Kinetics of Heterogeneous Reaction between *o*-Toluidine Nitrate & Red Fuming Nitric Acid

R. P. RASTOGI, H. J. SINGH & KAUSHAL KISHORE

Department of Chemistry, University of Gorakhpur, Gorakhpur 273001

Kinetics of heterogeneous reaction between o-toluidine nitrate(s) and red fuming nitric acid (aq.) has been studied. The results suggest that the reaction is chemically-controlled and not diffusion-controlled and the reaction involves consecutive reactions. The rate constant of the slowest step is found to be independent of the particle size or the degree of compactness of the solid nitrate whereas it increases with the increase in the strength of the acid. Ammonium metavanadate which acts as a burning rate catalyst is found to enhance the value of the rate constant of the slowest step.

THE chemical reactions leading to combustion of solid propellants[1-7] and liquid propellants[8-10] have been investigated by a number of workers. However similar studies on hybrid propellants, which have in most cases fuel in the solid state and the oxidizer in the liquid state have been negligible[11,12]. Although, in the conventional theories of hybrid combustion turbulent boundary layer is invoked[13,14], the role of chemical reactions can not be overlooked. This is further substantiated by the recent work of Bernard *et al.*[15,16], and Rastogi and Desh Deepak[17] on the pressure dependence of the hybrid regression rate. The special feature of chemical reactions in hybrid combustion s the heterogeneous nature of some of the steps. A study of these is vital for controlling the internal ballistics of hybrid rocket engines.

Accordingly, the reaction between *o*-toluidine nitrate (solid) and red fuming nitric acid (liquid) was investigated in detail. Since the reaction between *o*-toluidine nitrate and red fuming nitric acid is highly exothermic and leads to ignition, the kinetics was followed by using dilute red fuming nitric acid. The kinetics has been studied as a function of (i) particle size of the fuel, (ii) concentration of the acid, (iii) temperature, (iv) amount of the catalyst (ammonium metavanadate). The experiments have been performed with *o*-toluidine nitrate in powder form as well as in pellet form. The latter was done since a cast of fuel grain is used in actual rocket motor. Effect of compression of the fuel grain on the heterogeneous kinetics has also been investigated.

Materials and Methods

o-Toluidine nitrate — It was prepared in the laboratory and recrystallized from a mixture of ethyl acetate and ethyl alcohol (50%, v/v)[18]; m.p. 185°.

Pellets of *o*-toluidine nitrate were prepared as follows: *o*-toluidine nitrate (0·5 g, particle size 150-240 mesh) was taken in a die (int. diam. 1 cm) Using a compression machine (Associated Instru-

ment Manufacturers, India) the pellets were prepared by applying known pressures so that the degree of compression could be varied at will.

Red fuming nitric acid (RFNA) (*d*, 1·5/cm³) containing 10% oxides of nitrogen was obtained from Basic and Synthetic Chemicals, Calcutta. Aqueous solution of red fuming nitric acid was prepared by mixing desired amounts of red fuming nitric acid and water in a freezing mixture in order to prevent oxides of nitrogen to escape.

Experimental set-up and procedure — The experimental set-up used for studying the kinetics is shown in Fig. 1. The apparatus consisted of a reaction tube *A* (20 cm long, 3·5 cm int. diam.) fitted with a mercury sealed stirrer *D*. The tube *A* had a side limb *B* through which acid was added in the reaction tube. The stirrer *D* had a side arm *C* which was connected to a U-tube *E* filled with KOH pellets in order to absorb carbon dioxide, moisture and oxides of nitrogen. The tube *E* was connected to a graduated glass burette *F* which was enclosed in a glass jacket filled with water in order to keep the temperature of the gas constant. The residual gas which was nitrogen could be collected over water at atmospheric pressure. Reaction tube *A* was
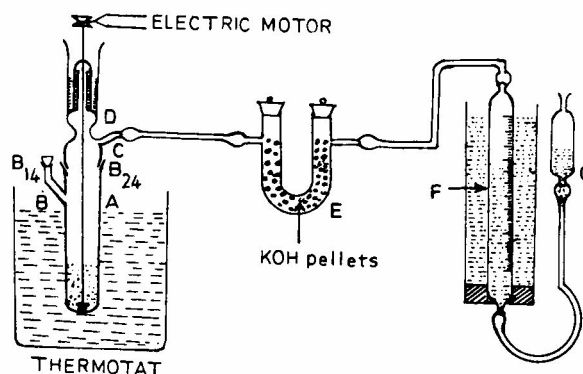

