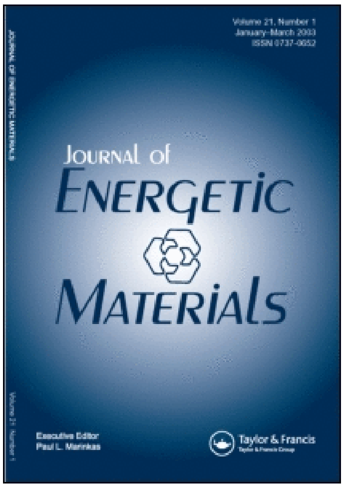

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Effect of La_2O_3 , Pr_2O_3 and Nd_2O_3 on the Thermal Decomposition of Ammonium Perchlorate.

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ABSTRACT

The effect of 'p' type rare earth oxides with partially filled 'f' orbitals like La_2O_3 , Pr_2O_3 and Nd_2O_3 on the thermal decomposition of ammonium perchlorate (AP) has been studied using isothermal and non-isothermal methods of thermal analysis. Differential thermal analysis (DTA) and thermogravimetry (TG) results reveal that these oxides influence the thermal decomposition pattern of AP significantly and bring down the decomposition temperature substantially. Isothermal studies showed substantial acceleration of the decomposition of AP with the incorporation of these oxides as little as 0.05 %. Isothermal data were analyzed using various kinetic models. The activation energy for the catalyzed decomposition of AP was significantly lower. The catalytic effect is explained on the basis wherein the 'p' type oxides act as conduites through metal cation in the electron-transfer mechanism for AP decomposition.

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INTRODUCTION

Catalytic decomposition of ammonium perchlorate (AP) is of strategic importance as it has great potential in the realm of the development of high burn-rate composite propellants, a futuristic requirement. Catalyzed decomposition of AP with wide variety of additives have been reported [1-5] Enhancement of decomposition rate by metal oxides has been attributed to the latter's ability to act as a bridge in the electron transfer from the anion to the cation of the AP molecule, which is considered the primary step in the decomposition process, leading to a chain process. When such a mechanism is operative "p' type rare earth oxides which can abstract electrons more effectively because of their incomplete 'f' shells as in lanthanide series are expected to be more effective catalysts. In order to fathom this possibility the rare earth oxides, La_20_3 , Pr_20_3 and Nd_20_3 , have been studied as catalysts for AP decomposition using mainly thermal analysis[6-7]

EXPERIMENTAL

All the chemicals used were of high purity. AP conforming to specification No. IND/ME, 105 (A) obtained from WIMCO, Bombay was used after recrystallization from distilled water. La_20_3 , Pr_20_3 and Nd_20_3 were of G.R. grade, the purity quoted was greater than 99.9% . Average particle size of AP was 11.79 µm and specific surface area 0.2610 m^2/gm. The particle sizes of La_20_3,

Pr_2O_3 and Nd_2O_3 were 7.52, 7.82 and 5.52 μm respectively and specific surface areas were 0.7980, 0.7668 and 1.0856 m^2/gm respectively.

AP and the oxides were separately dried in an oven at about 100°C for three hours and stored in a desiccator. Mixing of the oxides with AP was done by pestle and mortar and passing repeatedly through 300 mesh sieve.

For thermal analysis NETZSCH-409 simultaneous thermal analyzer was used with Pt-Ir thermocups and Pt-Pt 10% Rh thermocouples. 20 mg sample was heated at a heating rate of 10°C/min. Isothermal weight loss study was done on a thermobalance assembled in the laboratory, of sensitivity ± 0.1 mg, in the temperature range, 300 to 330°C, with 80 mg of sample. Temperature could be maintained within±1°C.

RESULTS

DYNAMIC STUDIES:

TG/DTA curves of AP and AP + oxides are shown in Fig 1a, 1b, 1c and 1d.

