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TEMPERATURE PROFILES OF REACTIVE BILIQUID SYSTEMS PRIOR TO IGNITION

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A thin-film thermometric device was used to record the temperature profiles of the exothermic reactions occurring between various substituted benzenes and anhydrous nitric acid. A comparison of the profiles indicated that the extent of exothermicity and the rate of heat evolution depend on the substituent/s on the benzene ring. The initial reaction was identified as nitration, which is accompanied by other exothermic reactions, especially in systems leading to ignition. The profiles of the self-igniting systems, amine-HNO_3 and amine-N_2O_4, suggest that, apart from their individual exothermicities, the specific nature of the fuel-oxidizer reaction also plays an important role in the onset of ignition.

Fuel-oxidizer combinations capable of igniting simply by mutual contact have been extensively used as rocket propellants. The hypergolic ignition in these systems is primarily a result of the highly exothermic reactions occurring between the fuel and the oxidizer in the preignition stage. Study of these reactions is important for controlling the ignition delay, an important parameter in hypergolic propellant rockets. Several attempts have been made in the recent past [1-3] to unravel their mechanisms. However, the complexity of these reactions has so far precluded an understanding of the preignition process. It is generally believed that, with oxidizers such as HNO_3, several types of reactions occurring simultaneously within milliseconds contribute to the overall exothermicity of the process. The sequence in which these reactions occur and their individual contributions to the overall exothermicity have not yet been explored.

In a continuation of our studies on hypergolic systems [4-6], we have examined the transient temperature profiles of various biliquid systems comprised of aromatic amines and anhydrous nitric acid, particularly in the preignition stage. It was felt that the profiles of these systems could be inter-

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preted better if simpler but related systems, such as those consisting of substituted benzenes and HNO_3, were studied. These reactions may provide an insight into the effects of substituents on the overall exothermicity, and also the predominance of certain types of reactions in the initial stage.No detailed study relating to the nature of these exothermic reactions appears to have been made even on simple systems such as benzene-HNO_3, with the components taken as neat liquids. It is likely that the reactions in dilute solutions are quite different. For example, in amine-HNO_3 systems, only the neutralization reaction occurs in dilute aqueous solutions, which may not be predominant when the reactants are mixed as neat liquids. Further, an examination of the temperature profiles may lead to valuable information concerning the rate of heat evolution, reaction times, and possibly the number of reactions occurring during the course of these highly exothermic processes.

In the present investigation, we report a temperature profile study of the reactions of benzene and substituted benzenes with pure HNO_3, using a thin-film thermometric technique. The profiles have been compared with the self-igniting (hypergolic) systems involving aromatic amines and HNO_3 or N_2O_4.

Experimental

Benzene, substituted benzenes and amines purchased from commercial sources were purified by known procedures prior to use. The oxidizers, anhydrous HNO_3 and N_2O_4 were prepared in the laboratory following standard procedures [7]. On analysis, the acid was found to contain 98.9% HNO_3; 0.1% H_2O and 1.1% NO_2.

Transient temperature profiles

The transient temperature profiles were recorded by using a thin-film resistance thermometry technique, as described earlier [8]. In this set-up, the transient surface temperature is measured in terms of the changes in electric resistance of a micron-thin platinum film deposited on the surface of a glass cup which is used as the probe as well as the reaction vessel. A known amount of the oxidizer is added via a modified graduated dropper onto the fuel taken in the cup. The platinum film acts as a fast-responding temperature-sensing element. The change in resistance of the film connected via a DC wheatstone bridge is obtained as the change in voltage on a digital storage oscilloscope (KIKUSUI Model DSS 6520-A) as a function of time. The flame in igniting systems is sensed with a sensitive photodiode. The signals from the flame-sensing and temperature profile devices are recorded on the oscilloscope simultaneously. The stored data on the scope are transferred to an X-Y plotter to obtain a hard copy of the same. A block diagram of the set-up used for this purpose is given in Fig. 1.

