Kinetic Studies on o-Toluidine Nitrate/Nitrogen Peroxide System

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o-Toluidine nitrate (OTN) and N_2O_4 system has been shown to act as a convenient hybrid rocket propellant. The kinetics of heterogeneous chemical reaction between o-toluidine nitrate and NO_2 has been investigated by measuring the reaction zone thickness as a function of time. An empirical relation $\xi^n = k_t$, where ξ is the reaction zone thickness at time t and k and n are constants, is found to fit the experimental data. The values of k and n are found to be pressure and temperature sensitive. The values of k and n also depend on particle size of o-toluidine nitrate at temperature below 40°C but above 40°C these are independent of particle size. The value of k is found to be enhanced by the addition of ammonium metavanadate to OTN.

THE studies on hybrid propellants are meagre as compared to those for solid and liquid propellants. Earlier studies on hybrid propellants are confined to engineering aspects[1-10] and the role of chemical factors in influencing the ballistic properties of the propellants seems to have been overlooked. Rastogi and co workers[11,12] investigated the role of physicochemical factors in the combustion of polymeric fuel/O_2 hybrid system. The role of surface reactions in hypergolic ignition of solid-liquid systems has been investigated by Bernard et al.[13]. Rastogi and coworkers[14] showed that these factors influence the pressure dependence of burning rate of hybrid propellants.

Hybrid propellant systems employing solid aromatic amines and nitric acid or nitrogen tetroxide as the oxidiser have recently attracted considerable interest[13,15,16]. Heterogeneous combustion studies on aniline nitrate and red fuming nitric acid (RFNA) were made by Rastogi and Bisht[17,18]. Heterogeneous chemical reaction occurring between o-toluidine nitrate (OTN) and RFNA has been investigated by Rastogi et al.[19] Preliminary experiments show that OTN is spontaneously ignitable with N_2O_4 and that the system can be a potential hybrid propellant. OTN + N_2O_4 system has the advantage that available oxygen is larger as compared to the simple amines. Impingement of hot vapours ($\approx 80°C$) of RFNA on OTN brings about spontaneous combustion. It is also observed that interaction between hot NO_2 and OTN also brings about spontaneous ignition†. It is obvious that combustion is preceded by solid-gas reaction. Hence, in order to understand the combustion behaviour of this system a detailed study of the kinetics of the heterogeneous reaction at the solid-gas interface was undertaken. The kinetics was followed as a function of (i) pressure of NO_2 in the reaction cell, (ii) particle size of OTN and (iii) temperature of the reaction cell. The role of additives like ammonium metavanadate has also been investigated.

Materials and Methods

o-Toluidine nitrate (OTN) was prepared in the laboratory and purified in a manner described earlier[19].

Nitrogen peroxide was prepared in the laboratory[20] by heating lead nitrate and passing the liberated gas through a U-tube immersed in a freezing mixture. Another flask (50 ml capacity) was attached to the lower part of the U-tube in which N_2O_4 could be collected. N_2O_4 thus prepared was always kept below 10°C in order to prevent the dissociation of N_2O_4.

Ammonium metavanadate (REACHIM, USSR) was used as such.

Polyvinyl chloride, grade SR-10 (Rajasthan Vinyl & Chemical Industries, New Delhi) was used as the binder.

Ignition studies — Finely powdered OTN (3g, 100-150 mesh) mixed with 10% ammonium metavandadate was taken in a flat bottom glass tube of 4 cm length and 2 cm diameter. The content was packed to a length of 1.8 cm in the tube. Hot NO_2 vapours at $\sim 80°C$ were allowed to impinge the surface of OTN. Spontaneous ignition was observed.

In another experiment a compact mixture of finely powdered (2g, 100-150 mesh) OTN mixed with 10% ammonium metavanadate was put in a porcelain dish. Liquid N_2O_4 was added to it with the help of a special dropper. The jet of the dropper had a large diameter ($\sim 5mm$) so that the entire liquid was ejected all at once. Spontaneous ignition was observed.

In the third experiment ignition was studied with OTN with PVC as binder. The experimental details are as follows : Grannular PVC (1 g) was taken in a porcelain dish and methylene dichloride (15 ml) added to it. The contents were warmed.