It is seen from Fig 1a that there are, as expected, two distinct stages of weight loss in TG of AP, the first stage occurs in the range of 271 to 341°C with 23.5% weight loss and second stage in the temperature range of 341 to 395°C with 76.5% loss. After these two stages no residue remains. DTA curve shows that there is an endothermic change at 249°C, a small exotherm at 310°C followed by a large deflagration exotherm at 379°C. Fig 1b shows the TG/DTA curves of

AP + La_2O_3 . It is seen that there are two distinct stages of weight loss in TG. The first stage begins around 271°C where 20% weight loss is observed up to 331°C ; the remaining 80% weight loss occurs over the second stage in the temperature range of 331 to 374°C. DTA curve shows that there is an endotherm at 249°C, a small exotherm at 310°C followed by a large exotherm at 353°C.

Fig. 1c represents TG/DTA curves of AP + Pr_2O_3 . In this case also there are two stages of weight loss, the first stage is over the temperature range of 271 to 339°C with about 20% loss and the second stage is over 339 to 363°C with 80% weight loss. From DTA curve it is observed that there is an endotherm at 249°C, a small exotherm at 310°C and a large exotherm at 337°C.

Fig. 1d shows TG/DTA curves of AP + Nd_2O_3 . It is seen that in TG there is only one stage from 271 to 369°C with 100% weight loss. From the DTA curve it is noted that there is an endotherm at 249°C and a sharp exotherm at 315°C. In this case two exotherms are apparently merged into one sharp exotherm.

Isothermal Studies:

Mixture of AP + rare earth oxides (1%) which were used for the dynamic study were tried for isothermal study at five different temperatures 310, 315, 320, 325 and 330°C but it was found that the reaction was going out of control i.e. the total mass decomposed within few minutes. Similar results were found with 0.5%

oxides also. However mixtures of AP with 0.05% by weight of rare earth oxides[4] were found to be amenable for kinetic study using isothermal TG.

Isothermal TG data of AP are presented in Fig. 2. Here 'α' has been expressed as the amount of AP decomposed at time 't'. Fig. 3 represents the α - t plots of AP + La_2O_3. In this case there are two stages of weight loss as also appearing in pure AP. It is seen from these plots that as compared to AP the rate of weight loss is increased and the period for 100% decomposition is decreased. The time taken for 100% decomposition is 115 minutes at 310°C; 100 minutes at 315°C, 75 minutes at 320°C. 60 minutes at 325°C and 50 minutes at 330°C. Similar results are obtained for AP + Pr_2O_3 and AP + Nd_2O_3 and the α - t curves are shown in Figs. 4 and 5 respectively. These α - t curves were analyzed for various kinetic model functions. Equations which gave better fit are given in Tables 1-4 along with the corresponding kinetic data.

DISCUSSION

The relative catalytic activity may be computed as

$$\text{Catalytic activity} = \frac{\text{Rate of catalysed decomposition}}{\text{Rate of uncatalysed decomposition}}$$

DTA-TG data reveal that the rate of overall catalysed decomposition for the systems investigated follows the order,

$$AP + Nd_2O_3 >> AP + La_2O_3 \approx AP + Pr_2O_3$$

The activation energy barrier "E" is lower in the order

$AP + Nd_20_3 << AP + La_20_3 \approx AP + Pr_20_3$ and
the log A is in the order

$AP + La_20_3 \approx AP + Pr_20_3 > AP + Nd_20_3$

The specific surface area of the oxide catalyst is as :

$Nd_20_3 >> + La_20_3 \approx Pr_20_3$

As such the catalysed decomposition of AP follows a complex pattern with certain definite trends.

If we study the electrons in a group in the periodic table, generally a slow but steady increase in the atomic and ionic radii is observed with increasing atomic number. In case of lanthanides, the nuclear charge steadily increases from cerium to lutetium as the electrons are added to the same 4 'f' orbitals. Thus the effective charge increases resulting in the atomic contraction in the size of the covalent or ionic radius with increase in the atomic number of lanthanides.