Fig. 1 — Experimental set-up for the kinetic study of the reaction between *o*-toluidine nitrate and red fuming nitric acid

placed in an oil thermostat maintained correct to ±0·5°. The actual experiment was done as follows.

o-Toluidine nitrate (0·3 g) of a definite particle size was taken in the reaction tube A. The particles of different sizes were collected with the help of appropriate sieves. Dilute RFNA (100 ml) of definite percentage was taken in a separate tube and was placed in the thermostat which was maintained at a definite temperature. When dilute RFNA had attained the temperature of the bath, it was added to the reaction vessel all at once. The side limb B was subsequently stoppered. The mixture was stirred continuously. The volume of nitrogen gas evolved was measured at different time intervals by levelling the water columns in C and gas burette F.

The accuracy of the experiment was checked by calculating the volume of N_2 gas expected to be evolved under the experimental condition from 0·3 g of o-toluidine nitrate after complete reaction. The agreement between experimental and calculated values was good (within ±1%). However, deviations are observed with higher percentages of nitric acid and at higher temperatures. This might be due to unabsorbed oxides of nitrogen.

The experiments were repeated with powdered samples as well as pelletized samples.

Results and Discussion

Volume of the nitrogen gas evolved at various intervals of time has been plotted in Figs. 2-6. Experiments have been repeated for o-toluidine
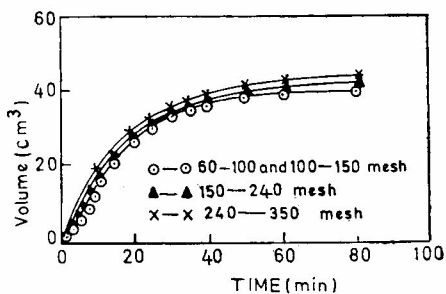

Fig. 4 — Volume of nitrogen evolved at various time intervals in the reaction of o-toluidine nitrate (150-240 mesh) with red fuming nitric acid at 35° in the presence of varying amounts of ammonium metavanadate

Fig. 5 — Volume of nitrogen evolved at various time intervals in the reaction of o-toluidine nitrate (0·5 g in powder as well as pellet forms) with red fuming nitric acid at 35°

Fig. 2 — Volume of nitrogen evolved at various time intervals in the reaction of o-toluidine nitrate of different particle sizes with red fuming nitric acid (5%) at 35°
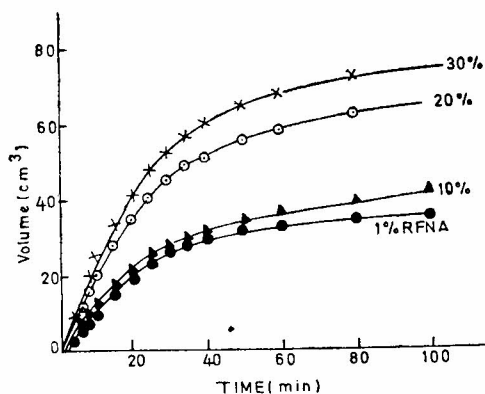

