

THE CATALYTIC EFFECT OF RARE EARTH OXIDES ON THE THERMAL DECOMPOSITION OF AMMONIUM PERCHLORATE

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The kinetics of the decomposition of ammonium perchlorate (AP) in the presence of rare earth oxides, yttrium oxide (Y_2O_3) and lanthanum oxide (La_2O_3) as catalysts have been investigated. The Prout-Tompkins and contracting-cube equations have been found to fit the isothermal thermogravimetry data of catalysed AP decomposition. Gases evolved during catalytic decomposition of AP were analysed by infrared spectroscopy by matrix isolation technique. The mechanism of the catalysed thermal decomposition of AP has also been discussed in terms of an electron transfer process.

Ammonium perchlorate (AP) has been found to play a key role in the combustion of composite solid propellants. The thermal decomposition of AP has been studied over an usually wide range of temperature [1]. Ammonium perchlorate is stable at room temperature but decomposes to a measurable extent at temperature exceeding 150° . It has also been observed that the decomposition and burning properties of AP can largely be improved by using various catalysts [2, 3]. As a result chromium oxide, zinc oxide, copper oxide, copper chromite etc., find use in propellants. The effect of catalysts on the combustion of composite propellants has also been dealt with by many authors [4, 5]. Solymosi has reviewed the effect of different oxides and salts on the slow and fast decomposition of AP [2]. The Prout-Tompkins, Avrami-Erofeyev and the contracting-cube equations have been found to fit the data. Furthermore, kinetic parameters for the catalytic AP decomposition in the acceleratory as well as deceleratory periods have also been reported by some workers [6, 7].

We have studied the kinetics of the thermal decomposition of AP in the presence and absence of catalysts. Rare earth oxides, yttrium oxide (Y_2O_3) and lanthanum oxide (La_2O_3) were used as catalysts. The Prout-Tompkins and contracting-cube ($n=3$) equations were found to fit the TG data for the catalysed thermal decomposition of AP. Also, an attempt is made to identify the gases evolved at different temperatures during the decomposition in the presence and absence of catalysts by infrared spectroscopy.

Experimental

Material

Ammonium perchlorate (AP) obtained from Wimco, Bombay was used after recrystallization from distilled water. Crystals of AP were ground in a mortar and sieved through 300 mesh sieve ($< 54 \mu\text{m}$). Yttrium oxide (Y_2O_3 AR grade) and lanthanum oxide (La_2O_3 AR grade) were used in the form of fine powders. The ammonium perchlorate and the oxides were separately dried in an oven at about $100\text{--}120^\circ$ and stored in desiccator. Mixing with the oxides was done in a mortar and repeatedly passed through a 300 mesh sieve.

Methods

(A) Isothermal TG of AP

Isothermal studies on AP + Y_2O_3 (3.5% by wt.) and AP + La_2O_3 (3.5% by wt.) were undertaken using a Netzsch simultaneous thermal analyser, in the temperature ranges $200\text{--}240^\circ$ and $220\text{--}270^\circ$ respectively, whereas the decomposition of AP samples was studied in the range $240\text{--}270^\circ$. The sample (~ 10 mg) under investigation was put in a platinum crucible in a tube furnace which was controlled within ± 1 deg. The weight loss was recorded with the help of a sensitive balance.

(B) Evolved gas analysis by IR

Gases evolved during catalytic decomposition of AP were analysed by spectroscopy by matrix isolation technique [8] using a Perkin-Elmer 683 IR spectrophotometer. Nearly 50 mg of the sample was placed in a Pyrex tube (18 cm length \times 1 cm diameter), the open end of which was attached to a bulb leading to infrared transmitting window. Gases evolved were passed through KBr pellet. The rise in temperature was controlled by Stanton Redcrofts Universal temperature programmer. The spectra were recorded at every 10 deg rise of temperature.

