (evolved gas analysis). The performance of the technique was described in our earlier paper [10]. The changes in the amount of the collected and titrated gaseous decomposition products against temperature are demonstrated by curves 1,3 and 5 in Fig.1. These curves were calculated with the equivalent weight of the $NO_2+NO+1.5O_2$ gas mixture. DTA curves in Fig.2 were recorded partly of the original (curve 1) partly of partially decomposed (curves 2-6) $AgNO_3$ samples. Latter ones were prepared by using the quasi isothermal heating technique. The individual samples were heated as long as their weight decreased with 15,30,45, 65 and 85 % of the theoretical weight change. The decomposition

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was quenched by a rapid cooling. After this the DTA curves were recorded in the conventional way, at a 0.5 $\%\mathrm{min}^{-1}$ heating rate.

DISCUSSION

The decomposition of $AgNO_3$ was found to be a one step process (curves 5 and 6 in Fig.1) when investigated by applying a dynamic heating program. In contrast, under the conditions of the quasi isothermal quasi isobaric measuring technique the decomposition took place in the majority of the cases in two steps (curves 3 and 4 in Fig.1). It was rather difficult to find a proper explanation for this phenomenon.

$$2AgNO_3 = 2Ag + NO_2 + NO + 1.5O_2 \tag{1}$$
$$2AgNO_3 = Ag_2O + NO_2 + NO + O_2 \tag{2}$$
$$AgO = 2Ag + 0.5O_2 \tag{3}$$
$$AgNO_3 = AgNO_2 + 0.5O_2 \tag{4}$$
$$2AgNO_2 = 2Ag + NO_2 + NO + 0.5O_2 \tag{5}$$
$$7AgNO_3 = (Ag_2O)_3.AgNO_3 + 3NO_2 + 3NO + 3O_2 \tag{6}$$
$$2(Ag_2O)_3.AgNO_3 = 14Ag + NO_2 + NO + 2.5O_2 \tag{7}$$

The possibility that in the first step AgO_2 is being formed (equ.2) had to be rejected because it had comprehensively been proved that Ag_2O decomposes upto 300°C i.e. at a lower temperature than $AgNO_3$. It seemed even more implausible that the formation of $AgNO_2$ intermediate had caused the gradual decomposition (equ.4 and 5) since this decomposes at 210° i.e. at a temperature even lower than Ag_2O.

Beside the two compounds there exists only a single compound which could be brought in connection with the existence of the supposed intermediate. By means of anodic oxidation a compound of the composition $Ag_5^{3+}Ag_2^{+}O_8NO_3$ can be prepared which according to Náray and Popp [11] loses in three steps oxygen between 120 and 150°C while transitionally $Ag_7^{+}O_3NO_3$ is being formed. This latter can also be written as $(Ag_2O)_3.AgNO_3$. With other words, there exists an Ag_2O phase which contains still a small amount of NO_3^- anions. According to this observation the NO_3^- anion is capable to stabilize the Ag_2O phase and shift the decomposition upto 440°.

We had every ground to suppose that in every case when the Q-TG and Q-TGT curves resp. indicated a two step decomposition (curves 3 and 4 in Fig.1) first (at 390°C) the mentioned phase of $(Ag_2O)_3.AgNO_3$ composition was being formed (equ. 6). Thereupon between 390 and 520°C, with a maximal rate at about 440°C also this intermediary phase decomposed (equ.7). However, even under quasi isothermal-quasi isobaric conditions the decomposition of $AgNO_3$ did not take place in every instance in the described round about way. Some times it occurred that the sample decomposed according to equ. 1 as shown by curves 1 and 2 in Fig. 1. Viz. the experimental conditions under which these curves were traced were the very same as in the case of curves 3 and 4.

The formation of the supposed intermediate is supported by the condition that the Q-TGT curve which was constructed by calculating with the equivalent weight according to equ. 1 was not congruent with the Q-TG curve in the temperature interval 390-500°C but run below it (curves 3 and 4 in Fig.1). That means that more O_2 and less NO_2 + NO were liberated in this period than in the earlier one.

The maximum rate of the decomposition of the intermediate was at about 440°C. This also makes the formation of the $(Ag_2O)_3.AgNO_3$ probable, since Náray and Popp [11] found the same temperature for the decomposition of their intermediate.

The $AgNO_3$ suffers at 160°C a modification change and melts at 210°C. Each of these processes is (curve 1 in Fig.2) endothermic. If the decomposition had been taken place in the sense of equ. 1 then the peak area of the DTA curves (Fig.2) should have linearly decreased with the progress of decomposition. In contrast, upon the effect of 25 percent conversion the shape of the 210°C peak changed while after 50 percental conversion the 165°C peak disappeared. In our opinion, this makes, although in an indirect way, the correctness of our supposition probable.

The decomposition of $AgNO_3$ was examined also in O_2, air and N_2 atmospheres resp. by using open crucibles and by applying the two different kind of heating techniques. Despite the different atmospheres the course of the obtained TG curves became nearly identical with that of the corresponding curves to be seen in Fig. 1. From this follows that the transformation does not lead to equilibrium. If the examination was carried out in N_2 atmosphere, then only 93 percent of the nitrogen oxides could be titrated probably therefore, because under the given conditions also N_2 and N_2O were being formed.

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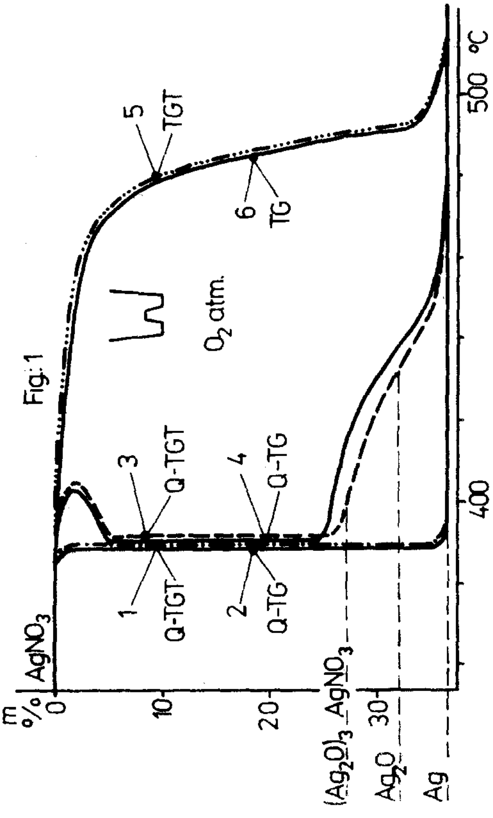

Fig.1

Fig.:2.