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Mechanism of Catalysed & Inhibited Decomposition of Ammonium Perchlorate

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A physicochemical model of ammonium perchlorate (AP) decomposition based on chemisorption-desorption process has been developed which yields the equation,

$$\frac{d\alpha}{dt}=\frac{a\alpha-b\alpha^2}{1+h\alpha}$$

between α, the fraction decomposed, and time t. The equation is known to satisfy thermal decomposition of AP for a wide range of temperatures in the presence and absence of catalysts and inhibitors. The model shows that constant (a) is associated with nucleation process and (h) is associated with adsorption of $HClO_4$. This is confirmed by adsorption experiments which show that there is significant adsorption of $HClO_4$ on catalysts for which h value is large while the adsorption is negligible for inhibitors for which $h \approx 0$. Greater adsorption of $HClO_4$ in the case of catalysts and negligible adsorption in case of inhibitors is also suggested by pH studies of partially decomposed samples of AP. The model is found to support the data on thermal decomposition of metal perchlorates.

A unified model of thermal decomposition of ammonium perchlorate (AP) has been advanced recently which holds good for a wide range of temperatures and also for catalysed and inhibited decomposition[1,2]. The model is based on relation (1),

$$\frac{d\alpha}{dt}=\frac{a\alpha-b\alpha^2}{1+h\alpha} \quad \ldots (1)$$

where α denotes the fraction decomposed at time t and a, b and h are constants which depend upon temperature and the nature of additives. The analytical studies suggest that a is associated with nucleation process and h with adsorption of $HClO_4$. It may be noted that $h \sim 0$ for inhibitors, whereas it is very significant for catalysts at the same temperature. We became interested in understanding the physicochemical basis of Eq. (1) primarily for having a deeper understanding of AP decomposition and the mechanism of catalysis and inhibition. Accordingly a physicochemical model has been advanced in this paper, which confirms that a is associated with nucleation process and h with adsorption of $HClO_4$.

Materials and Methods

Ammonium perchlorate (Alwaye, ISRO, Kerala), $MnCO_3$ (BDH), basic copper carbonate, $HClO_4$ (Merck, 70%), and $CaCO_3$, $SrCO_3$, $BaCO_3$ and CaO, (all of AR grade) were used as such. Copper chromite was prepared in the laboratory as described in previous communication[1].

Adsorption of $HClO_4$ vapour on various additives

Isothermal TG of different additives under $HClO_4$ and argon atmospheres was studied using a set up which had a long corning glass tube in which a platinum bucket was suspended with a long silver wire attached to a quartz fibre spring (Fig. 1). The lower part of the long tube was kept in a furnace maintained at 350° ± 2°C. The extension of the spring was measured by a cathetometer (least count = 0.001 cm). The spring was calibrated prior to experiment by noting the extension for different standard weights. The plot of extension versus load was found to be linear for small weights. The sensitivity of the spring was 717.92 mg/cm.

Using Ar as a carrier gas, $HClO_4$ vapour was passed at a constant rate through the long corning glass tube containing the sample (300 mg) via two U-tubes, one of which had fused $CaCl_2$. The other U-tube was used to collect the $HClO_4$ condensed occasionally during the experiment. After flushing the long tube for 5 min the upper and lower ends of it were closed with the help of vacuum stopcocks. The mass gain/mass loss of the sample was estimated by measuring the extension/contraction of the spring as a function of time. Similar experiments were repeated in pure argon atmosphere. The difference in weights, in the atmosphere of argon and $HClO_4$ vapour, gave the extent of adsorption on the additives.

Determination of H^+ and Cl^- concentrations

Samples of AP or AP + 4% additive (~ 1 g each) were taken in a platinum bucket and decomposed to different extents at 220°C. Aliquots (0.65 g each) of these decomposed samples were dissolved in doubly distilled water (50 ml) and the pH of these solutions