Results and discussion

The rate of decomposition (30% decomposition) for AP with and without catalyst at various temperatures has been calculated from TG plots (Figs 1-3) and the data are given in Table 1. The catalytic activity (C_A) of the catalysts has also been estimated using Eq. (1) and the results are given in Table 1.

$$C_A = \frac{\text{Rate of catalysed decomposition of AP}}{\text{Rate of uncatalysed decomposition of AP}} \quad (1)$$

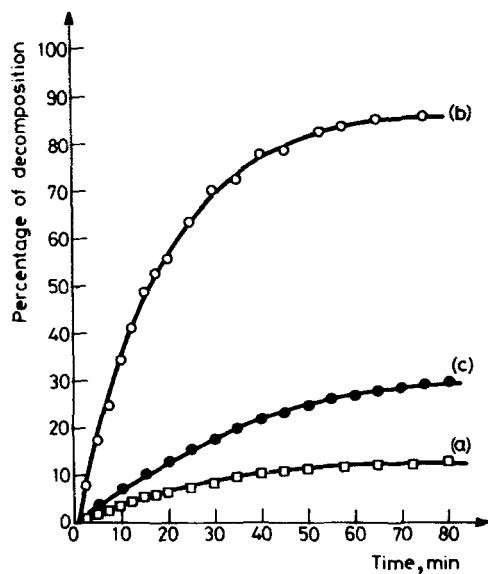


Fig. 1 Isothermal thermal decomposition curves of AP and catalysts at 240 °C. a – Ammonium perchlorate (AP); b – AP + Yttrium oxide (3.5%); c – AP + Lanthanum oxide (3.5%)

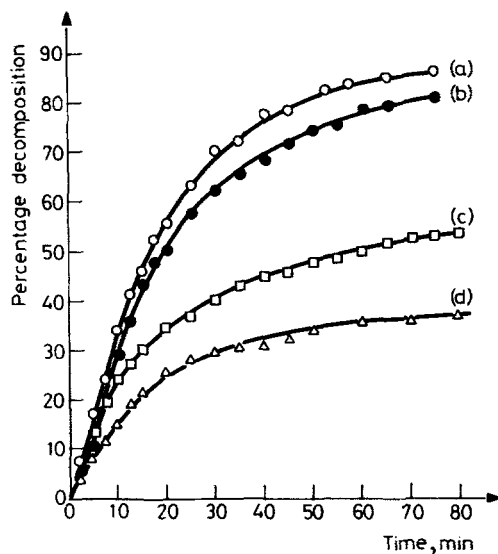


Fig. 2 Isothermal decomposition of AP + yttrium oxide at (a) 240 °C, (b) 235 °C, (c) 232 °C, (d) 224 °C

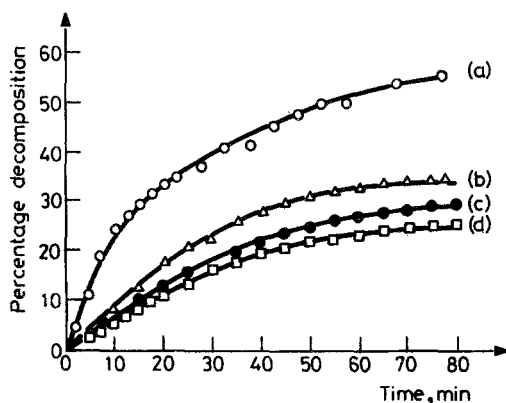


Fig. 3 Isothermal decomposition of AP + lanthanum oxide at (a) 270 °C, (b) 256 °C, (c) 240 °C, (d) 227 °C

Table 1 Effect of catalysts on the thermal decomposition of AP (catalyst conc. 3.5% by weight)

| Temperature, °C | Sample | Rate (for 30% decomposition) min ⁻¹ | Catalytic activity, C_A |
|-----------------|-------------------------------------|--|------------------------------|
| 240 | AP | 0.12 | — |
| 240 | AP + Y ₂ O ₃ | 3.14 | 26.16 |
| 235 | AP + Y ₂ O ₃ | 2.85 | — |
| 232 | AP + Y ₂ O ₃ | 2.00 | — |
| 224 | AP + Y ₂ O ₃ | 1.00 | — |
| 270 | AP + La ₂ O ₃ | 2.00 | — |
| 250 | AP + La ₂ O ₃ | 0.66 | — |
| 240 | AP + La ₂ O ₃ | 0.27 | 2.25 |

The rate of decomposition of AP, AP + Y₂O₃ and AP + La₂O₃ has been fitted by the Prout–Tompkins and contracting-cube equations (Eqs 2 and 3).

$$\text{Log} \frac{\alpha}{1-\alpha} = k_1 t + C \quad (2)$$

$$1 - (1-\alpha)^{1/3} = k_2 t \quad (3)$$

where α is the fraction decomposed, t is the time, and k_1 and k_2 are the rate constants which depend on temperature. Rate constants obtained at various temperature in each case are given in Table 2. The typical plots using Eqs (2) and (3) for AP + Y₂O₃ and AP + La₂O₃ are given in Figs 4 and 5, respectively. The activation energies (E) for the thermal decomposition of AP and AP + catalysts have been calculated and the values are given in Table 2.