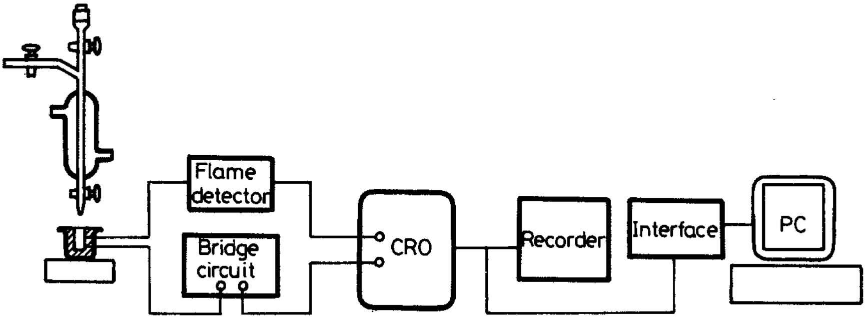


Fig. 1 Block diagram of the temperature profiling set up

All experiments were carried out at room temperature (25 ±2°) except those involving N_2O_4, which was pre-cooled to 5 ±2° before being added onto the fuel kept at room temperature. The temperature profiles are presented as voltage *vs* time plots as recorded on the plotter. A change of 1 mV (Y-axis) corresponds to 0.45 deg. The profiles could be recorded with fair accuracy except in those cases where spurting occurred. For consistent reproduction, at least three profiles were recorded in each case. The profiles chosen for comparing various systems were recorded under identical experimental conditions, using reactants in 1:1 molar ratio, unless otherwise stated. The amount of nitric acid used in a typical experiment was about 0.3 g. In the igniting systems, the onset of ignition is denoted as a solid dot on the profile.

Analysis of the reaction product of benzene-HNO_3

In order to ascertain the types of reactions occurring between benzene and HNO_3, the reaction products were examined on a dual packed column gas chromatograph (AIMIL NUCON series 5500) in the TCD mode, with helium as the carrier gas, using a 100% Carbowax 20M on Chromosorb W-HP 80/100 mesh column. The mixture was injected immediately after the reaction. Only two peaks, corresponding to benzene and nitrobenzene, were observed. The intensity of the nitrobenzene peak increased, while that of the benzene peak decreased with time. No other product could be detected, even after reaction for five minutes.

Results

A qualitative summary of the reaction behaviour of the various neat benzene-HNO_3 systems studied is given in Table 1. It is apparent that many of these reactions are highly exothermic and are often accompanied by loud noise and turbulence, causing spurting.

Table 1 Reaction behavior of various biliquid systems

Sl. No.	Systems*	Observations	Remarks
1	Benzene-HNO_3	Immediate reaction with spurting and crackling noise	Red color changes immediately to pale-yellow
2	Toluene-HNO_3	same as above	Red color changes immediately to pale-red
3	*p*-Xylene-HNO_3	Immediate reaction with spurting and loud crackling noise	Red color changes slowly to pale-red
4	*m*-Xylene-HNO_3	same as above	same as above
5	Anisole-HNO_3	Very fast reaction with gushing noise accompanied by reddish-brown fumes	Blood-red color
6	Brombenzene-HNO_3	Fast reaction with noise	–
7	Phenol-HNO_3	Violent reaction with loud exploding noise	–
8	Aniline-HNO_3	Vigorous reaction with white fumes	Brownish-black mass
9	*o*-Toluidine-HNO_3	Vigorous reaction with white fumes and occasional ignition	Brownish-black mass
10	Nitrobenzene-HNO_3	Virtually no reaction	No change
11	Benzaldehyde-HNO_3	Slow reaction, proceeds smoothly	No change
12	Aniline-N_2O_4	Vigorous reaction with dense brown fumes and ignition	Reddish-brown mass
13	*o*-Toluidine-N_2O_4	Vigorous reaction with dense brown fumes and ignition	Reddish-brown mass

* Reactants taken in 1:1 mole ratio

The temperature profiles of the typical reactions of some of the benzenes with HNO_3 are reported in Fig. 2. It is evident that the sharp rise in temperature in a time interval of about 0.5 to 1 sec is representative of the highly exothermic stage of the reaction in these systems. Soon after, the benzene-HNO_3 reaction profile shows a steady state, with no or only an insignificant further rise in temperature. The small kinks or dips observed in the initial exothermic portion of the profile could be attributed to the disturbances caused mainly by the turbulent nature of the reaction. The reaction profile of benzene-HNO_3 is closely similar to that of toluene-HNO_3. Each profile shows a rather sharp rise, followed by a small lowering in the temperature and then by a steady state. The effect of substitution by an additional methyl group on the ring is shown by the p-xylene-HNO_3 system. In this case, although the profile again shows a close similarity with those of benzene and toluene in the initial stage, there is a further increase in temperature after the lowering before the steady state is reached. The reaction of anisole with HNO_3 is relatively smooth and gives a highly reproducible temperature profile, which essentially shows a close similarity with that of the toluene-HNO_3 reaction.