Fig. 3 — Volume of nitrogen evolved at various time intervals in the reaction of o-toluidine nitrate with red fuming nitric acid of different compositions at 35°
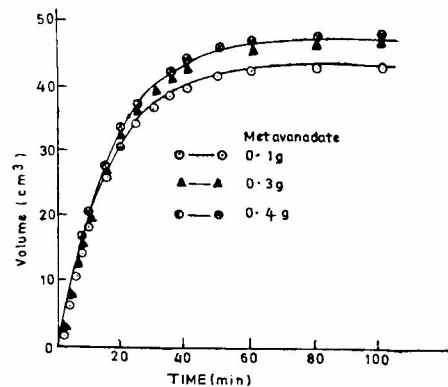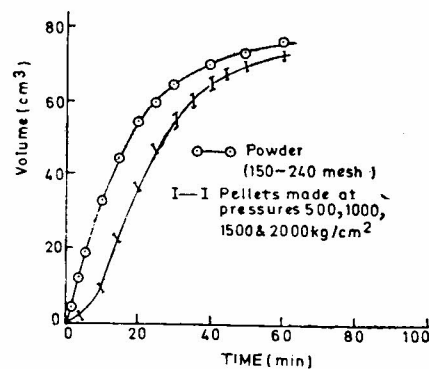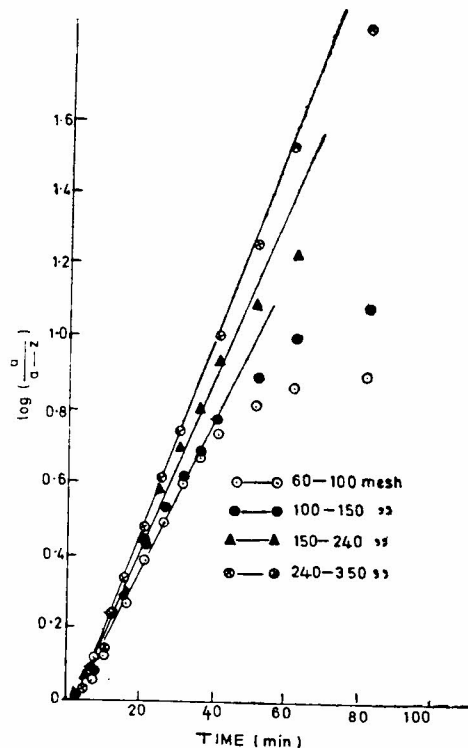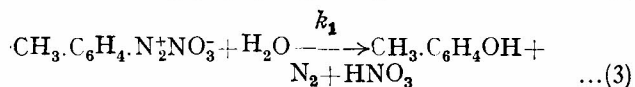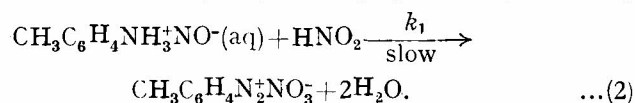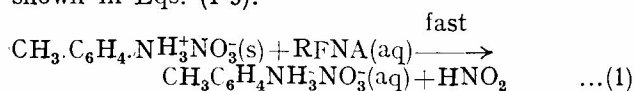

Fig. 6 — Plots of log $(a/a-z)$ versus time for the results plotted in Fig. 2

nitrate of different particle sizes and at different concentrations of nitric acid, etc. Results plotted in Figs. 2-5 show that the kinetics is fairly complex.

In order to examine the nature of the kinetics involved, attempts were made to use the concept of ion-exchange kinetics. Neither the film diffusion model nor the particle diffusion model could explain the results[19].

Kinetics of homogeneous reaction between aniline and nitric acid had earlier been studied by Rastogi and Munjal[10] who found that aniline nitrate is one of the intermediate products. Kinetic results obtained were found to support a reaction scheme involving series of consecutive reactions. Incidentally, the volume versus time plot in the present case are similar to those obtained by Rastogi and Munjal[10]. It follows therefore, that in the present case also we should expect to have series of consecutive reactions.