In the present non-isothermal kinetic study of AP with rare earth oxides (1%) , it is seen that the rate of decomposition is considerably enhanced and temperature of second exotherm is lowered by 10 -30°C. From the TG of AP with rare earth oxides it is observed that the weight loss starts at lower temperatures than the virgin AP. These results indicate that the rare earth oxides catalyze the thermal decomposition of AP. In the isothermal studies on the thermal decomposition of AP with rare earth oxide (0.05%) activation energy for thermal decomposition is significantly reduced.

Due to the lanthanide contraction law the rare earth metals do not shield the outermost electrons from the nuclear charge and this facilitates electron transfer from perchlorate ion to metal to form perchlorate radical and the rare earth metal undergoes reduction. This rare earth metal being in the reduced state donates an electron to the ammonium ion leading to the formation of ammonium radical and rare earth metal gets oxidized to the original state like transition metal oxide[8].

The presence of the positive holes in 'd' and 'f' orbital of rare earth oxides would favour the electron-transfer mechanism because they can accept electrons from the perchlorate ion thus enhancing the decomposition. The properties of the cations of the oxides may play an important role in the decomposition of AP. The rare earth oxides are classified as 'p' type semiconductors[9] and due to their half-filled shells can help the electron-transfer process.

Mechanism of Catalytic Decomposition:

The catalytic effect of rare earth oxides on the thermal decomposition of AP may therefore be explained based on the electron-transfer mechanism:

$NH_4ClO_4 \rightleftharpoons NH_4^+ + ClO_4^-$ .. 1

$M^{3+} + ClO_4^- \rightarrow M^{2+} + ClO_4^\bullet$ .. 2

$M^{2+} + NH_4^+ \rightarrow M^{3+} + NH_4^\bullet$ .. 3

This mechanism is consistent with the kinetic parameters obtained in the present study as well as the reported literature [10-12].

When the specific surface area of the oxide catalyst is larger there will be corresponding increase in the interfacial contact area between the oxide and AP particles leading to easier and fast diffusing path ways for the oxide into the AP lattice where in the metal oxide facilitates the electron transfer between the ammonium and perchlorate ions resulting in lower activation energy barrier. Significantly lower "E" value observed for Nd_20_3 catalysed AP decomposition, thus may be attributed to its higher surface area. Particle size, shape, surface structure and texture of the oxide and AP in addition to electronic and other properties play a crucial role in the decomposition as the surface defect structure facilitates diffusion process into solid matrix.

CONCLUSION:

La_20_3 , Pr_20_3 and Nd_20_3 catalyzed the thermal decomposition of AP significantly and hence are expected to be very good burn rate accelerators for AP based composite propellants. These oxides perhaps offer the best catalytic effect among the oxides so far reported as catalysts for the thermal decomposition of AP.

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TABLE 1

Ap (Pure)

Correlation coefficient "R" obtained for various F (α) and rate parameters by isothermal TG.

Sr No.	F (α)	Isothermal temperature °C					E/k	
		310	315	320	325	330	J mol^{-1}	Log A s^{-1}
1.	α	0.9823	0.9857	0.9884	0.9881	0.9835	158	12.0
2.	$1-(1-\alpha)^{1/2}$	0.9959	0.9968	0.9968	0.9969	0.9994	162	12.1
3.	$1-(1-\alpha)^{1/3}$	0.9911	0.9935	0.9961	0.9943	0.9979	169	12.7
4.	$[-1n(1-\alpha)]^{3/2}$	0.9935	0.9954	0.9962	0.9954	0.9943	173	13.5
5.	$[-1n(1-\alpha)]^{1/2}$	0.9988	0.9993	0.9992	0.9992	0.9972	166	12.7
6.	$[-1n(1-\alpha)]^{1/3}$	0.9956	0.9955	0.9950	0.9959	0.9916	159	11.9
7	$1n\,[\alpha/(1-\alpha)]$	0.9940	0.9953	0.9971	0.9972	0.9944	163	13.0