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†It should be noted that in the liquid state we have pure N_2O_4 but in the vapour N_2O_4 dissociates into NO_2 and a mixture of N_2O_4 and NO_2 is obtained, the composition of which depends on temperature. In this paper N_2O_4 denotes the liquid while NO_2 represents the mixture in the gaseous state.

OTN (9g, 100-150 mesh) and ammonium meta-vanadate (1g) were thoroughly mixed with the viscous PVC in a dish to give a cylindrical mould. Care was taken to eliminate air bubbles in the cast. The moulds were allowed to cure in an oven maintained at 60°C. Adequate amount of liquid N_2O_4 was added in the porcelain dish with the help of a dropper all at once. Spontaneous burning occurred.

Kinetic studies — The apparatus shown in Fig. 1 was used for the study of kinetics. The design is similar to that adopted by Rastogi and Bisht[17]. The madifications are self-explanatory.

OTN (3g) of a known particle size was taken in the reaction tube L (int. diam. 1.6 cm and length 8 cm). The content of the tube was packed to a definite length, the tube L was fixed at the proper position and connected to the container B by the stop-cock A. The container B was connected to the manometer and the vacuum pump through stop-cock C. The whole assembly was evacuated with the help of a vacuum pump by suitably turning the stopcock D. The vacuum was of the order of 10^{-3} mm Hg. The stopcock A was closed. Now stop-cock D was connected to NO_2 reservoir and NO_2 introduced into the system. In order to remove air, the system was again evacuated. The assembly was again filled with NO_2 and again evacuated. This was repeated once again. Finally the NO_2 was filled to a desired pressure.

The reaction cell was allowed to attain the temperature of the thermostat. The stopcock A was now opened carefully in order to allow NO_2 to come in contact with OTN. A brown black product was formed at the surface layer of the solid fuel in the reaction tube L. The progress of the reaction was followed by measuring the thickness of the reaction zone with the help of a cathetometer (model OSAW, India) at different intervals of time. The pressure of NO_2 in tube B could be maintained constant during the course of the experiment with the help of NO_2 reservoir and that of mercury reservoir J.

Experiments were performed at various pressures of NO_2. The experiments were also performed for various particle size of OTN, at several temperatures and by varying the amount of ammonium metavanadate used as an additive. The experiments were repeated several times and the reproducibility was found to be within ± 5%.

Results and Discussion

Experimental observation on ignition of OTN and NO_2 system show that the system can be used as a hybrid propellant. The kinetics of the solid-gas heterogeneous reaction between OTN and NO_2 was followed by measuring the increase in the thickness of the reaction zone as a function of time. The results are plotted in Figs 2-6 under different conditions. An equation of the type.

$$\xi^n = kt \qquad ..(1)$$

where ξ is the reaction zone thickness at time t and k and n are constants, has been found to fit the experimental data. When log ξ was plotted against log t, linear plots were obtained in each case. A typical fit of Eq. (1) is shown in Fig. 7. Both k and n values are found to increase with pressure of NO_2 and temperature (Figs 8 and 9). The values of k and n also depend on particle size of OTN. The finer the particles the higher the values of k and n. This increase is more pronounced at lower temperaturers (30-35°C) whereas at 40°C
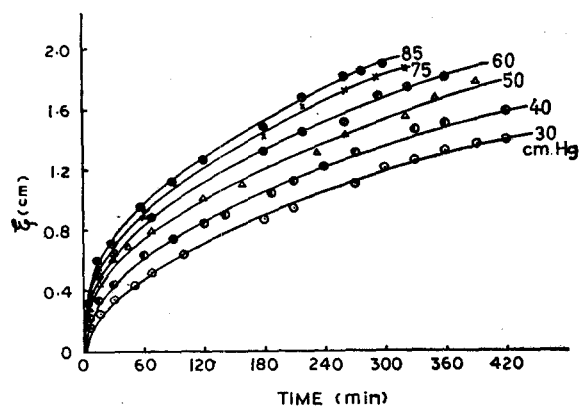

