HYPERGOLIC BURNING OF FORMYLIDENE AND FURFURYLIDENEAMINES WITH RED FUMING NITRIC ACID AS OXIDIZER

S.P. PANDA & S.G. KULKARNI

Institute of Armament Technology, Poona

Six p-formylidene and six p-furfurylideneamines were synthesized and their ignition delay with red fuming nitric acid (RFNA) were measured by cup test method using a high speed camera. Structure—hypergolicity correlation revealed that a p-methyl group inhibits hypergolicity whereas a p-methoxy group accelerates it. Similarly oxidizable non-conjugated benzene rings increase hypergolicity whereas conjugated benzene rings decrease it. On compacting, the p-formylidene anisidine was found to be hypergolic with an ignition delay less than 100 milliseconds.

Some of the formylidene- and furfurylideneamines are known hybrid rocket fuels which are self-ignitable (hypergolic) with the most commonly used oxidizer, red fuming nitric acid (RFNA)[1,2]. It is believed that like amines these Schiff's bases undergo salt formation, nitration and oxidation with RFNA in the pre-ignition stage [13]. However no comparative study establishing structure and hypergolicity correlation has appeared in literature for Schiff's base—RFNA systems. This prompted us to synthesize several formylidene- and furfurylideneamines and study their hypergolicity with RFNA to arrive at certain interesting structure—hypergolicity correlations.

METHODS AND MATERIALS

Preparation of Formylidene and Furfurylideneamines

The amines used to synthesize the Schiff's bases were either liquid like aniline or solids like p-anisidine, p-toluidine, benzidine, diaminodiphenylmethane and p-phenylenediamine. While using aniline to make Schiff's bases following procedure of D'Alelio[4] was used.

Aniline (0·1M) was added slowly with stirring to fomaldehyde (0·1M, 37% Formalin). Mixture was allowed to stand and stirring was continued till the reaction produced a solid material. The precipitate was filtered, washed with water and dried in oven at 75°C. The product was recrystallised from ethanol. While making the furfurylideneaniline by the above procedure, solid did not separate readily from the reaction mixture when formaldehyde was replaced by furfuryaldehyde. However the whole reaction mixture solidified after keeping for a week. The solid was washed with dilute ethanol, dried and used without further purification.

Schiff's bases starting from solid amines were prepared by the method described by Hanumanthu and Ratnam[5] for benzidine-benzaldehyde anil, replacing benzaldehyde with formaldehyde or furfuraldehyde and using different amines. For example, p-anisidine (0·05M) was dissolved in methanol (60 ml) and to the clear solution, formaldehyde or furfuraldehyde (0·05M) was added dropwise with stirring. The precipitate was filtered and washed with methanol and dried in oven. These Schiff's bases, however, could be recrystallised from ethanol. When diamines were used to make the Schiff's bases, 1 : 2 molar proportion of the amines and the aldehydes was employed. The Schiff's bases were characterised by their melting points and IR spectra taken for the mulls in nujol in a Perkin-Elmer No. 457 double beam spectrometer. The characteristic data are given in Tables 1 and 2.

Measurement of Ignition Delay

The ignition delays (I.D.) of different Schiff's bases (particle dia, 223.6μ; passing through a '72' mesh sieve) with RFNA (HNO_3, 76%, N_2O_4, 21%; H_3PO_4, 1.0%; HF, 0.3−0.5%; H_2O, 1.7%) were measured by the 'cuptests'[2,6] method at the room temperature and pressure. The weighed quantity of fuel (0·75 gm) was taken in a cylindrical glass dish (dia 5 cm) and the requisite quantity of RFNA was added to this with the help of a graduated dropping tube (inner dia, 0·2 cm) by releasing the vacuum applied to the tube to suck the acid in. Ignition delay was measured as the difference in time between the acid touching the fuel and the appearance of a flame using a stopwatch where the I.D. values are more than 0·1 sec. For I.D. values

less than 0·1 sec, an Acmade high speed camera (500 frames per second) was used. Better records were obtained by photographing the shadows obtained by selectively illuminating the graduated dropping tube and the cup beneath it against a white screen in a dark background. The results are given in Tables 1 and 2.