Table 2 Kinetic parameters for thermal decomposition of AP, AP + Y₂O₃ and AP + La₂O₃

| Sample | Temp., °C | $K_{a_1} \times 10^2$ | $k_{d_1} \times 10^2$ | E_{a_1} | E_{d_1} | $k_{a_2} \times 10^2$ | $k_{d_2} \times 10^2$ | E_{a_2} | E_{d_2} |
|-------------------------------------|-----------|---------------------------|-----------------------|----------------|-----------|---------------------------|-----------------------|----------------|-----------|
| | | min ⁻¹ (Eq. 2) | | kJ/mol (Eq. 2) | | min ⁻¹ (Eq. 3) | | kJ/mol (Eq. 3) | |
| AP | 240 | 5.0 | 0.62 | | | 0.13 | 0.06 | | |
| | 250 | 5.2 | 0.7 | 56 | 56 | 0.21 | 0.09 | 55 | 62 |
| | 260 | 8.54 | 0.54 | | | 0.33 | 0.11 | | |
| | 270 | 11.2 | 0.80 | | | 0.38 | 0.11 | | |
| AP + Y ₂ O ₃ | 224 | 9.00 | 0.55 | | | 0.60 | 0.10 | | |
| | 232 | 10.6 | 0.69 | 106 | 214 | 0.95 | 0.24 | 112 | 207 |
| | 235 | 12.4 | 1.6 | | | 1.33 | 0.50 | | |
| | 240 | 16.8 | 2.9 | | | 1.50 | 0.62 | | |
| AP + La ₂ O ₃ | 227 | 4.16 | 0.59 | | | 0.18 | 0.10 | | |
| | 240 | 5.28 | 0.71 | 85 | — | 0.25 | 0.12 | 80 | — |
| | 256 | 8.40 | 0.94 | | | 0.40 | 0.17 | | |
| | 270 | 11.40 | 0.97 | | | 0.44 | 0.20 | | |

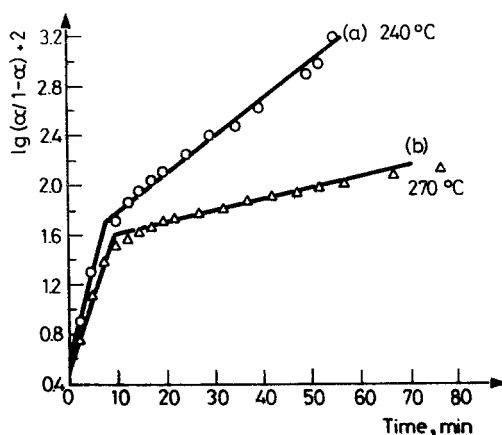

Fig. 4 Kinetic analysis of (a) AP + yttrium oxide and (b) AP + lanthanum oxide by the Prout-Tompkins equation

Table 1 clearly shows that the rate of thermal decomposition of AP is increased in presence of Y₂O₃ and La₂O₃. The order of catalyst activity (C_A) in AP decomposition was found to be Y₂O₃ > La₂O₃.

The kinetic parameters reported in Table 2 show that the rate constants for AP + La₂O₃ systems increase with increase in temperature in both the acceleratory and deceleratory periods. The energy of activation (E) for the catalysed decomposition of AP are higher than that of pure AP. Many previous investigators have also reported higher activation energy in the case of catalysed AP decomposition [2].