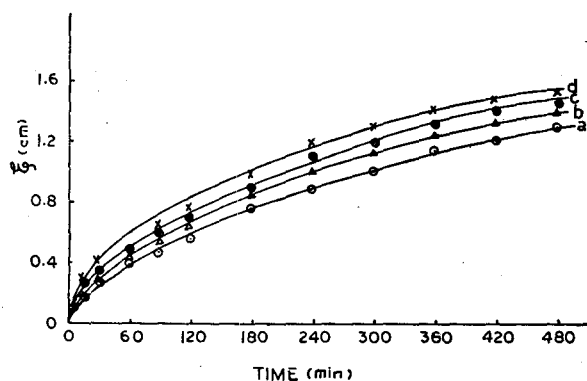Fig. 2 — Effect of varying pressure of NO_2 on reaction rate [Particle size of OTN=100-150 mesh; temp. = 40°C]

Fig. 3 — Effect of varying particle size of OTN on reaction rate at 30°C [NO_2 pressure = 40 cm Hg. Particle size : (a) 50-100; (b) 100-150 ; (c) 150-240 ; (d) 240-350 mesh]
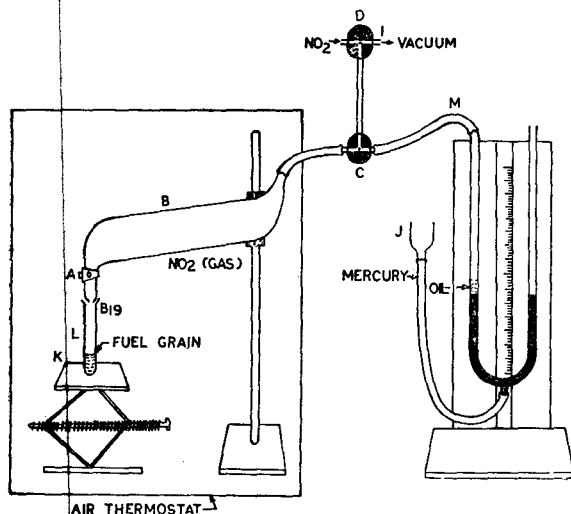

Fig. 1 — Experimental set-up for the study of kinetics of heterogeneous reaction between o-toluidine nitrate and NO_2
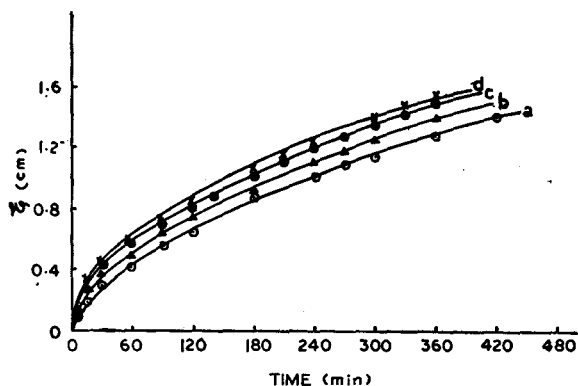
Fig. 4 — Effect of varying particle size of OTN on reaction rate at 35° [Other conditions as outlined in Fig. 3]
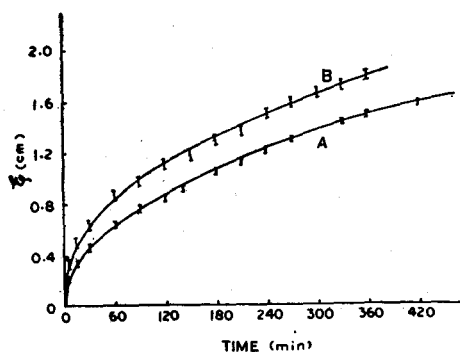

Fig. 5 — Effect of varying particle size of OTN on reaction rate at 40° (A) and 50°C (B) [Single plots cover the particle size 50-100, 100-150, 150-240, · 240-350 mesh; NO₂ pressure= 40 cm Hg]

and above k and n both become independent of the particle size. Nevertheless, the values of k and n are higher than the corresponding values at lower temperatures. Energy of activation of the overall process has been obtained from the linear Arrhenius plots and the values thus calculated for different particle sizes and at 40 cm Hg of NO₂ pressure are : 12.0, 9.3, 8.8 and 7.0 kcal mol^{-1} for particle sizes 50-100, 100-150, 150-240 and 240-350 mesh respectively.