On the other hand, the reactions of HNO_3 with substituted benzenes containing an electron-withdrawing substituent are less exothermic. The profile of benzaldehyde-HNO_3, for example, exhibits a much lower exothermicity, while there is hardly any evidence of heat evolution in the nitrobenzene-HNO_3 reaction, in spite of the profile being recorded at higher sensitivity.

The temperature profiles of the reaction of HNO_3 with benzenes substituted with amino groups, i.e. aniline and o-toluidine, look deceptively similar to that of the benzene-HNO_3 system in the initial stage. However, the profile of the aniline-HNO_3 reaction shows a continuously enhanced exothermicity with time, in contrast with the benzene-HNO_3 system, which displays a steady state after the initial reaction.

The carefully resolved temperature profiles of the reactions of substituted benzenes with HNO_3 (Fig. 3) show that there is an initial sharp rise, followed by a slight lowering or steady-state region, and a subsequent gradual rise in temperature. The benzene-HNO_3 reaction however, exhibits only a sharp rise, followed by a steady state. High-resolution profiles of a few selected systems in the 500 msec period (not presented here) from the start of the reaction reveal that the slopes of the profiles in the initial stage vary from system to system. The initial rates of temperature rise for the anisole and aniline reactions are significantly higher than that for benzaldehyde. The slopes of the benzene, toluene and p-xylene reaction profiles are steeper than that for benzaldehyde.

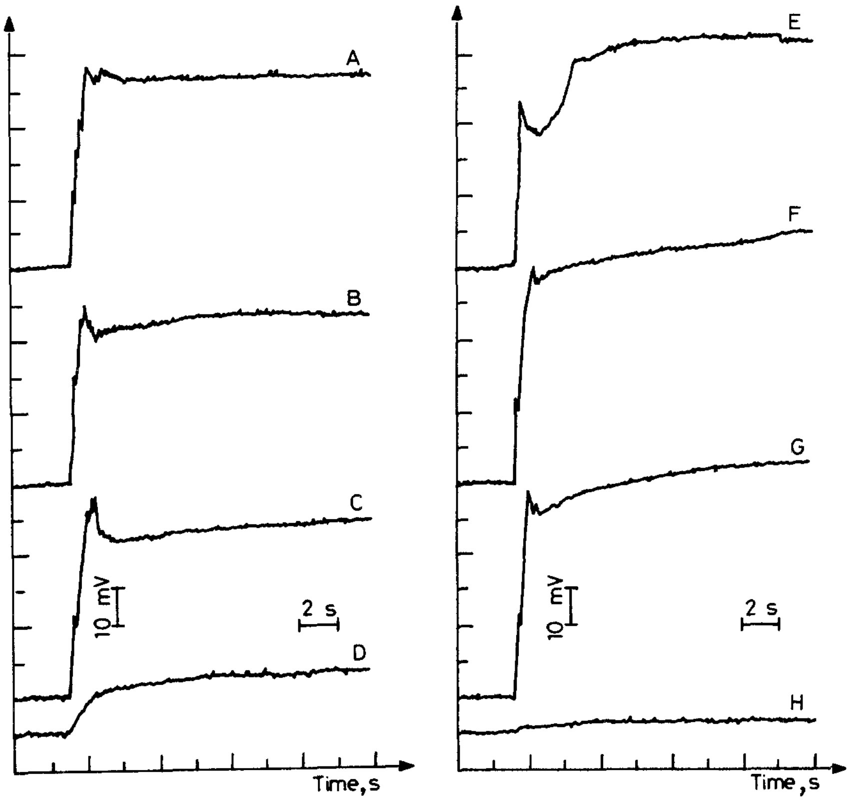


Fig. 2 Temperature profiles of the reactions between HNO_3 and (A) benzene, (B) toluene, (C) anisole, (D) benzaldehyde, (E) p-xylene, (F) aniline, (G) o-toluidine and (H) nitrobenzene, in 1:1 mole ratio

The effects of change of the reactant ratio (oxidizer/fuel, O/F, in moles) on the profiles are depicted in Fig. 4a, b. The anisole-HNO_3 reaction was chosen for this purpose as this is a smooth reaction. It is seen that, after the initial sharp rise, the temperature changes are insignificant up to a certain increase of the HNO_3/anisole ratio. At an O/F ratio of 7:1, the temperature fulls almost to that for the initial stage of the reaction. This is in contrast with the aniline-HNO_3 system (Fig. 4b), where the temperature actually rises with increase of the O/F ratio. In fact, the system ignites at a higher

O/F ratio and the ignition delay (ID) decreases with increase of the amount of the oxidizer.

