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EFFECTS OF DIFFERENT ADDITIVES ON THE THERMAL DECOMPOSITION OF AMMONIUM PERCHLORATE

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IR spectral investigations on ammonium perchlorate (AP) in the presence of varying amounts of ammonium permanganate (APm) and 2% by weight of different rare earth oxide additives were made over the temperature range 25-290°. Heating and spectral scanning were done simultaneously and the peak intensity was presumed to be proportional to the amount of undecomposed AP. Presence of 10% APm lowered the temperature of AP decomposition from 200 to 110° and increased the rate by several folds. Mixed oxide produced as a result of deflagration of APm are considered catalyzing the process. In the presence of rare earth oxides additives, the NH_4^+ stretching peak intensity decreased considerably, the extent followed the trend $Gd_2O_3 > MnO_2 > Nd_2O_3 > Pr_2O_3 > Dy_2O_3 > Y_2O_3 > La_2O_3 >$ virgin AP. An electron transfer mechanism is envisaged to explain the results.

Thermal stability of AP is known to be sensitive to the presence of additives [1-3]. Depending on their structure and chemical properties additives increase the decomposition and combustion rates and lower the ignition temperature. Solymosi and others [4] have investigated the catalytic effect of oxides on the isothermal decomposition of AP. Our data on the mixtures of AP + KBr/KCl showed that the presence of KBr/KCl influence the thermal characteristics of AP [5]. Systematic studies are presented here to understand the effect of different rare earth oxide additives and also of MnO_2 and NH_4MnO_4 on the IR spectral peak intensities while heating was going on concurrently.

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Experimental

Freshly prepared [6] ammonium permanganate was recrystallized from doubly distilled water, ground well and the particles passing through 0.053 mm sieve were collected. Its mixtures with AP of the same particle size were prepared on weight basis as 10:90, 30:70 and 50:50. Mixtures of rare earth oxides were prepared by adding 2% by weight of analytical grade oxides. A Perkin-Elmer Model 683 infrared spectrophotometer was employed for the in situ infrared analysis. The technique has been described elsewhere [7]. Pellets of the mixtures prepared in the KCl/KBr matrix were heated dynamically over the temperature range 25-290° at a rate of 5 deg/min^{-1}. A single scanning of the spectra required 3 1/2 minutes.

Results and discussion

Changes in the NH_4^+ stretching, NH_4^+ bending, ClO_4^- stretching and ClO_4^- bending frequencies were followed using KCl as the matrix. A typical plot for the NH_4^+ stretching frequency presented in Fig. 1 indicates that the change in peak intensity is negligibly small up to 80° and beyond this temperature the intensity starts diminishing, closing on to 100% loss at

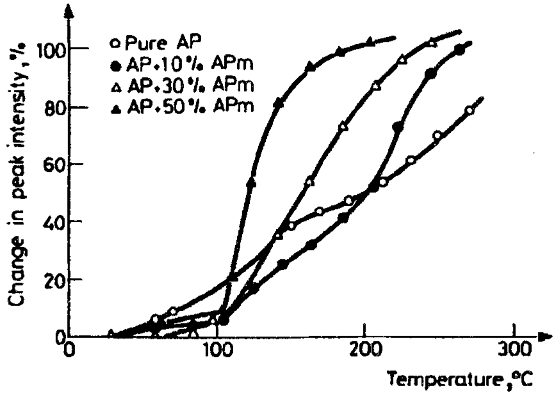

Fig. 1 Effect of ammonium permanganate (APm) impurity on the intensity of NH_4^+ stretching (KCl matrix); heating rate: 5 deg min^{-1}

about 250°. Further, the rate of intensity loss and hence the temperature at which the entire peak disappears depends on the amount of APm initially present. A sudden change in the peak intensity is also exhibited by the ClO_4^- stretching frequency after 110° (See Fig. 2) and the loss closes on to 95% at 270°.