Effect of the addition of burning rate catalyst such as ammonium metavanadate on the kinetics has also been investigated. In the presence of 1.0, 2.5, 5.5 and 8.0% (w/w) of ammonium metavanadate the values of k increase to 14.5, 18.1, 24.2 and 29.2 × 10^{-3} cm^n min^{-1} respectively as compared to the value 8.3 × 10^{-3} cm^n min^{-1} in the absence of ammonium metavanadate at 40 cm Hg of NO₂, temp. = 45°C and OTN particle size=100-150 mesh.

We shall now discuss the mechanism of surface reactions. There would be two competing processes : (a) the rate of diffusion of NO₂, and (b) the rate of reaction at the surface.

Molecules of NO₂ collide with the particles of OTN and initially reaction takes place on the surface of the fuel particles. A blue black product is formed at surface of fuel grain whose thickness grows with time. This shows that adsorption of NO₂ takes
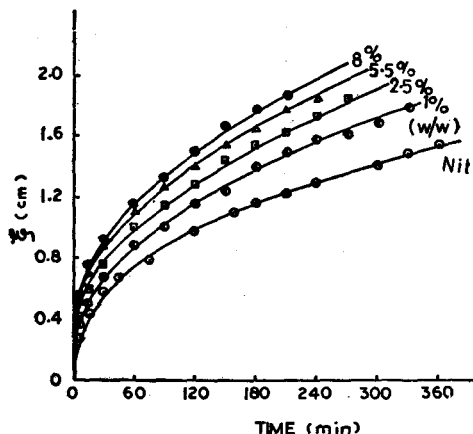

Fig. 6 — Effect of additive ammonium metavanadate at different concentrations on reaction rate at 45°C [Particle size of OTN = 100-150 mesh]
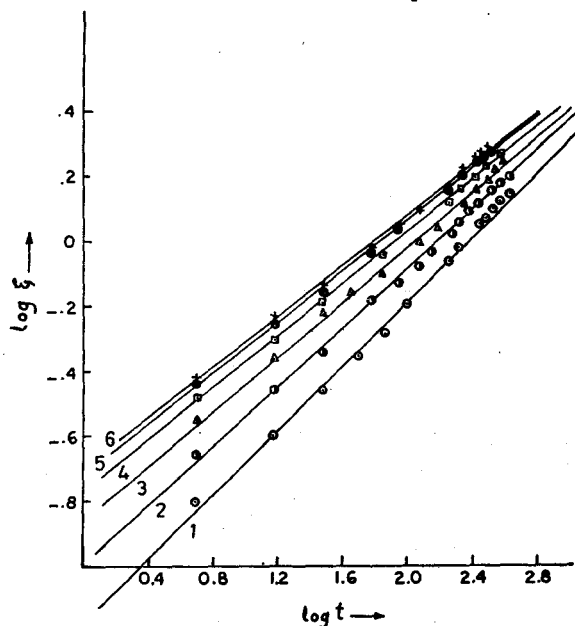

Fig. 7 — Typical fit of Eq. (1) to the kinetic data [OTN particle size = 100-150 mesh; NO₂ pressure (cm Hg) : (1) 30; (2) 40; (3) 50; (4) 60; (5) 75; and (6) 85; temp. = 40°C]
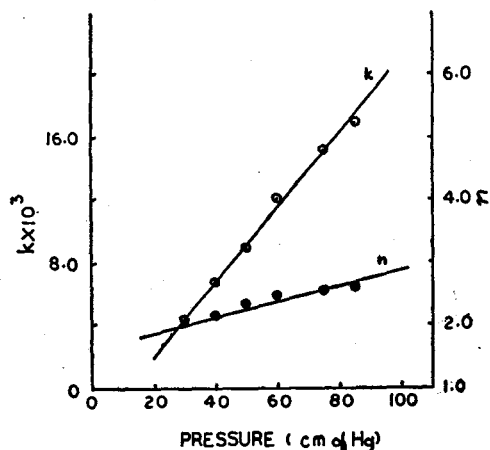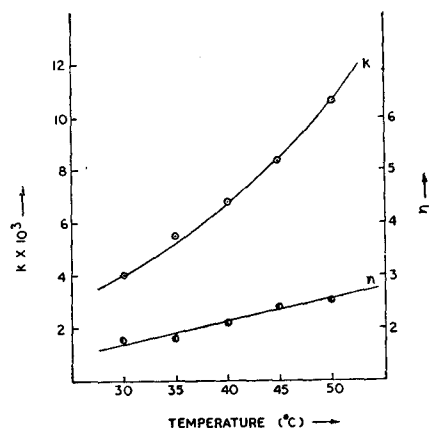