Results plotted in Figs. 2-5 show a small induction period in the beginning which is shorter when finely powdered toluidine nitrate is taken. It becomes longer as the particle size increases and it is of the order of 10 min in the case of pellets. It is also observed that after this interval, toluidine nitrate completely dissolves in solution. Consequently we can postulate the reaction sequence to proceed as shown in Eqs. (1-3).

$$CH_3.C_6H_4.NH_3^+NO_3^-(s)+RFNA(aq)\xrightarrow{\text{fast}}$$
$$CH_3C_6H_4NH_3^+NO_3^-(aq)+HNO_2 \qquad ...(1)$$

$$CH_3C_6H_4NH_3^+NO^-(aq)+HNO_2\xrightarrow[\text{slow}]{k_1}$$
$$CH_3C_6H_4N_2^+NO_3^-+2H_2O. \qquad ...(2)$$

$$CH_3.C_6H_4.N_2^+NO_3^-+H_2O\xrightarrow{k_1}CH_3.C_6H_4OH+$$
$$N_2+HNO_3 \qquad ...(3)$$

This reaction sequence (1-3) is in many ways similar to that postulated by Rastogi and Munjal[10].

Since, dissolution is a faster process, the kinetics would be essentially governed by slower consecutive reactions.

If *a* is the initial molar concentration of *o*-toluidine nitrate in solution and *z* the number of moles of N_2 evolved, the kinetic equation for the first order consecutive reaction[20] is given by Eq. (4)

$$z = a\left(1-\frac{k_1'e^{-k_1 t}}{k_1'-k_1}+\frac{k_1 e^{-k_1' t}}{k_1'-k_1}\right) \qquad ...(4)$$

where k_1 would depend on the concentration of HNO_2 or N_2O_4. We assume that the concentration of HNO_2 is much greater than that of toluidine nitrate.

When $k_1 \ll k_1'$ we get,

$$z = a(1-e^{-k_1 t}) \qquad ...(5)$$

On, rearranging Eq. (5), we have

$$\log \frac{a}{a-z} = \frac{k_1}{2\cdot3026}\cdot t \qquad ...(6)$$

Thus, if first order consecutive reactions are taking place in the reaction system a plot of $\log\left(\frac{a}{a-z}\right)$ against time should be linear. The linear plots in Figs. 6-9 confirm this. It should be noted that the plots are linear up to a time when *o*-toluidine nitrate is completely consumed. Thereafter no increase in volume of evolved gas takes place and the curves tend to become parallel to the time axis. Further, it follows that the reaction rate is faster than the diffusion of the reactants to the solid grain.