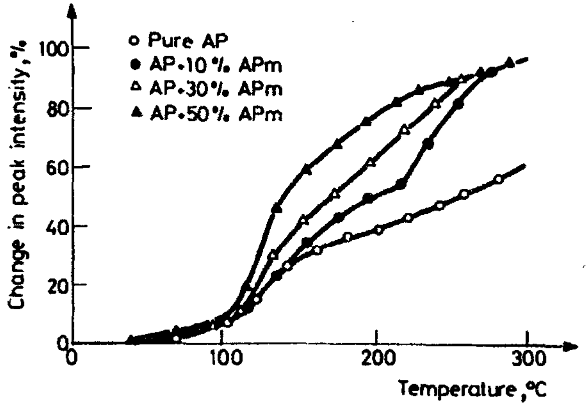

Fig. 2 Effect of APm impurity on the intensity of ClO_4^- stretching (KCl matrix); heating rate: 5 deg min^{-1}

As the concentration of APm is increased, the loss over the temperature range of 110-180° also increases and beyond this range the change in intensity is much slower in all the cases. The data on NH_4^+ and ClO_4^- bending frequencies are qualitatively similar but differing in the extent of intensity loss. These results are summarized in Table 1.

We have shown that deflagration of APm occurs between 105-110° following a proton-transfer [8] mechanism and the stable end-products were found to be mixed oxides of manganese. When produced in the AP + APm mixture such oxides are likely to catalyse the thermal decomposition of AP. Such catalytic action by manganese oxides is known [9] but occurring to a varying degree depending on the oxidation state of manganese. Besides the catalytic action, a variety of defects like, dislocations, point defects and additional nuclei produced in AP crystals during the deflegration of APm, will also enhance the decomposition of AP.

Thus, even though physical contact of AP taken in a large matrix material and containing a very small amount of the additive is expected to be very much limited, there is a profound influence of the additive when actual decomposition process begins.

Table 1 Effect of ammonium permanganate additive on the peak intensities of AP at different temperatures; heating rate 5 deg/min^{-1}

APm by weight, %	Temp., °C	Percentage loss			
		NH_4^+ stretch.	NH_4^+ bend.	ClO_4^- stretch.	ClO_4^- bend.
0	25	0	0	0	0
	50	4	2	1	1
	100	16	9	7	8
	150	39	18	29	14
	200	49	27	39	21
	260	74	40	52	32
10	25	0	0	0	0
	50	2	2	1	2
	100	5	4	7	8
	150	27	16	32	16
	200	48	33	51	27
	260	97	60	85	54
30	25	0	0	0	0
	50	0	1	1	1
	100	5	7	7	8
	150	42	9	41	21
	200	81	28	63	37
	260	100	59	91	57
50	25	0	0	0	0
	50	4	2	1	2
	100	8	9	10	12
	150	85	39	57	31
	200	100	49	78	45
	260	100	63	91	60

The intensity - temperature plots obtained using KBr pellets containing 0.5% AP and just 0,001% of a lanthanide oxide are shown in Fig. 3. It is revealed that the loss of any peak, depends on both, the additive and the temperature. The minimum influence is shown by lanthanum oxide which enhances the AP decomposition at 290° by 15% while at the same temperature the effect of gadolinium oxide is as high as 45%. This change in terms

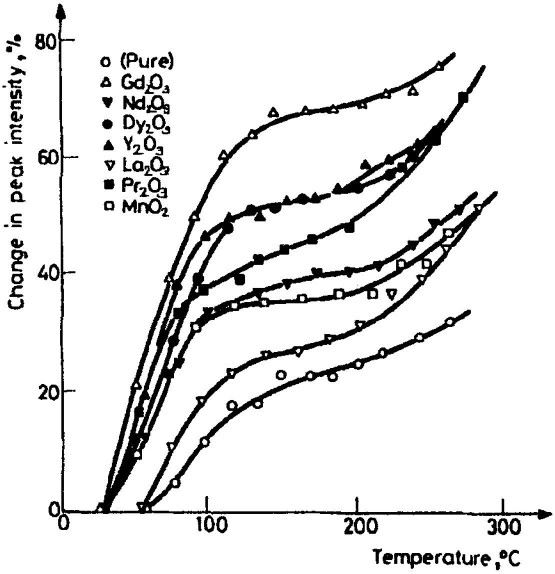

Fig. 3 Influence of rare earth oxide additive (2%) on the NH_4^+ stretching band (KBr matrix); heating rate: 5 deg min^{-1}

