# Catalyzed and Inhibited Decomposition of Ammonium Perchlorate

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## Introduction

THERE has been active interest in recent years in the study of thermal decomposition of ammonium perchlorate (AP) in the presence of catalysts[1,2] and inhibitors[3] because of its importance in solid-propellant rockets. Some recent studies have shown that for composite propellants at atmospheric pressure carbonates are more effective burning rate catalysts[4,5] than oxides of chromium and copper and that calcium oxide and carbonates of calcium, barium, and strontium act as burning rate inhibitors.[6] From the viewpoint of rocket technology, it is desirable to investigate how these catalysts and inhibitors influence the thermal decomposition of AP. This is particularly important in view of the recent finding that the data on AP decomposition for different temperature ranges and for different particle sizes can be represented by the general equation[7]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\frac{a\alpha-b\alpha^2}{1+d\alpha} \qquad (1)$$

where $a$, $b$, and $d$ are constants. $\alpha$ is the fraction decomposed at time $t$. At lower temperatures, $\mathrm{d}\alpha \ll 1$, resulting in

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=a\alpha-b\alpha^2 \qquad (2)$$

where the $\alpha$-$t$ curves are sigmoidal. However, at higher temperatures, $\mathrm{d}\alpha \gg 1$ so that

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=a'-b'\alpha \qquad (3)$$

where $a'=a/d$ and $b'=b/d$.

The purpose of the present investigation was to make a comparative study of catalysts and inhibitors in order to investigate how they affect the values of $a$, $b$, and $d$. It was hoped the study would provide a deeper insight into the nature of catalysis and inhibition.

## Criteria of Catalysis and Inhibition

If an autocatalytic reaction of the type

$$A+B \rightleftharpoons 2B$$

is considered, the result[8] is Eq. (2) where $\alpha$ is the fraction decomposed at time $t$. The point of inflexion of the sigmoidal curve would be given by $\alpha_i=a/2b$, $t_i=1/(a+b)\ln(a/b)$. It is easy to show that both $a$ and $b$ would then be related to the autocatalytic rate constants. Further, $\alpha$-$t$ curves can be characterized by 1) the time lag; 2) the coordinate point of inflexion $\alpha_i$ and $t_i$; 3) $\alpha_0$, the fraction decomposed at infinite time; and 4) the percentage of decomposition after a fixed interval of time.

Thus, the question is which of these characteristics can be used as an operational criterion for catalysis and inhibition. Characteristic 4 has been used arbitrarily to assess the relative catalytic activity. This is obviously not justified. Similarly, since $\alpha_i$ is related to the ratio of the rate constants, it cannot also be used as a criterion. Further, $t_i$ is inversely proportional to $(a+b)$. Hence, if the rate is enhanced, $t_i$ would be reduced. Therefore, $t_i$ can be used as a measure of catalytic activity. Similarly when $\alpha \ll 1$ at time $t \to 0$, $\mathrm{d}\alpha/\mathrm{d}t=a\alpha$ and $a$ is thus related to the time lag or initial slope. Experimental estimates of these quantities to a fair degree of accuracy are difficult. Nevertheless, the time lag and the time interval corresponding to the point of inflexion are good measures of the rate constant and can be used as criteria for catalysts and inhibitors. However, a more definitive measure of catalysis and inhibition would be the constant $a$. Hence, an attempt has been made to compare $a$ for the catalyzed and inhibited decomposition of AP.

## Experimental

### Materials

The AP was supplied by ISRO, Alwaye, Kerala. Calcium oxide and calcium, barium, and strontium carbonates (British Drug House) were used as received without purification.

### Experimental Procedure

Isothermal Thermogravimetric Analysis (TGA) of AP and AP+ additives was studied at 245°C in the usual manner. The

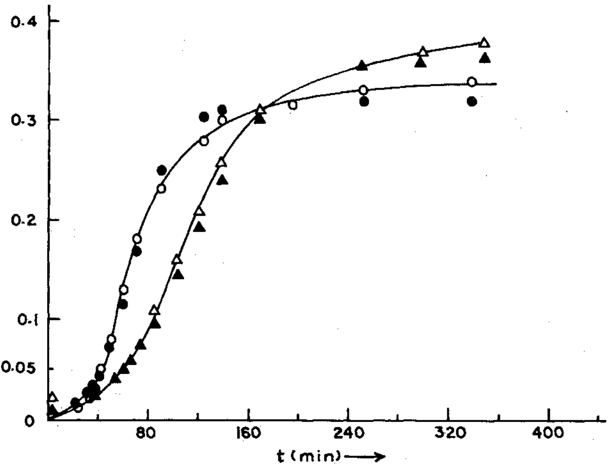

**Fig. 1** Plot of $\alpha$ vs time: ○, experimental; ●, theoretical for AP (100-200 mesh) +4% $BaCO_3$ (<100 mesh) at 245±1°C; △, experimental; ▲, theoretical for AP (100-200 mesh) +4% CaO (<100 mesh) at 245±1°C.

