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# EFFECT OF GAMMA/NEUTRON IRRADIATION AND PERMANGANATE ADDITIVES ON THERMAL DECOMPOSITION OF AMMONIUM PERCHLORATE

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When mixed with 2% by weight of either $KMnO_4$, $Ba(MnO_4)_2$ or $NH_4MnO_4$, an enhanced thermal decomposition of cubic ammonium perchlorate, AP, was observed over the temperature range 255–300°. A still more pronounced effect was observed when AP was subjected to a radiation dose of 10 Mrad. The activation energy involved over the acceleratory stage was found to be 46 kJ $mol^{-1}$ for the irradiated AP, as against the normal value of 85 kJ $mol^{-1}$. The value remained unaltered in the case of the first two additives, while in the presence of $NH_4MnO_4$ it decreased to 55 kJ $mol^{-1}$. Neutron bombardment did not change the decomposition characteristics of AP; the $^{38}Cl$ activity produced following the $(n, \gamma)$ reaction showed highly damaged centres with the activity distribution ratio *0 : 8.5 : 20 : 71.5 for* $ClO_4^- : ClO_3^- : (ClO^- + ClO_2^-) : Cl^-$. Heating above 220° created further disorder through complete reduction of the recoil oxyanions.

The physical incorporation of a number of metal oxides and salts [1–3], and also $\gamma$-irradiation [4–6], are known to influence the thermal decomposition characteristics of AP. In the presence of $MnO_2$ desensitization of decomposition was found to take place at 257°, while at and above 265° marked sensitization occurred [3]. It was of interest to study the kinetics of thermal decomposition of AP mixed with small quantities of thermally unstable permanganates, the decomposition products of which may potentially function as catalysts. The effects of $\gamma$-radiation and the $(n, \gamma)$ reaction, which also produce highly damaged centres, are studied in this paper.

## Experimental

Mixtures containing 2% by weight of AnalaR grade $KMnO_4$ or $Ba(MnO_4)_2$ or freshly-prepared $NH_4MnO_4$ [7] and once-recrystallized commercial grade (purity > 99%) AP were prepared and ground to yield particles of size 77–60 microns. The samples were exposed either to $\gamma$-radiation from a $^{60}Co$ source (dose $\sim$100 rad $s^{-1}$) or to thermal neutrons from a $^{252}Cf$ source ($\varnothing\, 10^8 n\ s^{-1}$) in sealed glass ampoules. The neutrons were accompanied by a $\gamma$-flux corresponding to 0.2 rad $s^{-1}$. The radioactive products were analyzed as described elsewhere [8]. 100 mg of the sample was taken in a platinum cup and the loss in weight upon decomposition was recorded using a single-pan balance of 0.05 mg sensitivity and an electronically-controlled furnace which maintained the desired temperature within ±0.5°.

## Results and discussion

Typical isotherms showing the effects of permanganate additives and radiation treatment on the thermal decomposition of AP are presented in Fig. 1. The results obtained in each case showed that the plots of fractional AP decomposition, $\alpha$, *vs.* time are sigmoid in shape, with only acceleratory and decay periods and with a practically negligible induction period. Both the rate and the extent of thermal decomposition of AP increase in the presence of the additives over the temperature range studied, *viz.* 255–300°. This effect follows the order $NH_4MnO_4 > > Ba(MnO_4)_2 > KMnO_4 > AP$. In the presence of 2% $MnO_2$, on the other hand, it was shown that the decomposition is desensitized at 257° [3]. $NH_4MnO_4$ seems to be the most effective additive [9], bringing down the AP retention practically to zero on heating at 280°. As $NH_4MnO_4$ was found to explode at around 80°, it is likely that the observed sensitization of the thermal decomposition of AP may be due to the creation of dislocation and point defects and decomposition nuclei on the surface of AP particles.

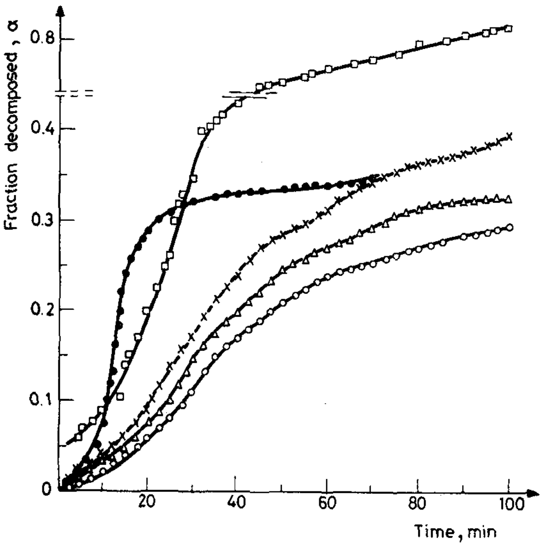

Fig. 1. Isothermal decomposition characteristics of AP at 255 °C. ○ Pure AP; △ AP + 2% $KMnO_4$; × AP + 2% $Ba(MnO_4)_2$; □ AP + 2% $NH_4MnO_4$; ● AP + 10 Mrad dose

