THERMAL DECOMPOSITION OF AMMONIUM PERCHLORATE DURING X-RAY IRRADIATION

COUNTRY: USSR

TECHNICAL TRANSLATION

This document has been approved for public release and sale; its distribution is unlimited. It may be released to the Clearinghouse, Department of Commerce, for sale to the general public.

Reproduced by the CLEARINGHOUSE for Federal Scientific & Technical Information Springfield Va. 22151
THERMAL DECOMPOSITION OF AMMONIUM PERCHLORATE 
DURING X-RAY IRRADIATION

by

A. I. Skorik, V. V. Boldyrev 
V. E. Komarov and A. I. Baranov

SOURCE: IVUZ. KHIMIYA I KHIMICHESKAYA 
TEKHOLOGIYA 
Vol. 11, No. 7, pp. 744-747 
1968 
USSR

Translated for FSTC by Techtran Corporation

This translation is an unedited rendition of the original foreign text. Statements or theories advocated or implied are those of the source and do not reflect the position or opinion of the US Army Foreign Science and Technology Center. This translation is published with a minimum of copy editing and graphics preparation in order to expedite the dissemination of information. Requests for additional copies of this document should be addressed to the Defense Documentation Center, Cameron Station, Alexandria, Virginia, ATTN: TSR-1.
THERMAL DECOMPOSITION OF AMMONIUM PERCHLORATE DURING X-RAY IRRADIATION

The effect of various factors on the kinetics of the thermal decomposition of ammonium perchlorate has been investigated by several authors (for instance, see references [1,2]).

We obtained data on the effect of x-ray irradiation at the moment of decomposition on the kinetics of the decomposition of pure ammonium perchlorate and of ammonium perchlorate containing additives of solid inorganic semiconductors.

EXPERIMENTAL PART

In our tests we used a recrystallized preparation of "pure" quality. The samples were made by pressing at a pressure of 5 tons/cm² of the initial substance, carefully ground in a mortar, into tablets with a diameter of 5 mm and 18-20 mg. The additives were introduced to the original substance in the form of a fine powder prior to pulverization. The source of radiation was a RUP-200-20-5 x-ray instrument with a 3-BTN 200 tube. The radiation dose at the location of the sample was 300 r/min. We investigated the effect of preliminary irradiation and of irradiation at the moment of decomposition on the rate of thermal decomposition of perchlorate, both pure and containing 5% by weight of the additive, by the volumetric method on the apparatus and by the procedures outlined earlier [3]. It was established that irradiation for 45 minutes at the moment of decomposition has no effect on the decomposition of pure ammonium perchlorate (Fig. 1), and of samples of ammonium perchlorate containing 5% CdO, Fe₂O₃, CdS, WO₃, CuI,
PbO and MoO$_2$. During the time of irradiation at the moment of decomposition, the decomposition of ammonium perchlorate containing Ni$_2$O$_3$, NiO and Co$_3$O$_4$ in the very same quantities accelerates. As an example, data on the decomposition of ammonium perchlorate containing PbO and Ni$_2$O$_3$ are given in Figure 2. At the same radiation dosage, preliminary 30-minute irradiation of samples of ammonium perchlorate with additives, as in the case of pure ammonium perchlorate, accelerates its subsequent thermal decomposition (Figs. 1 and 2, curve 1). In this case the preliminary irradiation causes the acceleration of the decomposition both of the original, and of the partially decomposed pure ammonium perchlorate (Fig. 3).

![Figure 1](image1.png)

**Figure 1.** Thermal decomposition of pure ammonium perchlorate preliminarily irradiated for 30 minutes (1), irradiated at the moment of decomposition (2), and not irradiated (3), at 272°C.