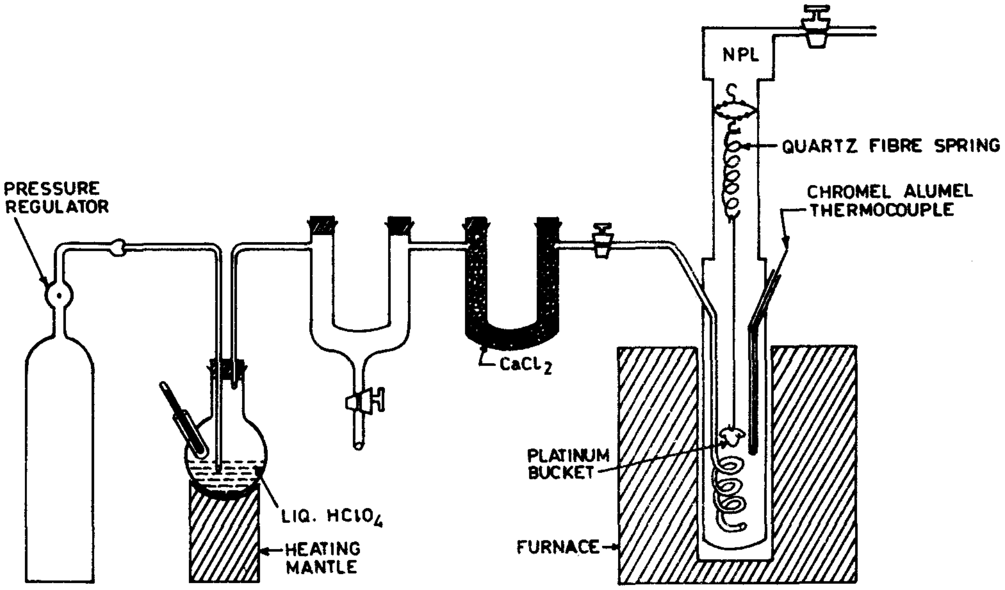

Fig. 1 – Quartz fibre spring assembly for adsorption experiments.

measured using a Systronics digital pH meter having a least count of 0.01 log units. Chloride ion concentration in the solution was estimated by Volhard's method.

Physicochemical model of AP decomposition

It has been shown recently that for a wide range of temperatures, the data on uncatalysed, catalysed and inhibited decomposition of AP[1,2] are fitted by the empirical Eq. (1).

In order to understand the processes which are associated with the constants a and h, Eq. (1) is derived on the basis of a physico-chemical model. This is based on reaction mechanism, shown in Scheme 1, which is supported by the findings of several workers[3-6].

$$NH_4ClO_4(s) \rightleftharpoons NH_3(a) + HClO_4(a)$$
$$HClO_4(a) \rightleftharpoons HClO_4(g)$$
$$NH_3(a) \rightleftharpoons NH_3(g)$$
$$HClO_4(g) + NH_4ClO_4(s) \rightarrow 2HClO_4(g) + NH_3(a)$$
$$HClO_4(g) + NH_3(g) \rightarrow \text{Products and sublimate}$$
$$NH_3(a) + HClO_4(a) \rightarrow \text{Products}$$

Scheme 1

For developing a quantitative model based on the above mechanism, we make the following reasonable assumptions:

(i) All the lattice sites of AP are not the nucleation sites. The nucleation sites are only those where adsorption and desorption of $HClO_4$ is possible; (ii) $HClO_4(g)$ may react with $NH_3(a)$ giving $NH_4ClO_4(s)$; (iii) the total number of active sites is proportional to the mass of sample (AP or AP + additive) at time t, since the material is porous; and (iv) fraction decomposed per unit time ($d\alpha/dt$) is proportional to the number of nuclei[7].

Let N be the number of active sites per unit area, θ_{HClO_4} be the fraction of nucleation sites (nuclei) and θ_{NH_3} be the fraction of sites where adsorption of NH_3 is possible. Then the number of nuclei per unit area would be $N\theta_{HClO_4}$

Using assumption (iv), we can write,

$$\frac{d\alpha}{dt} = k'NH\theta_{HClO_4} \qquad \ldots (2)$$

Now again it is clear from assumption (iii) that NS is proportional to m_t

or

$$NS = m_0 k_1 (1-\alpha) \qquad \ldots (3)$$

Combining Eqs (2) and (3) we get,

$$\frac{d\alpha}{dt} = k' k_1 m_0 (1-\alpha)\theta_{HClO_4}$$

or

$$\frac{d\alpha}{dt} = k_2 (1-\alpha)\theta_{HClO_4} \qquad \ldots (4)$$

θ_{HClO_4} can be estimated in the following manner. r_d, the rate of desorption of $HClO_4$, would depend on θ_{HClO_4} so that