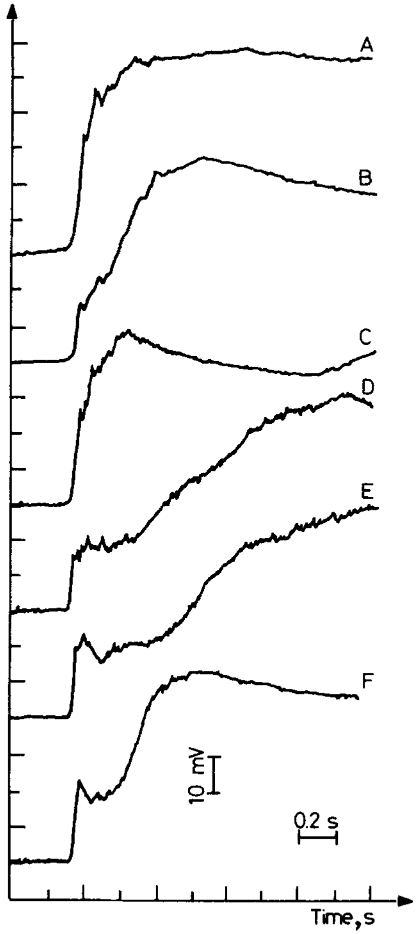


Fig. 3 Temperature profiles of the reactions between HNO_3 and (A) benzene, (B) toluene, (C) p-xylene, (D) anisole, (E) aniline and (F) o-toluidine, in 1:1 mole ratio at high resolution (time scale)

The reaction between amine and N_2O_4 is smoother, and yields highly reproducible profiles. The profiles of the reactions of aniline and o-toluidine with N_2O_4 as the oxidizer in 1:1 mole ratio (Fig. 5a, b), show a sharp rise region, which is followed by the ignition of the system. The temperature rises further after the ignition and soon reaches a steady state.

The ignition delay seem to increase with increase of the O/F ratio.