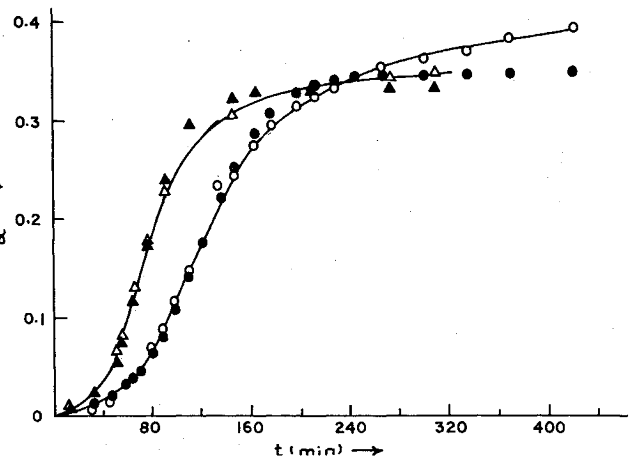

**Fig. 2** Plot of $\alpha$ vs time: ○, experimental; ●, theoretical for AP (100-200 mesh) +4% $CaCO_3$ (<100 mesh) at 245±1°C; △, experimental; ▲, theoretical for AP (100-200 mesh) +4% $SrCO_3$ (<100 mesh) at 245±1°C.

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**Table 1 Constants of Eq. (1) for AP decomposition at 245°C in presence of typical catalysts and inhibitors**

| Additive | *a*, $\min^{-1}$ | *b*, $\min^{-1}$ | *d* |
|---|---|---|---|
| Nil | 0.125 | 0.387 | 10 |
| Basic copper carbonate (BCC)[a] | 0.125 | 0.30 | 10 |
| Copper chromite (CC)[a] | 0.246 | 0.60 | 30 |
| $CaCO_3$ | 0.037 | 0.107 | ~0 |
| CaO | 0.032 | 0.09 | ~0 |
| $BaCO_3$ | 0.06 | 0.189 | ~0 |
| $SrCO_3$ | 0.063 | 0.192 | ~0 |

[a] Data from Ref. 7.

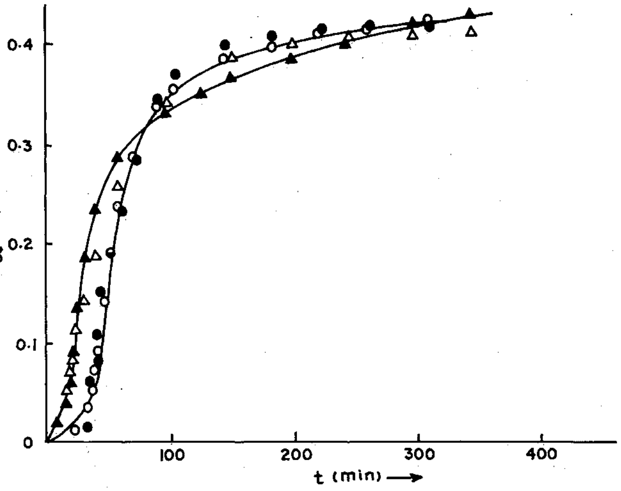

**Fig. 3 Plot of $\alpha$ vs time: ○, experimental; ●, theoretical for AP (100-200 mesh) +4% BCC (100-200 mesh) at 245±1°C; ▲, experimental; △, theoretical for AP (100-200 mesh) +4% CC (100-200 mesh) at 245±1°C.**

temperature of the furnace was controlled to within ±1°C. The studies were made with 102-104 mg of samples in each case.

The experiments were repeated with additives such as $CaCO_3$, $BaCO_3$, $SrCO_3$, and CaO. In the samples, the percentage of additives was 4%. Plots of $\alpha$ against $t$ for these additives are shown in Figs. 1 and 2.

### Analysis of the Experimental Data and Results

The data were analyzed in a manner described elsewhere.[7] The values of the constants *a*, *b*, and *d* for different additives are shown in Table 1.

The results clearly show that *a* and *d* are enhanced in the case of catalysts, while being appreciably reduced in the case of inhibitors. The sigmoidal character of the $\alpha$-$t$ curves is retained in the case of inhibitors. However, the curves in the case of catalysts are nonsigmoidal as shown in Fig. 3, which was drawn using the data of Ref. 7 for comparison purposes.

There is strong experimental evidence to suggest that the thermal decomposition of AP proceeds according to the following reaction sequence[9]:

$$\begin{tikzcd}
 & NH_4^+ClO_4^- \arrow[r, "(1)"] \arrow[d, "(2)"] & NH_3(a)+HClO_4(a) \arrow[r, "(4)"] \arrow[d, "(3)"] & \text{Products} \\
\text{Sublimate} & NH_3(g)+HClO_4(g) \arrow[l, "(6)"'] \arrow[r, "(5)"] & \text{Products} &
\end{tikzcd}$$

Reaction 1 involves proton transfer and the subsequent formation of $NH_3$ and $HClO_4$ in the adsorbed state. The weight loss occurs with reactions 2-4. It has been suggested that nucleation occurs first, after which the decomposition is accelerated. Nucleation is an autocatalytic process. Thus, it seems justified to associate the nucleation process with the autocatalytic rate constant *a*.

## Acknowledgment

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