$$r_d = k_d \theta_{HClO_4} \qquad \ldots (5)$$

On the other hand r_a, the rate of adsorption for $HClO_4$, would depend on the fraction of sites unoccupied $(1-\theta_{HClO_4}-\theta_{NH_3})$ and the number of molecules in gaseous phase $(\alpha m_0/M)$. Therefore

$$r_a = k'' \alpha \frac{m_0}{M}(1-\theta_{HClO_4}-\theta_{NH_3})$$

or

$$r_a = k_a\alpha(1-\theta_{HClO_4}-\theta_{NH_3}) \quad \ldots (6)$$

For the steady state $r_a = r_d$ so that

$$k_d\theta_{HClO_4} = k_a\alpha(1-\theta_{HClO_4}-\theta_{NH_3}) \quad \ldots (7)$$

Similarly, equating r'_a, the rate of adsorption of ammonia and r'_d, the corresponding rate of desorption, at equilibrium we get

$$k'_d\theta_{NH_3} = k'_a\alpha(1-\theta_{HClO_4}-\theta_{NH_3}) \quad \ldots (8)$$

Dividing Eq. (7) by Eq. (8), we get

$$\frac{k_d\theta_{HClO_4}}{k'_d\theta_{NH_3}} = \frac{k_a}{k'_a}$$

so that,

$$\theta_{HClO_4} = k_s\theta_{NH_3} \quad \ldots (9)$$

and

$$\theta_{NH_3} = k'_s\theta_{HClO_4} \quad \ldots (10)$$

Substituting the value of θ_{NH_3} from Eq. (10) into Eq. (7) we get,

$$k_d\theta_{HClO_4} = k_a\alpha(1-\theta_{HClO_4}-k'_s\theta_{HClO_4})$$

so that,

$$\theta_{HClO_4} = \frac{k_a\alpha}{k_d + k_a\alpha(1+k'_s)} \quad \ldots (11)$$

Substituting the value of θ_{HClO_4} from Eq. (11) into Eq. (4) we get,

$$\frac{d\alpha}{dt} = \frac{a\alpha - a\alpha^2}{1+h'\alpha(1+k'_s)} \quad \ldots (12)$$

Now taking into account for back formation of NH_4ClO_4 (assumption iv), i.e.

$$-\frac{d\alpha}{dt} = k'''\alpha\theta_{NH_3} \quad \ldots (13)$$

Now putting the value of θ_{HClO_4} from Eq. (9) into Eq. (8) we can show that

$$\theta_{NH_3} = \frac{k'_a\alpha}{k'_d + k'_a\alpha(k_s+1)} \quad \ldots (14)$$

Substituting the value of θ_{NH_3} from Eq. (14) into Eq. (13) we get,

$$-\frac{d\alpha}{dt} = \frac{A\alpha^2}{1+H\alpha(k'_s+1)} \quad \ldots (15)$$

Combining Eqs (12) and (15), the net $d\alpha/dt$ can be written as

$$\frac{d\alpha}{dt} = \frac{a\alpha - a\alpha^2}{1+h'\alpha(1+k'_s)} - \frac{a\alpha^2}{1+H\alpha(1+k_s)}$$

Neglecting the α^3 terms in numerator and α^2 terms in denominator, we get,

$$\frac{d\alpha}{dt} = \frac{a\alpha - \alpha^2(A+a-ah'-aH)}{1+\alpha(2H+2h')}$$

Since H is small in comparison to h', therefore,

$$\frac{d\alpha}{dt} = \frac{a\alpha - \alpha^2(A+a-ah')}{1+2\alpha h'}$$

or

$$\frac{d\alpha}{dt} = \frac{a\alpha - b\alpha^2}{1+h\alpha} \quad \ldots (16)$$

which is identical to Eq. (1).

Thus the model predicts that *a* is associated with nucleation process while *h* with adsorption of $HClO_4$.

Further tests of Eq. (16)

Although the detailed test of the Eq. (16) has been reported earlier[1,2], it was thought of interest to test the equation for other perchlorates for which the data are available[8].

Equation (16) would reduce to Eq. (12) when the possibility of reaction between $NH_3(a)$ and $HClO_4(g)$ would be very small so that $a = b$. Further for such a case $\alpha \to 1$ when $\frac{d\alpha}{dt} \to 0$ and thus complete dissociation would take place regardless of magnitude of *h*. Equation (12) would hold for cases of complete thermal decomposition for metal perchlorates[8], $M(ClO_4)$ where M = Co, Mn, Li, Ni, Cr, Zn and Cd. For such a case the initial reaction would be,

$$2M^+ + 2ClO_4^- \rightarrow 2MO + 2ClO_2(a) + O_2$$

and the possibility of recombination would be remote. Accordingly $a = b$. In Table 1 values of *a* and *b* have been calculated as described earlier[1], from the available data[8] which fit Eq. (16). The near concordance between *a* and *b* shows that the model is correct.