A 10 Mrad dose of gamma radiation produced similar results upon subsequent heating as were obtained with the additives. On the other hand, the decomposition characteristics did not change when AP was neutron bombarded for 1 h with a flux of $10^8$ $n$ $s^{-1}$. From Fig. 1 it is seen that only the overall reaction period is decreased due to the radiation treatment, by way of increasing the rate constants for both the acceleratory and decay periods. The increase in the extent of decomposition, however, is always small, being 5% at 255°.

The data were analyzed according to the Prout–Tompkins equation [10], $\log(\alpha/(1-\alpha)) = k_n t + c$, where $k_1$ is for the acceleratory stage and $k_2$ for the decay stage. These rate constants were obtained from the straight line plots (Fig. 2). Typical values are listed in Table 1.

In each case it is observed that $k_1$ increases rapidly with temperature and at each temperature $k_1$ has the highest value for radiation treatment, the order

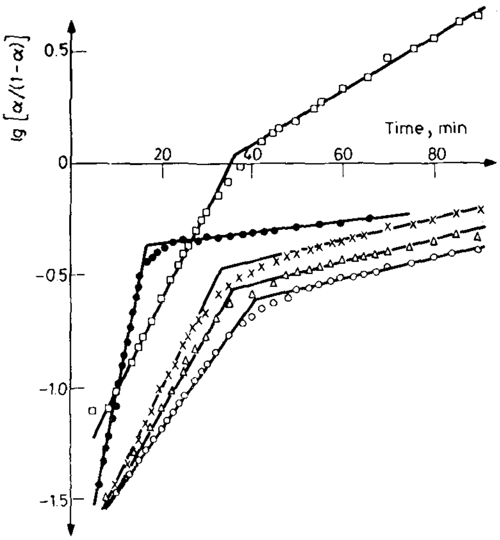

Fig. 2. Prout-Tompkins analysis of the kinetics of thermal decomposition of AP at 255 °C. ○ Pure AP; △ AP + 2% $KMnO_4$; × AP + 2% $Ba(MnO_4)_2$; □ AP + 2% $NH_4MnO_4$; ● AP + + 10 Mrad dose

Table 1

Constant $k_1$ and $k_2$ ($10^2k$ min$^{-1}$) and the corresponding activation energies $E_1$ and $E_2$ (kJ mol$^{-1}$) for the acceleratory and the decay stages of AP decomposition, respectively

| Temp., °C | 260 | | 280 | | 300 | | $E_1$ | $E_2$ |
|---|---|---|---|---|---|---|---|---|
| | $k_1$ | $k_2$ | $k_1$ | $k_2$ | $k_1$ | $k_2$ | | |
| AP | 2.6 | 0.5 | 7.1 | 0.5 | 8.8 | 0.6 | 85 | 6 |
| +2% $KMnO_4$ | 3.3 | 0.6 | 8.3 | 0.6 | 8.0 | 0.7 | 84 | 8 |
| +2% $Ba(MnO_4)_2$ | 3.9 | 0.6 | 9.7 | 0.7 | 13.6 | 0.9 | 85 | 10 |
| +2% $NH_4MnO_4$ | 8.6 | 2.8 | — | — | 40.0 | 8.6 | 55 | 69 |
| +10 Mrad dose | 10.4 | 1.9 | 17.3 | 0.4 | 20.1 | 0.3 | 46 | 56 |

being, radiation > $NH_4MnO_4$ > $Ba(MnO_4)_2$ > $KMnO_4$ > AP. The $k_2$ value, on the other hand, is almost constant at all temperatures for pure AP, as well as in the presence of additives, except in the presence of $NH_4MnO_4$ additive or on radiation treatment.

The activation energies $E_1$ for the acceleratory stage and $E_2$ for the decay stage were obtained by applying the Arrhenius treatment to the Prout–Tompkins constants, and the results are presented in the last column of Table 1. In the case of pure AP and that mixed with $KMnO_4$ or $Ba(MnO_4)_2$, the energy involved in the branching process over the acceleratory stage is seen to be much higher than that in the interfacial process over the decay stage. The constancy of the $E_1$ values suggests that these additives do not change the course of the decomposition reaction during the acceleratory stage, but provide an increased number of active sites on the surface. As a consequence of either pre-irradiation or the presence of $NH_4MnO_4$, on the other hand, $E_1$ diminishes considerably and $E_2$ increases severalfold. The decrease probably occurs due to dislocations, trapped charges and reduced products produced by gammas in the bulk of the AP, which modify the thermal decomposition process. Likewise, the process may be promoted through the greater ease of electron transfer from valence band to conduction band, facilitated by the manganese ions diffused into the AP lattice following $NH_4MnO_4$ decomposition.