TABLE 1

PHYSICAL AND COMBUSTION CHARACTERISTICS OF FORMYLIDENEAMINES

Compounds	M.P.	$\nu C = N$*	$\nu = CH_2$**	Fuel/Oxidiser, by weight (optimum)	I.D. (average)	Nature of the flame
	(°C)	(cm⁻¹)	(cm⁻¹)		(sec)	
1. Formylideneaniline	152	1610(s)	975(s)	1 : 1	0·15	Good flame, no residue left
2. p-Formylidenetoluidine	116	1640(s)	972(s)	1 : 1	0·45	Good flame, no residue left
3. p-Formylideneanisidine	126	1605(s)	972(s)	1 : 1	0·04	Very good flame, no residue left
4. 4, 4'-Diformylidenebenzidine	218–223	1625(s)	972(s)	1 : 2	0·70	Weak flame, small residue left
5. p, p'-Diformylideneaminodiphenyl-methane	158–160	1625(s)	972(s)	1 : 2	0·45	Good flame, small residue left
6. 1,4-Diformylidenephenylaminobenzene	192–193	1620(s)	972(s)	1 : 2	0·10	Very good flame, no residue left

* Assignment has been done after Nakanishi[11].
** Assignment has been done after Bellamy[12].

TABLE 2

PHYSICAL AND COMBUSTION CHARACTERISTICS OF FURFURYLIDENEAMINES

Compound	M. P.	$\nu C = N$	$\nu = CH$—	νFuran*	Fuel/Oxidizer, by weight (optimum)	I.D. (average)	Nature of the flame
	(°C)	(cm⁻¹)	(cm⁻¹)	(cm⁻¹)		(sec)	
1. Furfurylideneaniline	58	1650(w)	962(w)	890(s)	1 : 1	0·10**	Very good flame, no residue left
2. p-Furfurylidenetoluidine	44	1620(s)	962(2)	890(s)	1 : 1	0·30**	Very good flame, small residue left
3. p-Furfurylideneanisidine	52	1625(s)	965(s)	890(s)	1 : 1	0·046	Very good flame, resinous residue
4. 4, 4'-Difurfurylidenebenzidine	212–213	1640(s)	962(s)	890(s)	1 : 2	0·60	Good flame, small residue left
5. p, p'-Difurfurylideneaminodiphenylmethane	85–87	1630(sh)	965(s)	890(s)	1 : 2	0·45	Good flame, small residue left
6. 1, 4-Difurfurylidenephenylaminobenzene	164–165	1640(sh)	946(s)	880(s)	1 : 2	0·30	Very good flame, small residue left

*Assignment has been done after Nakanishi[11].
**I.D. values for the resinous solids melted and cooled to get flat surfaces.