Results and Discussion

The physicochemical model advanced above, shows that *a* is related to the autocatalytic rate constant and hence with the nucleation process. This is confirmed by the fact that in the case of catalysed decomposition of AP, the value of *a* is larger, as compared to that in inhibited decomposition[1,2]. This view is further supported by the fact that the energy of activation for the nucleation process reported by Boldyrev *et al.*[9] is 210 ± 20 kJ per mole which agrees well with the value of 190 kJ per mole reported by us[1]. The physicochemical model predicts that $h = 2k_a/k_d$, implying that *h* is larger when k_a is larger: In other words *h* is related to

Table 1 – Values of Constants of Eq. (16) for Thermal Decomposition of Metal Perchlorates

Compound	Temp. °C	*a* (min^{-1})	*b* (min^{-1})
$Co(ClO_4)_2$	195	0.600	0.625
$Mn(ClO_4)_2$	210	0.441	0.461
$LiClO_4$	418	$0.925(hr)^{-1}$	$0.967(hr)^{-1}$
$Ni(ClO_4)_2$	290	0.284	0.289
$Cr(ClO_4)_3$	160	0.310	0.319
$Zn(ClO_4)_2$	300	0.170	0.198
$Cd(ClO_4)_2$	392	0.110	0.143

Table 2 – Adsorption of $HClO_4$ on Different Additives [Temp of furnace = 350 ± 2°C; temp of $HClO_4$ vapour = 100°C; and time of heating for the sample = 240 min]

Sample	Particle size (mesh)	h	Adsorption of $HClO_4$ (mg)
$MnCO_3$	100-200	65	0.0862/mg of MnO
Copper chromite	—	30	0.0191/mg of copper chromite
Basic copper carbonate	100-200	10	0.0143/mg of copper oxide
CaO	< 100 mesh	~0	0
$CaCO_3$	< 100 mesh	~0	0
$BaCO_3$	< 100 mesh	~0	0
$SrCO_3$	< 100 mesh	~0	0

the adsorption of $HClO_4$. Following experiments justify this expectation.

Adsorption of $HClO_4$ vapour on various additives was measured. Results recorded in Table 2, along with reported values of $h^{1,2}$, show that for higher value of h, amount of $HClO_4$ adsorbed is higher and vice versa. Thus experimental results on adsorption of $HClO_4$ strongly support the model.

Further experimental support is provided by the measurement of $[H^+]$ and $[Cl^-]$ of aqueous solution of partially decomposed AP and AP + 4% additive samples.

Vernekar and Varada Raju[10] have suggested that the increase in $[H^+]$ during AP decomposition is due to the formation of HCl and HNO_3 (in traces) although Osada and Sakamoto[5] have claimed that $HClO_4$ is produced and remains in the condensed phase during the initial stages. Significant difference in the magnitude of $[H^+]$ and $[Cl^-]$ obtained in the experiments of Verneker and Varada Raju[10] suggests that the excess $[H^+]$ must have come from adsorbed $HClO_4$. This is also true in the present case.

Taking the above argument into account, it seems that experimental value of difference ($D = [H^+] - [Cl^-]$) is a better measure of the extent of adsorption, although complications in interpretation would arise when $HClO_4$ is decomposed by the additives.

From Fig. 2 it is clear that the value of D is greater for AP + $MnCO_3$ as compared to pure AP. However, for AP + copper chromite, it is still higher than pure AP in the initial stages of AP decompositon ($\alpha \approx .05$), but for larger values of α, value of D considerably decreases. This peculiarity is due to the fact that copper chromite is a good catalyst for $HClO_4$ decomposition and adsorbed $HClO_4$ is decomposed quickly. These experiments do not provide conclusive evidence about the relative extent of $HClO_4$ adsorption on AP, AP + $MnCO_3$ and AP + copper chromite but these do show that considerable adsorption of $HClO_4$ takes place in the case of catalysts.