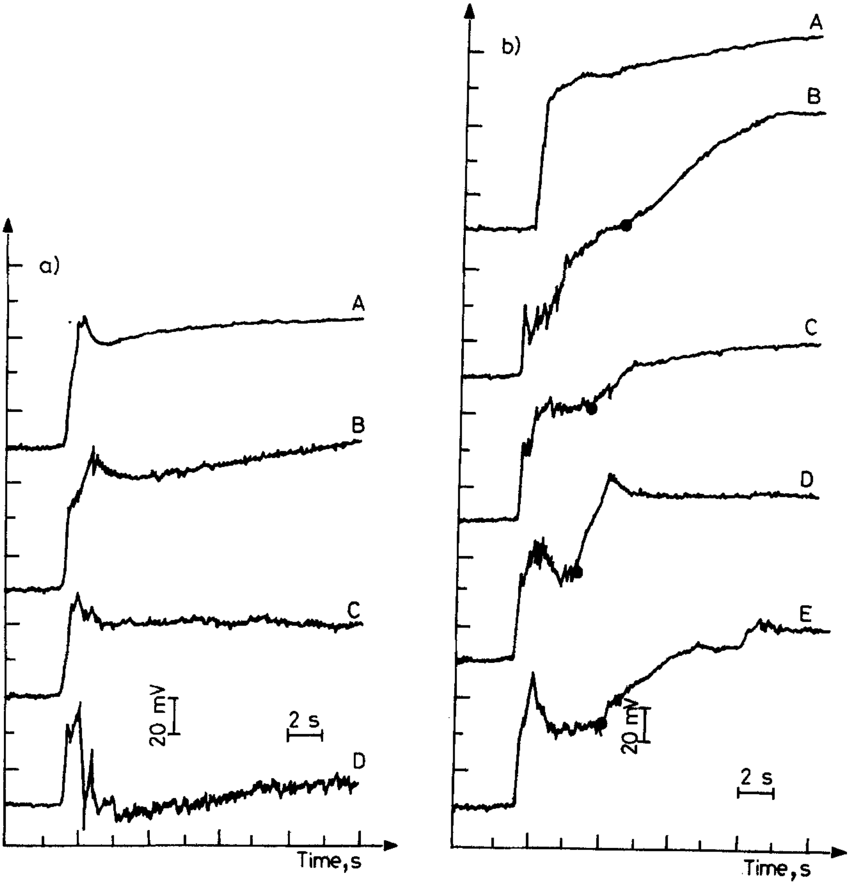


Fig. 4 The temperature profiles at different O/F ratios, of the reaction between (a) HNO_3 and anisole (A) 1:1, (B) 3:1, (C) 5:1 and (D) 7:1 and (b) HNO_3 and aniline (A) 1:1, (B) 2:1, ID-5.92 secs (C) 4:1, ID-4.06 secs (D) 6:1, ID-3.22 secs (E) 7:1, ID-4.4 secs

Discussion

The results of the present investigation could be understood, at least partly, in terms of the overall self-dissociation of anhydrous nitric acid:

$$2\,HNO_3 \rightleftarrows H_2O + NO_2^+ + NO_3^-$$

As it is rich in nitronium ion, this is an active nitrating agent for aromatic compound [9]. The nitration reaction is normally highly exothermic. The GC identification of nitrobenzene as the main product of the benzene-HNO_3 reaction, and the high exothermicity of the reaction as revealed by the profile data, demonstrate that the initial course of the reaction could be nitration. The intense variation in colour in the initial stage indicates that this reaction proceeds in a highly complex manner. When mixed in 1:1 mole ratio, the colorless reactants give an intense red coloration, which changes to yellow in a few moments.

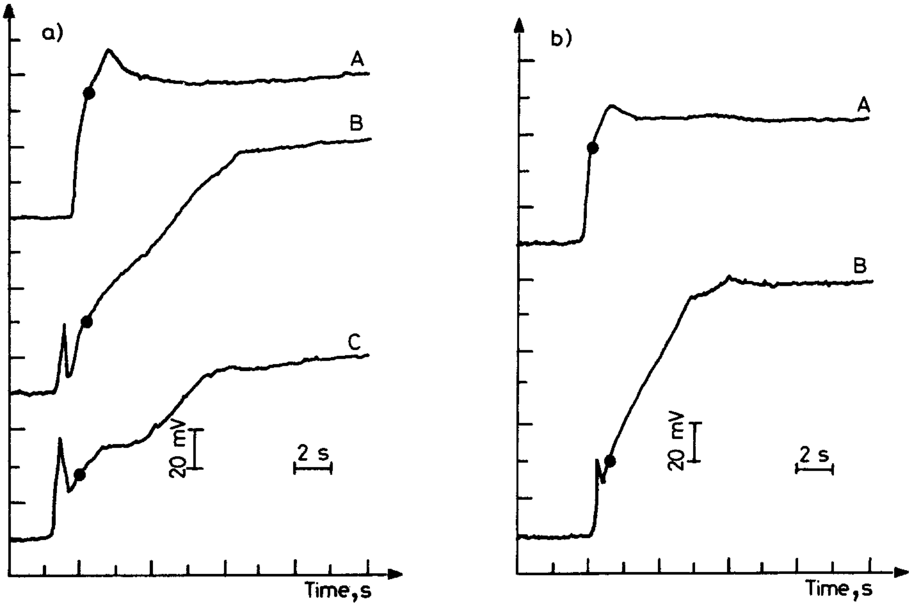


Fig. 5 The temperature profiles at different O/F ratios, of the reaction between (a) N_2O_4 and aniline (A) 1:1, ID-960 ms (B) 3:1, ID-1.6 secs (C) 4:1. ID-2.88 secs and (b) N_2O_4 and o-toluidine (A) 1:1, ID-800 ms (B) 4:1, ID-980 ms

Since the nitration reaction is an electrophilic substitution process, its rate is influenced by the polarity of the substituent on the benzene ring, which can activate or deactivate the aromatic nucleus towards the attack by the electrophile.