RESULTS AND DISCUSSION

It is well known that in the pre-ignition stage the amines and the Schiff's bases, hypergolic with RFNA' undergo several consecutive reactions involving salt formation as the first step followed by nitration and oxidation. This results in the production of gases which are raised to their ignition temperature by the heat of pre-ignition reactions minus the radiative and conductive loses, signalled by the appearance of a flame. If we assume the heat of salt formation is comparable for compounds, 1, 2 and 3 of Table 1 (Fig. 1), it looks that the heat of nitration and the rate at which it is produced is the deciding factor in fixing the I.D. values of these compounds. The oxidisability of these compounds containing one benzene ring may be assumed not to vary much from each other. The rate of nitration of the phenyl nucleus is expected to be higher for compound 3 containing the o-p orienting—OCH_3 group than that for compound 1. In case of compound 2, it seems that —CH_3 group gets easily oxidised to —$COOH$ group which deactivates the phenyl uncleus resulting in a decrease of rate of nitration. This is reflected in a higher I.D. value. Similar effect has been observed by us in case of p-methyl furfurylideneacetophenone[7]. Our argument is also in line with Urbanski[8] who describes the oxidation of the —CH_3 group to —$COOH$ group under nitration by concentrated nitric acid. In case of compounds 4, 5, 6, in Table 1 where two —$N=CH_2$ groups occur, the heats of salt formation also are expected
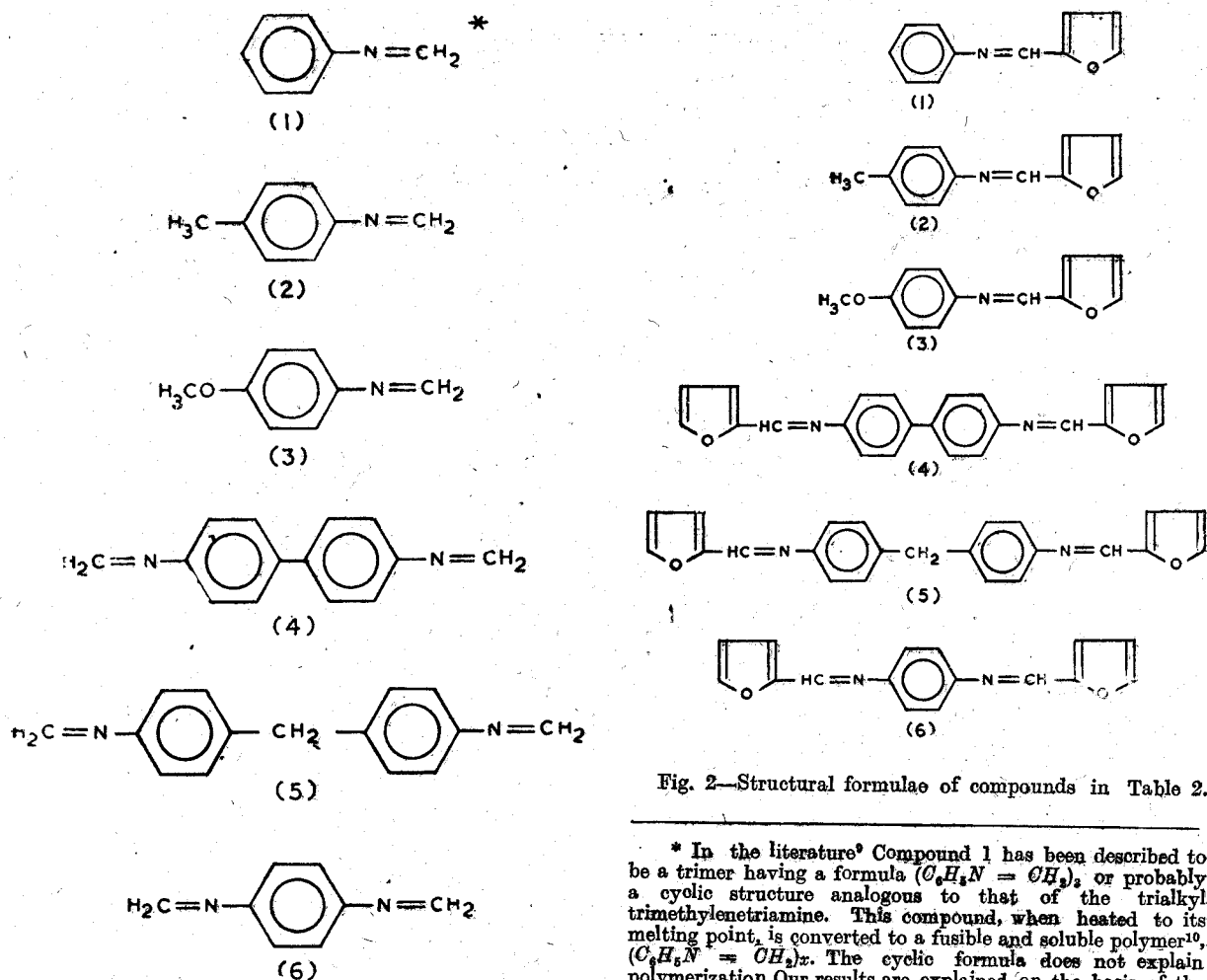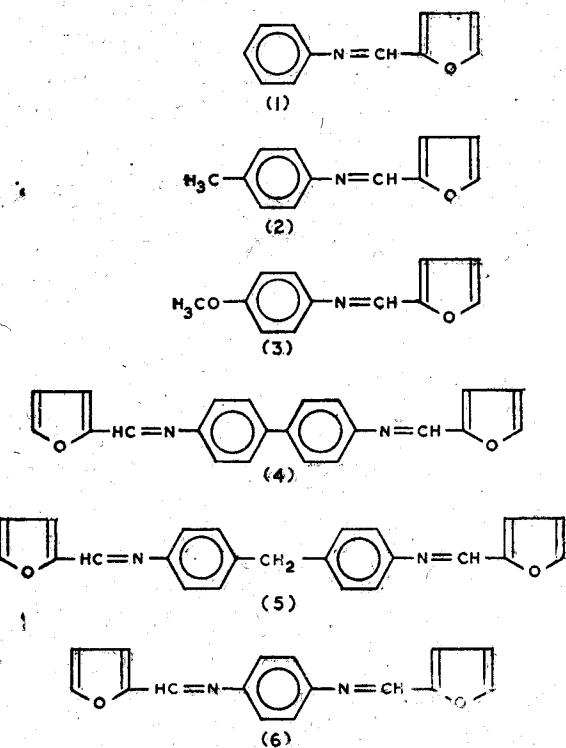