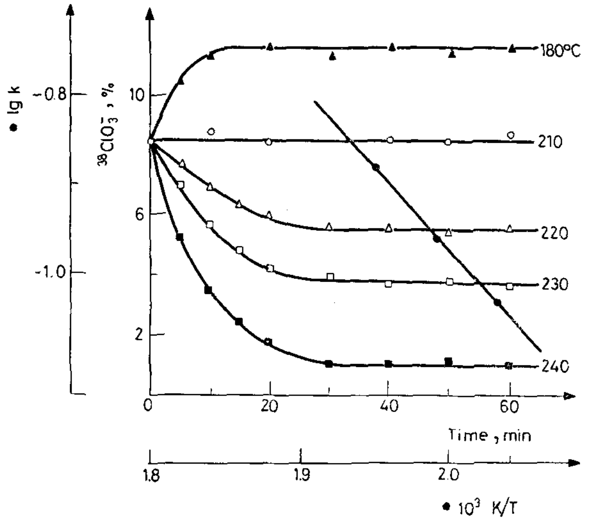

Fig. 3. Dependence of $^{38}ClO_3^-$ fraction on time of heating at different temperatures; plot of logarithm of k/min$^{-1}$ vs $1/T$

That each event of neutron capture by chlorine atoms in AP results in Cl–O bond rupture was indicated by practically zero $^{38}Cl$ activity in the AP fraction. The activity was distributed amongst the reduced fragments in the ratio 8.5 : 20 :

: 71.5 for $ClO_3^-$ : ($ClO^-$ + $ClO_2^-$) : $Cl^-$. Due to the sharing of the recoil energy between the neighbouring atoms, extensively damaged centres should be produced. In the presence of such disorder sites, AP decomposition was expected to commence at a lower temperature and to proceed further over the temperature range 220 – 240°. Instead, only the $ClO_3^-$ fragments containing $^{38}Cl$ were reduced to $Cl^-$ (Fig. 3), creating further disorder at the site without significantly affecting the AP decomposition characteristics. Above 240° all oxyanions collapsed due to thermal decomposition and the $^{38}Cl$ activity appeared wholly as $Cl^-$. The energy of activation involved in this reduction process was of the order of 43 kJ $mol^{-1}$.

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Résumé — Une décomposition thermique accélérée du perchlorate d'ammonium (AP) cubique a été observée entre 255 et 300° lorsque celui-ci est mélangé avec 2 p.c. en poids de $KMnO_4$, $Ba(MnO_4)_2$ ou $NH_4MnO_4$. Un effet encore plus prononcé est observé si le perchlorate d'ammonium est soumis à une irradiation de 10 Mrad. L'énergie d'activation nécessaire à l'étape d'accélération est de 46 kJ $mole^{-1}$, tandis que la valeur normale est de 85 kJ $mole^{-1}$. Dans le cas des deux premiers additifs, la valeur ne change pas, tandis qu'en présence de $NH_4MnO_4$ elle diminue à 55 kJ $mole^{-1}$.

Zusammenfassung — Bei dem Mischen mit 2 Gew.% $KMnO_4$, $Ba(MnO_4)_2$ oder $NH_4MnO_4$, wurde im Temperaturbereich von 255 bis 300° eine verstärkte thermische Zersetzung von kubischen Ammoniumperchlorat (AP) beobachtet. Ein noch auffälliger Effekt wurde beobachtet, wenn AP einer Bestrahlungsdosis von 10 Mrad unterworfen wurde. Die während der Beschleunigungsphase erforderliche Aktivierungsenergie betrug für das bestrahlte AP 46 kJ $Mol^{-1}$ gegenüber dem Normalwert von 85 kJ $Mol^{-1}$. Dieser Wert blieb im Falle der ersten beiden Additives unverändert, während er in Gegenwart von $NH_4MnO_4$ auf 55 kJ $Mol^{-1}$ herabgesetzt wurde.

Резюме — Для перхлората аммония кубической структуры, смешанного с 2 весовыми процентами $KMnO_4$, $Ba(MnO_4)_2$ или $NH_4MnO_4$, наблюдали более сильное термическое разложение в области температур 255—300°. Более ярко выраженный эффект наблюдали в том случае, когда перхлорат аммония был подвержен облучению дозой 10 *M* рад. В случае облученного образца, энергия активации процесса разложения составляла 46 кдж.$моль^{-1}$, по сравнению с нормальным значением 85 кдж.$моль^{-1}$ для необлученного образца. Эта величина не изменяется в случае первых двух добавок, тогда как в присутствии $NH_4MnO_4$ — значение уменьшается до 55 кдж.$моль^{-1}$.