k_1 was estimated for the reaction involving different particle sizes of *o*-toluidine nitrate. While k_1 was $(16\pm1)\times10^{-2}$ min^{-1} at 40° for particle sizes 60-100, 100-150, 150-240 and 240-350 mesh, the k_1
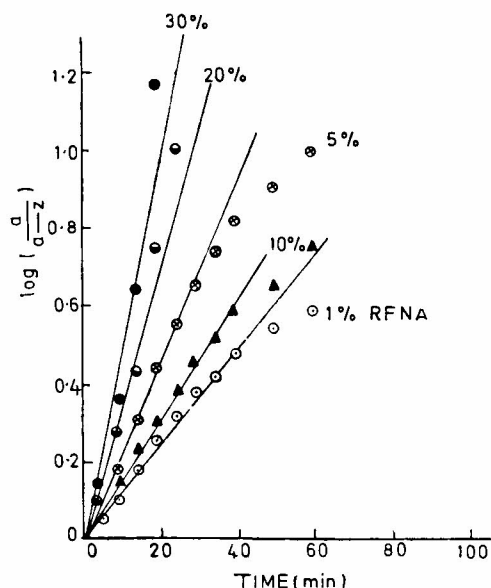
Fig. 7 — Plots of log $(a/a-z)$ versus time for the results plotted in Fig. 3 [Values for 5% were taken from Fig. 2]
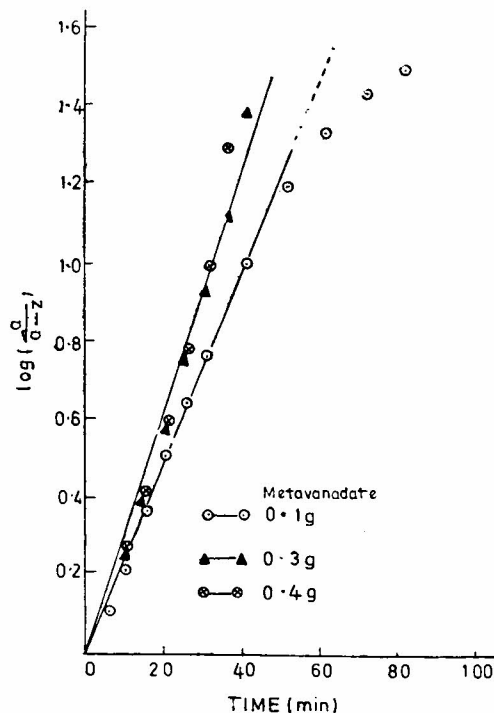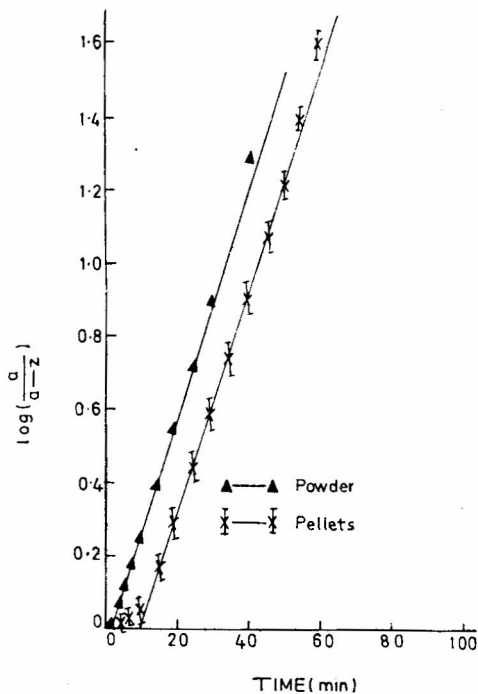
Fig. 8 — Plots of log $(a/a-z)$ versus time for the results plotted in Fig. 4

Fig. 9 — Plots of log $(a/a-z)$ versus time for the results plotted in Fig. 5

rate is bound to be enhanced. However, it is difficult to explain the value for 10% RFNA which was found to be reproducible. Results plotted in Fig. 5 show that volume of N_2 evolved increases with increase in the amount of the catalyst added. Values of $k_1(\times 10^2)$ for 0·1, 0·3 and 0·4 g/100 ml catalyst are $6·1 \pm 0·1$, $7·7 \pm 0·1$ and $7·7 \pm 0·1$ min^{-1} respectively.

Acknowledgement

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values at 35° for the particle sizes listed above were $5·1 \pm 0·1$, $5·1 \pm 0·1$, $5·6 \pm 0·1$ and $6·0 \pm 1 \times 10^{-2}$ min^{-1} respectively. Thus there is a weak dependence at 35° while at 40° k_1 is independent of particle size. This shows that film diffusion or particle diffusion is not the rate-controlling process. It follows from Fig. 9 that kinetic results with pellets of o-toluidine nitrate prepared by applying different pressures do not affect the value of k_1. Further, the values of k_1 for pellets and powders are found to be $(6·8 \pm 0·5) \times 10^{-2}$ and $7·7 \pm 0·1) \times 10^{-2}$ min^{-1} respectively. Since the difference is small, it further confirms that diffusion towards the solid grains of toluidine nitrate is not rate determining. k_1 increases with increase in the strength of acid. At 1·0, 5·0, 10·0, 20·0 and 30·8% (v/v) the values of $k_1(\times 10^2)$ are $2·9 \pm 0·1$, $5·3 \pm 0·1$, $3·5 \pm 0·1$, $7·7 \pm 0·5$ and $11·0 \pm 1$ respectively. This is understandable since with higher [acid] the concentration of NO_2 would be high and the reaction