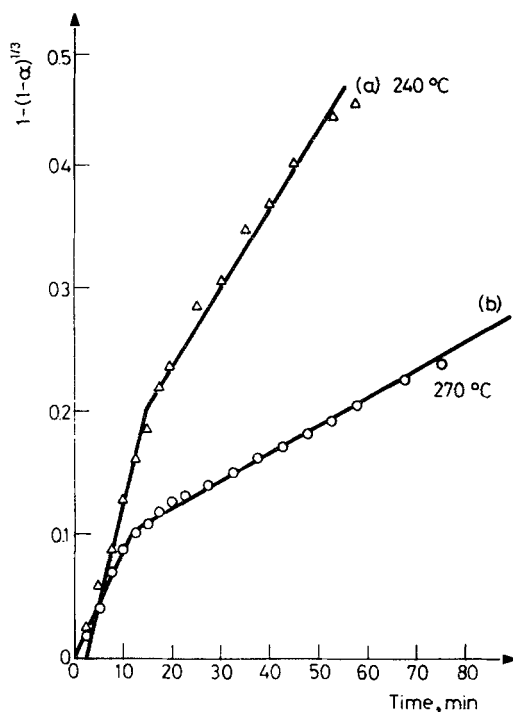
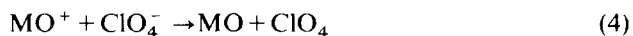


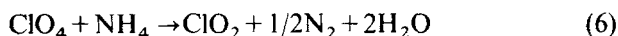
Fig. 5 Kinetic analysis of (a) AP + yttrium oxide and (b) AP + lanthanum oxide by the contracting-cube equation

The decomposition products of pure AP at 180° deduced from IR spectra, obtained by matrix isolation method, were perchloric acid (1590, 1364, 905 cm^{-1}) and ammonia (3350, 1850, 1550 cm^{-1}). The main decomposition product N_2O (two doublets 2275–2200, 1805–1780) forms only above 350°, while in the presence of the catalysts AP gives the above decomposition products at a much lower temperature. AP + Y_2O_3 at 232° gives N_2O and NO as main products, while AP + La_2O_3 gives them at about 300° only.

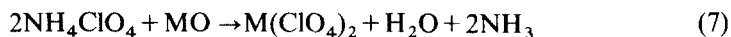
The mechanism of catalysed AP decomposition may be understood in terms of the following two effects: (i) Electron transfer process in AP decomposition which may be catalysed and (ii) the formation of metal perchlorate/amine.

The TG data of AP are recorded below 300° and it is known that the AP decomposition takes place by electron transfer process in this temperature range. It is possible that the metal oxide (MO) may enhance the decomposition of AP on account of the increase in the electron density as has been suggested by Solymosi et al. [7, 10].





However, the reaction of metal oxide with AP to form metal perchlorate/amine also seems to be quite possible as suggested by many workers [10].



From the kinetic data given in Table 2 it is clear that the catalysed reactions are characterised by an increased activation energy. This increase can be interpreted as being due to the change in the mechanism of the catalysed decomposition and of the rate determining step. It has been assumed earlier that the primary reaction is the decomposition of perchlorate ion, with the slowest process being the rupture of the Cl-O bond, since the dissociation energy of this bond (260 kJ/mol) is substantially larger than the activation energy obtained from kinetic data. Hence, it seems that both the electron transfer process and decomposition of perchlorate ion play key role in the decomposition of AP. However, more work is in progress to understand the mechanism of the decomposition of AP.

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Zusammenfassung — Es wurde die Reaktionskinetik der thermischen Zersetzung von Ammoniumperchlorat (AP) in Gegenwart der Seltenerdenoxide Yttriumoxid (Y_2O_3) und Lanthanoxid (La_2O_3) als Katalysatoren untersucht. Zum Fitting der isothermen thermogravimetrischen Daten der katalysierten Zersetzung von AP läßt sich die Prout-Tompkins- und die Schrumpfwürfelgleichung erfolgreich anwenden. Die bei der katalytischen Zersetzung von AP freigesetzten Gase wurden durch IR-Spektroskopie untersucht. Der Mechanismus der katalytischen thermischen Zersetzung wurde auch vom Gesichtspunkt eines Elektronentransferprozesses aus besprochen.

Резюме — Изучена кинетика термического разложения перхлората аммония в присутствии катализаторов оксида иттрия и оксида лантана. Найдено, что уравнения Праута–Томпкинса и сжимающегося куба хорошо описывают изотермические термогравиметрические данные каталитического разложения перхлората аммония. Выделяющиеся во время термического разложения газы анализировались ИК спектроскопией и методом матричной изоляции. Механизм термического разложения обсужден на основе электронного переноса.