From the profile data, it is observed that the slope of the initial temperature rise region, which is the start of the reaction, varies with the substituent on the benzene ring. Taking two cases of different polarity, i.e. the $-NH_2$ and $-CHO$ groups in aniline and benzaldehyde, respectively, it is seen that the rate of temperature rise is faster with $-NH_2$ (which is known to activate the benzene ring by electron donation) than with $-CHO$ (which deactivates it). Benzenes with a substituent of intermediate polarity, such as toluene and p-xylene, accordingly give moderate rates of temperature rise. The relative rates of temperature rise parallel the rate of a purely nitration reaction, in a qualitative sense, which is faster in aniline and slower in benzaldehyde [10]. However, the reactivity of benzene, which is reported to be one millionth of that of aniline or one twenty-fifth of that of toluene in the nitration [11] reaction, is not quantitatively reflected in the temperature profiles. Further, the nitration of aromatic compounds bearing an electron-withdrawing group does not occur unless forceful conditions are employed. The absence of an exothermic reaction in the nitrobenzene-HNO_3 system therefore argues in favor of a nitration reaction. Since the ring is already nitrated, there is no possibility of further nitration simply by mere mixing. Hence, the high exothermic reactivity of benzene substituted with electron donors and the slow or low reactivity of benzene substituted with electron acceptors strongly support the concept that the initial course of the reaction of benzene or substituted benzene with pure HNO_3 is nitration.

Besides the nitration reaction, HNO_3 is known to oxidize aromatic compounds fairly easily [12]:

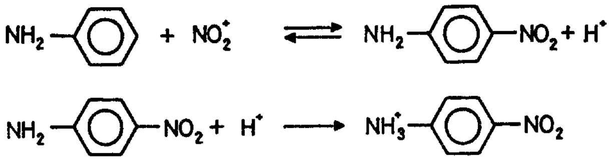
$$2\,HNO_3 \rightarrow H_2O + NO + NO_2 + O_2$$

The nitration of aromatic compounds containing electron-releasing groups needs milder conditions than those required for benzene. The high temperature generated in situ in these cases bring about polynitration and subsequent oxidative breakdown of the side-chains as well as the aromatic ring system. Oxidative cleavage or a breakdown process often accompanied by color changes (Table 1) is likewise an exothermic process, and this is evident in the resolved profile pattern (Fig. 3). The temperature profile of the benzene-HNO_3 reaction shows a steady state almost immediately after the initial reaction, whereas in those of the methyl-substituted benzenes-HNO_3 systems the temperature continues to rise slowly for a while (Fig. 2). A dip observed soon after the initial reaction, especially in the p-xylene-HNO_3 reaction, could be due to delay in the reactant species reaching the critical concentration.

The temperature profiles of aniline-HNO_3 and o-toluidine-HNO_3 are more complex. After the initial stage with no steady state in the temperature profile, the gradual rise is apparently indicative of other reactions taking place in the amine-HNO_3 systems. These reactions become more prominent as the reactant ratio O/F is gradually increased (Fig. 4a, b). Indeed, beyond a certain O/F ratio the amine-HNO_3 systems ignite spontaneously, i.e. they become hypergolic. The temperature rises up to ignition and beyond, in contrast with the changes observed in a non-igniting system. It may be pointed out here that the expected stoichiometric ratio for combustion reaction in the amine systems is approximately equal to 7:1 (O/F). The effect of variation of the O/F ratio in the non-igniting anisole-HNO_3 system, on the other hand, should be looked upon in a totally different context. Here, as seen in Fig. 4a, with the addition of excess oxidizer (O/F = 7:1) the temperature is found to decrease rather than increase as observed in the aniline-HNO_3 system. In this system, increase of the O/F ratio causes insignificant change in the initial stage where the nitration reaction is predominant. With increase of the acid content, oxidation of the nitrated product is more likely and this brings about slight changes in the latter region. Further addition of the oxidizer results in quenching of the reaction and dilution of the mixture, thereby producing a cooling effect. The effect of the O/F ratio on the exothermicity thus emphasizes the higher reactivity of the $-NH_2$ group as compared with $-OCH_3$ on the benzene ring.

Although a nitration reaction is indicated on the basis of the argument proposed earlier, the oxidation reaction could be much more extensive in the case of amine [13]. Further, the basicity of the $-NH_2$ group makes the amines susceptible to a highly exothermic acid-base reaction. Since the profiles do not exhibit any clear demarcation of these three types of reactions, it is likely that they occur simultaneously, possibly soon after the initial stage.