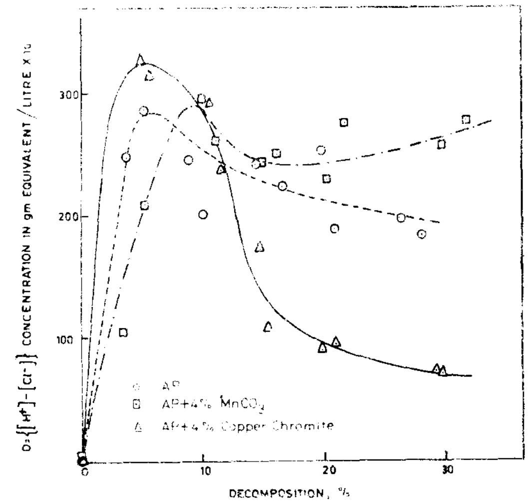

Fig. 2 — Plots of D versus % decomposition for partially decomposed samples of AP and AP + 4% additives, temp. of decomposition 220° ± 1°C

In case of $CaCO_3$ which acts as inhibitor in AP decomposition, the results are puzzling in the sense that $[Cl^-]$ is much more than $[H^+]$. This is due to the formation of calcium perchlorate as a result of double decomposition reaction between $CaCO_3$ and NH_4ClO_4 and which decomposes as $CaCl_2$ and $4O_2$ (ref. 8 pp. 165). $CaCl_2$ formed releases large amount of Cl^- and this accounts for higher $[Cl^-]$.

We can now speculate on the physicochemical basis of the mechanism of catalysis and inhibition of nucleation process during AP decomposition. Boldyrev *et al.*[9] have postulated following steps for the nucleation and growth processes: (a) separation of ammonia and perchloric acid in a pore due to different diffusion rate; (b) migration of perchloric acid into the neighbouring pore; (c) the decomposition of perchloric acid; and (d) interaction of the perchloric acid decomposition products with unreacted ammonium perchlorate on the walls of the pore. It is supposed that the stages (a) and (c) are responsible for nucleation while stages (a), (b) and (d) are associated with the growth of nucleus. Thus, accumulation and decomposition of perchloric acid in the zone of dislocation is responsible for the nucleation process. However, the pore model of nucleation cannot explain the manner in which external additives catalyse or inhibit the process of nucleation.

We believe that the mechanism of nucleation is closely associated with the adsorption of $HClO_4$. When $HClO_4$ is adsorbed preferentially on lattice sites occupied by perchlorate ions, the lattice forces around the ion are disbalanced resulting in the distortion of the lattice. Consequently NH_4^+ and ClO_4^- in the surrounding region come closer resulting in the proton transfer and subsequent desorption of NH_3 and $HClO_4$. Nucleation catalysts facilitate adsorption of $HClO_4$ while inhibitors retard this process.

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List of symbols

α = fraction decomposed;
a = k_2k_a/k_d = rate constants;
b = rate constant; $b = A + a - ah'$
h' = k_a/k_d
k_a = $k''m_0/M$, rate constant for the adsorption of $HClO_4$
k_d = rate constant for the desorption of $HClO_4$
r_a = rate of adsorption of $HClO_4$
r_d = rate of desorption of $HClO_4$
r'_a = rate of adsorption of NH_3
r'_d = rate of desorption of NH_3
θ_{HClO_4} = fraction of nucleation sites
N = No. of potentially active sites per unit area;
S = surface area
k' = proportionality constant
k'' = proportionality constant
m_0 = initial mass of the sample
m_t = mass of the sample at time t
k_1 = proportionality constant
k_2 = $k'k_1m_0$
M = molecular weight of $HClO_4$
k''' = rate constant for back formation of NH_4ClO_4
θ_{NH_3} = fraction of sites occupied by ammonia
k'_a = rate constant for the adsorption of NH_3
k'_d = rate constant for the desorption of NH_3
k_s = $\frac{K_aK'_d}{k'_ak_d}$
k'_s = $\frac{k'_ak_d}{k_ak'_d}$
k_s = $\frac{1}{k'_s}$
h = $2h'$
Hk_s = $\frac{k'_a}{k'_d} \times \frac{k_ak'_d}{k'_ak_d} = \frac{k_a}{k_d} = h'$
A = $k'''\frac{k'_a}{k'_d}$
$h'k'$ = $\frac{k_a}{k_d} \times \frac{k'_ak_d}{k_ak'_d} = \mathrm{H}$

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