of the oxide additives is in the order: $Gd_2O_3 > MnO_2 > Nd_2O_3 > Pr_2O_3 > Dy_2O_3 > Y_2O_3 > La_2O_3 >$ virgin AP. Interestingly, the influence of these additives on the other frequencies is negligibly small.

Electrical properties of the rare earth oxides should have a significant role in the AP decomposition process - probably by way of promoting an electrontransfer [10] process and thus acting as a catalyst. Transfer of an electron from a perchlorate anion to an ammonium cation located in the interstitial sites is facilitated, this yields unstable radicals

$$NH_4^+ + ClO_4^- \Leftrightarrow ClO_4^{\cdot} + NH_4^{\cdot} \quad (1)$$

$$NH_4^{\cdot} \Leftrightarrow NH_3 + H^{\cdot} \quad (2)$$

As a result of crystal stabilizing effect the perchlorate radical as such cannot break easily at lower temperature while ammonium radical dissociates practically instantaneously to form ammonia and hydrogen radical. The H radical may react with perchlorate radical to produce perchloric acid molecule

$$H^{\cdot} + ClO_4^{\cdot} \rightarrow HClO_4 \qquad (3)$$

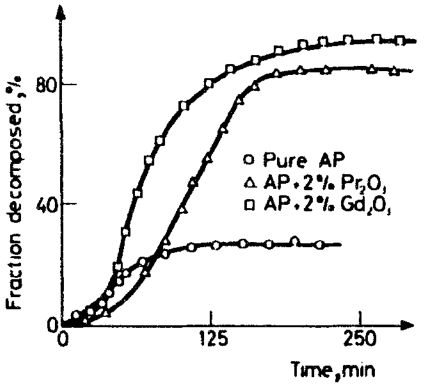

Fig. 4 Thermal decomposition of AP at 280°C

The subsequent reactions between NH_3; H and $HClO_4$ yield various products. Thermogravimetric analysis of such mixtures but in a powder form containing AP and a rare earth oxide showed a still larger influence (See Fig. 4). The decomposition of AP is enhanced from 28 to 98%. This greater influence is probably because of the unbound state of the mixture where a continuous and easier renewal of contact between AP and the oxide is possible.

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Zusammenfassung - Für den Temperaturbereich 25-290° wurden IR-Untersuchungen an Ammoniumperchlorat (AP) in Gegenwart von verschiedenen Anteilen an Ammoniumpermanganat (APm) und 2 Gew.-% verschiedener Seltenerdenoxide angestellt. Erhitzen und Spektrenaufnahme wurden in einem Schritt durchgefürt, dabei wurde angenommen, daß die Peak-Intensität proportional der Menge unzersetzten AP ist. Durch einen APm-Gehalt von 10% wird die Zersetzungstemperatur des AP von 200 auf 110° herabgesetzt und die Zersetzungsgeschwindigkeit um ein mehrfaches erhöht. Die als Produkt der Deflagration von APm entstehenden Mischoxide katalysieren den Vorgang. In Gegenwart von Seltenerdenoxiden als Additive nimmt die Intensität des Stretching-Peaks von NH^+ in folgender Reichenfolge beträchtlich ab: Gd_2O_3, MnO_2, Nd_2O_3, Pr_2O_3, Dy_2O_3, Y_2O_3, La_2O_3, unbehandeltes AP. Zur Interpretation der Ergebnisse wurde ein Elektrontransfer-Mechanismus zuhilfegenommen.