Fig. 1—Structural formulae of compounds in Table 1.

Fig. 2—Structural formulae of compounds in Table 2.

* In the literature[9] Compound 1 has been described to be a trimer having a formula $(C_6H_5N = CH_2)_3$ or probably a cyclic structure analogous to that of the trialkyl trimethylenetriamine. This compound, when heated to its melting point, is converted to a fusible and soluble polymer[10], $(C_6H_5N = CH_2)x$. The cyclic formula does not explain polymerization. Our results are explained on the basis of the hypothetical Schiff's base structure.

to be comparable. Here the oxidisabilities of the backbone structures have been purposefully maintained different. The highest ignition delay relates to the maximum stability of the two conjugated benzene rings of compound 4. In compound 5 this conjugation of the two benzene rings is broken by an intervening $—CH_2—$ group. Hence, oxidisability of the compound with RFNA goes up lowering the I.D. value. In compound 6 only one benzene ring is involved which provides comparatively less resistance to oxidation. This may be a possible explanation for its lower I.D. value. In Table 2 (Fig. 2) the corresponding furfurylidene derivatives of the compounds listed in Table 1 have been described. The pattern of variation of their I.D. values is exactly same as that in case of the compounds in Table 1. Therefore we assume that similar explanations are likely to hold good for the variation of their I.D. values. However it may be highlighted that the furan ring may undergo polymerization through an oxonium salt formation, followed by the ring opening in the pre-ignition stage with RFNA. This has been indicated by us in case of the hypergolic burning of the furfurylidene ketones with RFNA[7]. Polymerization as a pre-ignition reaction has been mentioned by Trent & Zucrow[13], while studying the hypergolicity of cyclopentadiene with WFNA.

The fuel is pressed or cast into grains from its powders to be used in the hybrid rockets. This decreases the surface area considerably. It is well established that I.D. values vary directly to the square root of the diameter of the fuel particles[3]. Therefore the I.D. values reported in Tables 1 and 2, though provide a qualitative indication of higher or lower hypergolicity, may not be directly useful in actual firing. We therefore pressed all the solids into small cylindrical grains (flat surface area, $7\cdot938\ cm^2$; height, $0\cdot239\ cm$; density, $1\cdot082$) and measured the ignition delay by dropping the acid on the flat surfaces of the grains. The least I.D. value was obtained for p-formylideneanisidine (nearly 100 m sec). This value could be further decreased by using various soluble catalysts like potassium dichromate with RFNA. Perhaps a p-me'hoxy group made the benzene ring highly oxidizable.

ACKNOWLEDGEMENT

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