TABLE 2

Correlation coefficient "R" obtained for various F (α) and rate parameters by isothermal TG for the TD of AP with La_2O_3

Sr No.	F (α)	Isothermal temperature °C					E/k	
		310	315	320	325	330	J mol^{-1}	Log A s^{-1}
1.	α^2	0.9975	0.9876	0.9924	0.9940	0.9986	156	12.0
2.	$1-(1-\alpha)^{1/2}$	0.9942	0.9969	0.9963	0.9977	0.9904	152	11.5
3.	$1-(1-\alpha)^{1/3}$	0.9984	0.9932	0.9980	0.9977	0.9961	155	12.7
4.	$[-\ln(1-\alpha)]$	0.9916	0.9809	0.9869	0.9840	0.9997	159	12.7
5.	$[-\ln(1-\alpha)]^{3/2}$	0.9954	0.9969	0.9987	0.9978	0.9923	153	12.0
6.	$[-\ln(1-\alpha)]^{1/2}$	0.9947	0.9990	0.9982	0.9994	0.9901	150	11.6
7	$(1-\alpha)[\ln(1-\alpha)]$	0.9979	0.9563	0.9886	0.9881	0.9959	161	12.4

TABLE 3

Correlation coefficient "R" obtained for various F (α) rate parameters

by isothermal TG for the TD of AP with Pr_2O_3

Sr No.	F (α)	Isothermal temperature °C					E/k J mol^{-1}	Log A s^{-1}
		310	315	320	325	330		
1.	$1-(1-\alpha)^{1/2}$	0.9939	0.9950	0.9900	0.9904	0.9516	151	11.5
2.	$1-(1-\alpha)^{1/3}$	0.9954	0.9964	0.9976	0.9943	0.9777	157	11.9
3.	$[\ln(1-\alpha)]^{3/2}$	0.9971	0.9978	0.9990	0.9925	0.9791	161	12.7
4.	$[\ln(1-\alpha)]^{1/2}$	0.9958	0.9886	0.9962	0.9987	0.9539	158	12.3
5.	$(1-\alpha)[\ln(1-\alpha)]+\alpha$	0.9792	0.9812	0.9940	0.9983	0.9939	156	11.9
6.	$[-(2/3)]-(1-\alpha)]^{2/3}$	0.9698	0.9715	0.9908	0.9942	0.9997	161	11.9
7	$\ln[\alpha/(1-\alpha)]$	0.9884	0.9948	0.9944	0.9560	0.9272	161	13.1

TABLE 4

Correlation coefficient "R" obtained for various F (α) and rate parameters by isothermal TG for the TD of AP with Nd_2O_3

Sr No.	F (α)	Isothermal temperature °C					E/k	
		310	315	320	325	330	J mol^{-1}	Log A s^{-1}
1.	α	0.9912	0.9899	0.9956	0.9966	0.9932	98	6.8
2.	$1-(1-\alpha)^{1/2}$	0.9983	0.9978	0.9980	0.9984	0.9982	104	7.2
3.	$1-(1-\alpha)^{1/3}$	0.9953	0.9951	0.9972	0.9987	0.9977	106	7.3
4.	$[-\ln(1-\alpha)]^{3/2}$	0.9957	0.9956	0.9942	0.9975	0.9957	107	7.8
5.	$[-\ln(1-\alpha)]^{1/2}$	0.9994	0.9996	0.9961	0.9979	0.9981	105	7.5
6.	$[-\ln(1-\alpha)]^{1/3}$	0.9959	0.9968	0.9894	0.9916	0.9922	103	7.1
7	$\ln[\alpha/(1-\alpha)]$	0.9965	0.9978	0.9896	0.9933	0.9932	104	8.0