Fig. 8 — Dependence of k and n on pressure [Particle size =100-150 mesh; temp. = 40°C]

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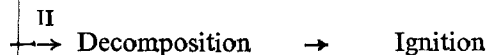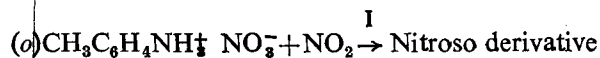TABLE 1 — DEPENDENCE OF k AND n ON THE PARTICLE SIZE OF OTN

[Pressure of NO_2 in the reaction cell $= 40$ cm Hg]

Particle size (mesh)	30°		35°		40°		45°		50°	
	$k \times 10^3$ cm^n min^{-1}	n	$k \times 10^3$ cm^n min^{-1}	n	$k \times 10^3$ cm^n min^{-1}	n	$k \times 10^3$ cm^n min^{-1}	n	$k \times 10^3$ cm^n min^{-1}	n
50-100	3.26	1.71	4.37	1.76	6.8	2.2	8.3	2.4	10.7	2.5
100-150	3.98	1.77	5.45	1.82	6.8	2.2	8.3	2.4	10.7	2.5
150-240	4.65	1.89	6.26	1.95	6.8	2.2	8.3	2.40	10.7	2.5
240-350	5.36	1.96	6.31	2.00	6.8	2.2	8.3	2.4	10.7	2.5

Fig. 9 — Dependence of k and n on temperature [Particle size $= 100$-150 mesh ; pressure $= 40$ cm Hg]

place followed by some interaction which does not initially lead to the formation of gaseous products. Subsequently, gaseous products are formed and desorbed. It has been reported by Bisht[21] that the gaseous products like CO_2, CO, O_2 and N_2 are amongst the products formed as a result of reaction between aniline nitrate and NO_2 indicating the ring rupture. Further, formation of nitroso derivatives has also been suggested by Kishore and Upadhyaya[22].

The following interface reaction seems to be more plausible, in view of the above arguments:

$$(o)CH_3C_6H_4NH_3^+ \overset{I}{\quad} NO_3^- + NO_2 \to \text{Nitroso derivative}$$

$$\overset{II}{\downarrow}$$

$$\longrightarrow \text{Decomposition} \quad \to \quad \text{Ignition}$$

There are three types of domains which are important in heterogeneous reactions : (a) a kinetic domain where the rate-controlling step is the chemical reaction; (b) a diffusion domain where the rate-controlling step is the diffusion to the reacting interface; and (c) a transition domain where diffusion and kinetics produce a marked effect at the same time.

It also follows from Eq. (1) that

$$\frac{d\xi}{dt} = K. \, t^{(1-n)/n} \qquad \ldots (2)$$

where

$$K = \frac{(k)^{1/n}}{n}$$

Since, n is always greater than unity (Table 1), the quantity $(1 - n)/n$ will always be negative. Therefore as $t \to 0$, $-\frac{d\xi}{dt} \to \infty$, showing thereby that initially the rate of reaction is extremely high. Further, it is found that the energy of activation is much lower as compared to that for usual chemical reactions. It follows that the reaction is controlled by diffusion. Diffusion of NO_2 into OTN may occur either by (a) surface migration, (b) grain boundary diffusion or (c) channels formed in the reactant mixture. Both (a) and (b) would require that the rate of reaction should depend on the particle size. Since k depends on particle size below 40°C and is independent of particle size above 40°C, it seems plausible that below 40°C grain boundary diffusion or surface migration occurs whereas above 40°C diffusion probably occurs through channels.

Acknowledgement

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