The first step, i.e. the sharp temperature rise, observed for aniline and also substituted benzenes could be attributed mainly to the nitration reaction, for in the anhydrous condition the chemistry is largely dominated by the NO_2^+ ion. The acid may not undergo any proton transfer at this stage. With the progress of the nitration, the displacement of a proton could cause formation of the hydroxonium ion:



As $[H^+]$ is initially small, the chances of neutralization associated with nitration may be negligible. However, as $[H^+]$ builds up, the neutralization reaction becomes important. Together with neutralization, the oxidation process to contributes too the exothermicity. It is also likely that the nitrate salt formed may decompose exothermally [14] and contribute to the overall exothermicity.

At this stage, it is worthwhile to compare the temperature profiles of the amine-HNO_3 and amine-N_2O_4 reactions. Both systems are self-igniting. The profiles of the amine-N_2O_4 reaction (Fig. 5a, b) are less exothermic and steeper than those of the amine-HNO_3 reaction (Fig. 2). Nevertheless, the amine-N_2O_4 systems ignite easily. In fact, the aniline-HNO_3 system does not ignite at all at low O/F ratio. The main reaction of an aromatic amine with N_2O_4 is apparently N-nitrosation leading to oxidation [15, 16]. The reaction pathways being different with the two oxidizers, the temperature profiles are expected to be dissimilar; more so, when the oxidizers are added at different temperatures. It is likely that the ease of ignition of the amine-N_2O_4 system may be related to the ease of gasification of N_2O_4. Since nitrogen tetroxide is highly volatile, a relatively slow temperature rise is enough to make it go into the vapor phase, wherein the ignition occurs. In contrast, HNO_3, being less volatile, requires a much higher temperature to vaporize.

It is further noted that a small amount of oxidizer is enough to cause ignition in the amine-N_2O_4 system. The reaction preceding ignition presumably occur in a series from nitrosation to oxidation, as postulated earlier, and cause a continuous rise in temperature. In contrast, in the amine-HNO_3 system, mainly the nitration reaction occurs to begin with, and subsequently neutralization and oxidation follow. The completion of the latter reactions requires a larger amount of the oxidizer and the ignition consequently occurs at a much higher O/F ratio.

The effect of the O/F ratio on the profiles in the N_2O_4 systems (Fig. 5) indicates that, although the initial course of the reaction is the same, the effect of cooling caused by the addition of precooled oxidizer and its vaporization is quite pronounced. This cooling effect leads to longer ignition delays.

Conclusions

The temperature profiles of the reactions between benzene or substituted benzenes and HNO_3, mixed in the neat state and monitored by using a thin-film thermometric probe, show the immediate occurrence of an exothermic reaction, most of which is completed within a second or so. The exothermicity and the rate of heat evolution depend on the substituent on the benzene ring. The first reaction between benzene and HNO_3 is apparently nitration. Other reactions occurring simultaneously following nitration also play an important role in raising the exothermicity, especially in the substituted benzene-HNO_3 reactions, and could be responsible for the self-ignition of aniline-HNO_3 systems. The self-ignition of aniline o-toluidine occurs more easily with N_2O_4 than with HNO_3. This study emphazises the role of preignition exothermic reactions in determining the ignition delay in biliquid systems.

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Zusammenfassung — Zur Aufzeichnung der Temperaturprofile bei exothermen Reaktionen zwischen verschiedenen substituierten Benzolen und wasserfreier Salpetersäure wurde eine dünnschichtthermometrische Apparatur benutzt. Ein Vergleich dieser Profile ergab die Abhängigkeit der Exothermizität und auch der Wärmeentwicklungsgeschwindigkeit von dem (den) Substituent(en) am Benzolring. Als Initiierungsreaktion wurde eine Nitrierung festgestellt, die - besonders bei Systemen, die sich entzünden - von anderen exothermen Reaktionen begleitet wird. Die Profile der selbstzündenden Systeme Amin-HNO_3 und Amin-N_2O_4 lassen darauf schließen, daß außer der jeweiligen Exothermizität auch die besondere Natur der Reaktion zwischen Brennstoff und Sauerstoffträger eine bedeutende Rolle für das Einsetzen der Entzündung spielt.