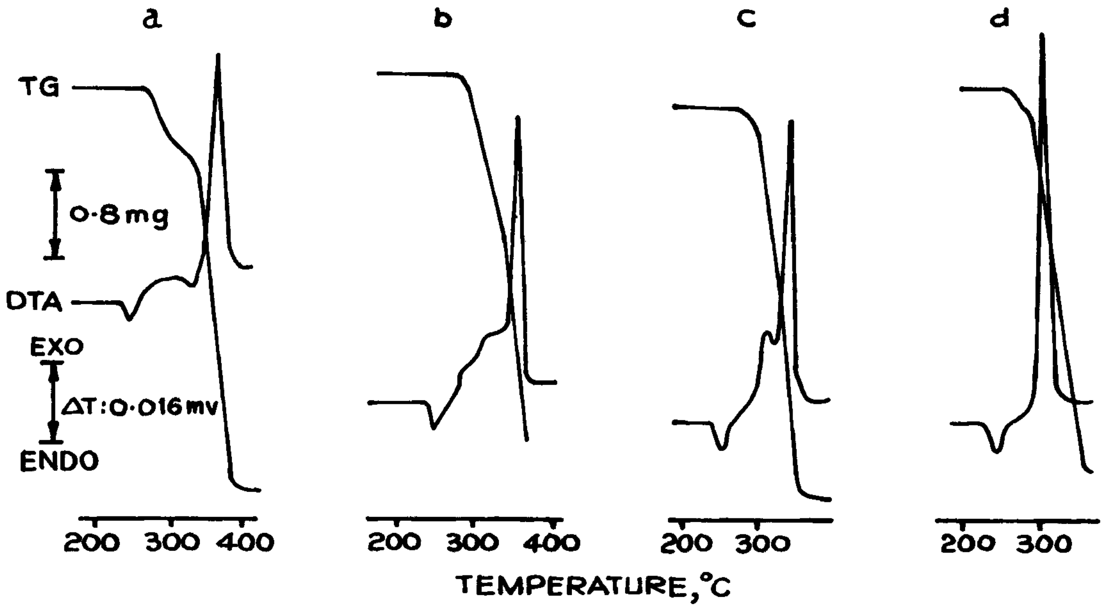
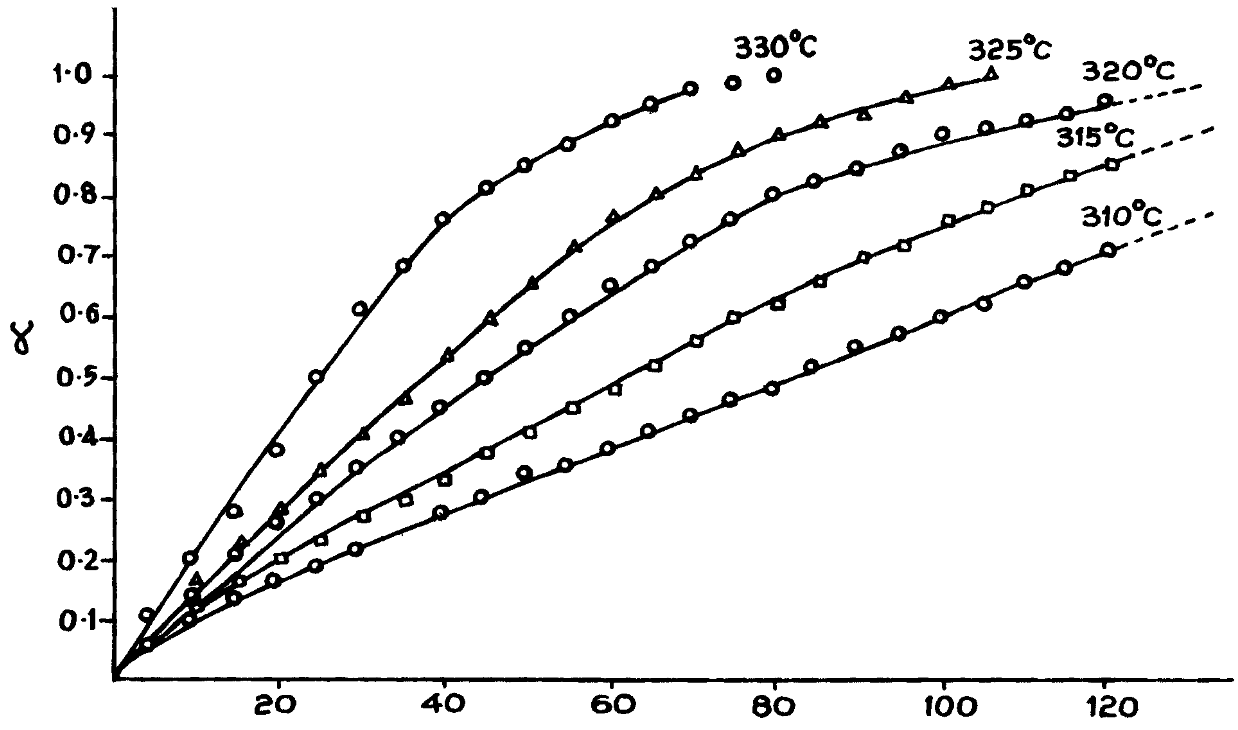