- a. Percent decomposition
- b. Time of decomposition, in minutes

![Figure 2](image2.png)

**Figure 2.** Thermal decomposition of ammonium perchlorate containing 5% Ni$_2$O$_3$ by weight (solid curves) and PbO (broken curves), preliminarily irradiated for 30 minutes (1), irradiated at the moment of decomposition (2), and not irradiated (3). The temperatures for decomposition are 233°C and 272°C, respectively.
a. Percent decomposition
b. Time of decomposition in minutes

c. Cooling and irradiation, 30 minutes

Figure 3. Effect of irradiation on the decomposition of partially decomposed pure ammonium perchlorate.

a. Percent of decomposition
b. Time of decomposition in minutes
c. Cooling and irradiation, 30 minutes

The study of the effect of the temperature at which preliminary irradiation was conducted on the acceleration of the subsequent thermal decomposition of ammonium perchlorate indicated that when the radiation doses are equal, a change in the temperature of preliminary irradiation from -28°C to +160°C, both in the case of pure ammonium perchlorate and in the case of ammonium perchlorate containing additives of Ni₂O₃, NiO, and Co₃O₄, does not alter the kinetics of the subsequent thermal decomposition.¹

Potentiometric determination in the irradiated samples of chloride and chlorate ions, which are the basic radiolysis products of ammonium chlorate [4], indicated that during irradiation by identical dosages (irradiation for 60 minutes at a dose of 1,000 r/min), the percent of the radiolyzed pure ammonium perchlorate does not change as the irradiation temperature changes from -20°C to +150°C. In the presence of 5% additives of Ni₂O₃, Co₂O₃, NiO, Fe₂O₃ and PbO, the percent of the radiolyzed ammonium perchlorate increases as the temperature rises. This effect is most pronounced in samples containing Ni₂O₃. The separate determination of Cl⁻ and ClO₃⁻ indicated that the increase in the percent of radiolysis is caused basically by processes which result in the accumulation of Cl⁻. The concentration of ClO₃⁻ in this case does not change significantly. Figure 4 gives data on the radiolysis.

¹ The tests were conducted on a heat balance apparatus in a nitrogen atmosphere.
of pure ammonium perchlorate (curve 1) and of ammonium perchlorate containing NiO₃ (curve 2) at various temperatures; curve 3 corresponds to the percent of ammonium perchlorate with the additive Ni₂O₃, radialized with the liberation of ClO₃⁻.

Figure 4. Temperature dependence of the radiallysis of NH₄ClO₄ (explanation in text).

a. Percent of decomposition
b. Temperature of irradiation, °C

Figure 5. Effect of irradiation on the catalytic properties of Ni₂O₃ (1 - catalyzer not irradiated; 2 - catalyzer irradiated prior to mixing).

a. Percent of decomposition
b. Time of decomposition in minutes

The test on the decomposition of ammonium perchlorate containing NH₄Cl, which was introduced into the original substance in the quantity of 0.6 mol percent by cocrystallization from solution, indicated that the presence of
Cl- retards the decomposition process.

Furthermore, it was determined that the irradiation of Ni$_2$O$_3$ by a dose of $2 \times 10^5$ results in increased catalytic activity in relation to the process of the thermal decomposition of ammonium perchlorate (Fig. 5).

DISCUSSION OF RESULTS

The mechanism of the effect of irradiation at the moment of decomposition on the rate of the process can be compared to the mechanism of the effect of preliminary irradiation on the rate of subsequent thermal decomposition, which usually is associated with stable, and sometimes irreversible, physical or chemical changes which occur in the substance under the effect of irradiation. The difference in the given case will be in that, first of all, at the moment of decomposition, irradiation takes place at a higher temperature, and secondly, the irradiation dosage received by the substance prior to the beginning of decomposition will be less than during the preliminary irradiation. On the other hand, during irradiation at the moment of decomposition, reversible changes which take place in a substance located in a radiation field, and which are characterized by a short lifetime, can have an effect on the kinetics.