FIGURE 1

TG/DTA Curves of

(a) Pure AP (b) AP + La_2O_3 (1%)

(c) AP + Pr_2O_3 (1 %) (d) AP + Nd_2O_3 (1%)



TIME IN MINUTE

FIGURE 2

α - t Plots for the thermal decomposition of pure AP at different temperatures.

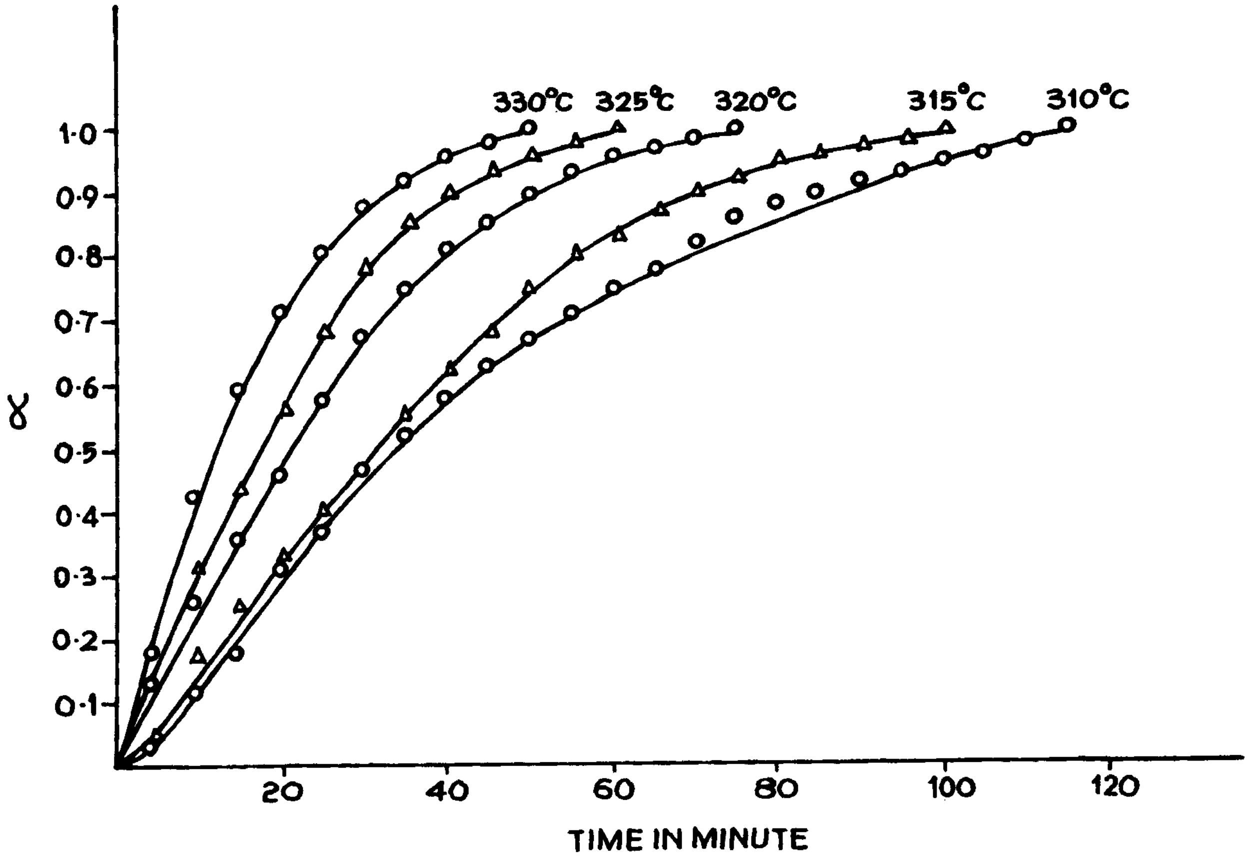


FIGURE 3

α - t Plots for the thermal decomposition of AP + La_2O_3 (0.05%) at different temperatures.

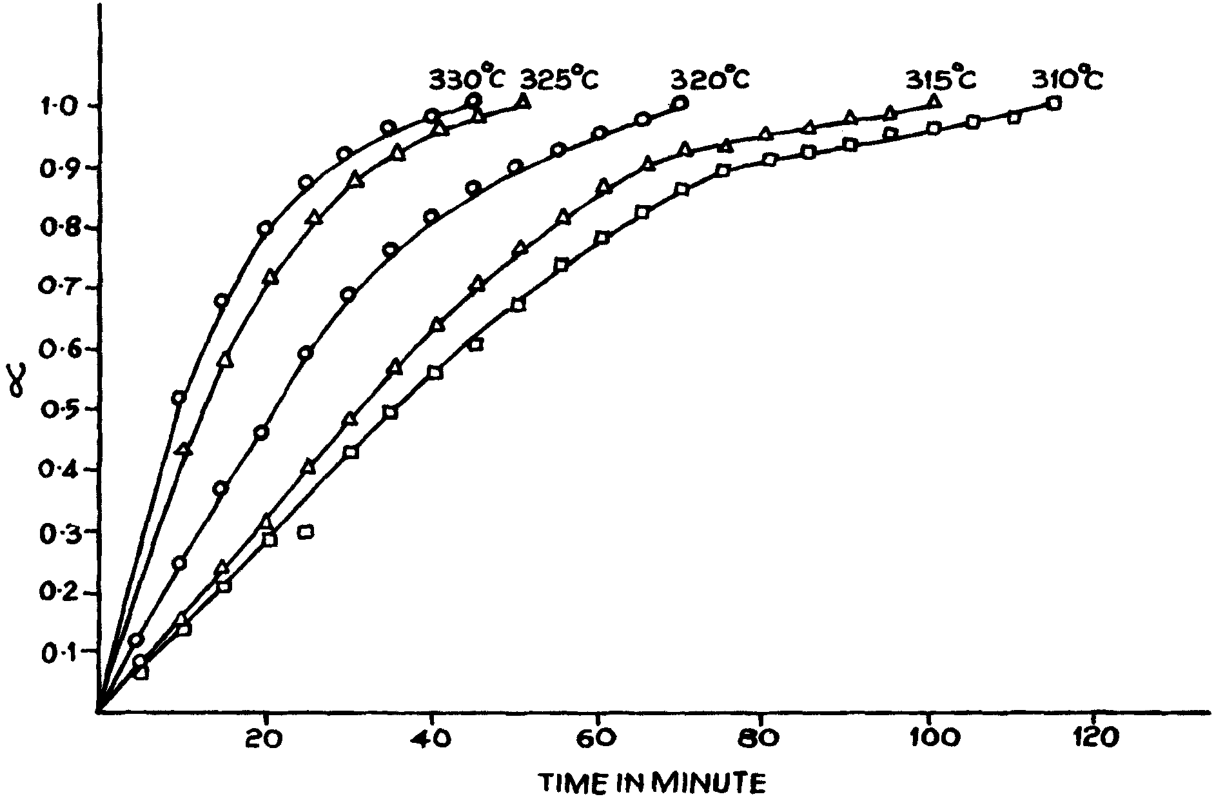


FIGURE 4

α - t Plots for the thermal decomposition of AP + Pr_2O_3 (0.05%) at different temperatures.