Acceleration of the thermal decomposition of ammonium perchlorate by preliminary irradiation is related to the accumulation in the original substance of ClO$_3^-$, which is formed during the radialysis of ammonium perchlorate [5, 6]. From this point of view, the absence of the effect of the temperature of preliminary irradiation on the acceleration of the subsequent thermal decomposition can be related to the constant concentration of ClO$_3^-$ in samples of ammonium perchlorate irradiated by equal dosages at various temperatures (Fig. 4, curve 3).

If we assume that the mechanism of the effect of irradiation at the moment of decomposition is similar to that of the effect of preliminary irradiation, then the absence of the effect of irradiation at the moment of decomposition on the rate of decomposition of pure ammonium perchlorate can be explained by the fact that the quantity of ClO$_3^-$ accumulated in the irradiated sample by the moment of the beginning of decomposition is small and cannot have a great effect on the rate of decomposition. However, in this case it remains unclear why the accelerating action of irradiation does not show up by the end of the irradiation, when the dose received by the sample becomes quite high, while, as seen from Figure 3, the decomposition of partially decomposed ammonium perchlorate is accelerated by irradiation.
Furthermore, from this same point of view, we should assume that the additives of Ni$_2$O$_3$, Co$_3$O$_4$, and NiO greatly accelerate the formation of ClO$_4^-$ due to dialysis, at least at higher temperatures, which insures the accumulation of ClO$_3^-$ in quantities that can affect the decomposition process at doses much smaller than those received by the sample during preliminary irradiation. But analytical data indicate that the concentration of ClO$_3^-$ in irradiated samples of ammonium perchlorate with these additives is less than in pure ammonium perchlorate, and does not change significantly as the irradiation temperature increases (for a sample with an additive of Ni$_2$O$_3$, see Fig. 4, curve 3). But at higher temperatures and in the presence of Ni$_2$O$_3$, the appearance of an extra quantity of Cl$^-$, which can be attributed to the slow thermal decomposition of the original substances at temperatures below the temperature of decomposition due to the catalytic effect of Ni$_2$O$_3$, can only retard the process.

Thus, the mechanism proposed for explaining the effect of preliminary irradiation on the rate of subsequent thermal decomposition of ammonium perchlorate does not completely explain the effects that take place during its decomposition in a radiation field. Apparently, in this case there are other changes at work, which are caused by irradiation in solid bodies, and whose effect on the decomposition process changes in the presence of additives of certain substances. Furthermore, we must consider the possibility of the change of catalytic activity of the additive under the effect of irradiation.

CONCLUSIONS

1. It has been established that irradiation at the moment of decomposition accelerates the decomposition of ammonium perchlorate containing additives of NiO, Ni$_2$O$_3$, and Co$_3$O$_4$, and has no effect on the kinetics of the decomposition of pure ammonium perchlorate and of ammonium perchlorate containing additives of CdO, CdS, Fe$_2$O$_3$, CuI, PbO, WO$_3$, MoO$_2$.

2. It has been shown that the existing theories on the mechanism of the effect of preliminary irradiation on the subsequent thermal decomposition of ammonium perchlorate do not explain the observed effect.

BIBLIOGRAPHY


The article establishes that irradiation at the moment of decomposition accelerates the decomposition of ammonium perchlorate containing additives of NiO, NiO, and CoO, and has no effect on the kinetics of the decomposition of pure ammonium perchlorate and of ammonium perchlorate containing additives of CdS, FeO, CuI, PbO, WO, and MoO.

It has also been shown that the existing theories on the mechanism of the effect of preliminary irradiation on the subsequent thermal decomposition of ammonium perchlorate do not explain the observed effect.
<table>
<thead>
<tr>
<th>KEY WORDS</th>
<th>LINK A</th>
<th>LINK B</th>
<th>LINK C</th>
</tr>
</thead>
<tbody>
<tr>
<td>irradiation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>decomposition</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ammonium perchlorate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>kinetics</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>preliminary irradiation</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>