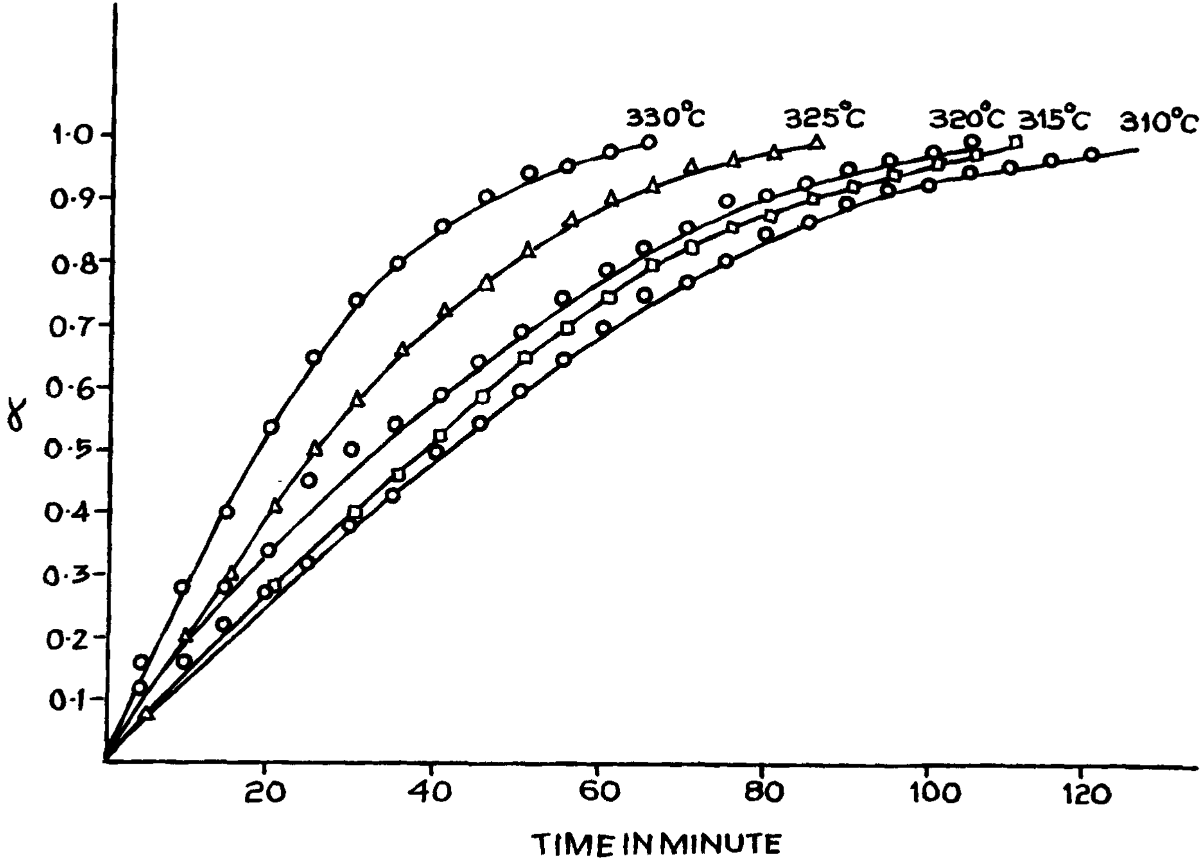


FIGURE 5

α - t Plots for the thermal decomposition of AP + Nd_2O_3 (0.05%) at different temperatures.