



Explosion Hazard of Aromatic Organic Compounds Containing One or Two Nitrogroups

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Abstract: Aromatic compounds containing one or two nitrogroups use in chemical industry commercially, in the first place there are mono- and di- nitroderivatives of benzene and toluene. Some industrial incidents at heat selfignition of them, and explosive properties of them were discussed in literature. This investigation deals with explosion hazard of less investigated in this regard class nitrocompounds – azo-dyes. All azo-dyes contain azo or amino groups, two benzene circles with substituents. Some of them contain one or two nitrogroups. Nitro- and azo- groups can give explosion hazard to organic substance. Temperature of fast decomposition beginning at heating and kinetic parameters of slow decomposition were experimentally measured for nine of them. The enthalpies of formation were measured experimentally, and explosion parameters were calculated for three of them. These results gave an opportunity to calculate the temperatures of heat explosion on a base of fundamental theory of heat explosion at convection heat transfer with environment. It was found that calculated temperatures of heat explosion agreed with experimental temperatures of fast decomposition beginning at heating, the divergence was 4.5% on average. Thus it was shown that investigated azo-dyes were the weak explosives, and theory of heat explosion could be quite applied to them.

Keywords: aromatic, decomposition, heat explosion, azo-dye

Introduction

Aromatic azo-compounds are produced by chemical industry and are widely used as organic colouring agents for textile and other materials. Some

of them contain chemical groups, that can add to chemical substance explosive properties: $-\text{NO}_2$, $-\text{N}=\text{N}-$ etc. Estimation of the parameters, that characterize explosion hazard of such compounds, needs for substantiation safe condition at realization of technology processes and compiling of technology documents. The methodology of reliability and safety estimation have been elaborated in the branch of industry of high explosives [1-3]. This approach was useful at estimation of explosion hazard of some organic peroxides [4-7] and azides [8], that were no applied as explosives but were widely used in another branches of industry. It has been shown that variety of explosive transition arising in substances of such classes most easily and propagating most strongly can be different one. This is heat explosion for one group, turbulent burning for second group, and low or high velocity detonation for the third group.

Results of the Experiments and Calculation

Computational estimation of such important parameters, that characterize explosion hazard of organic colouring agents as heat of explosion, detonation velocity, and ability to heat explosion was carried out in this work; the last parameter was compared with experimental value of the beginning of fast exothermal decomposition.

Chemical and commercial names of organic colouring agents (translation from Russian) are shown in Table 1. The kinetic parameters of slow thermal decomposition (activation energy and preexponential factor) and temperature of the beginning of fast exothermal decomposition were experimentally investigated in works [9-10] (Tables 1 and 4). Measurement of enthalpies of formation of several colouring agents at burning in oxygen in calorimeter bomb was carried out in work [9] (Table 2). The elemental analysis of them coincided with theoretical values (Table 3).

Experimental values of enthalpies of formation were used at calculation of the parameters of explosive transformation of these colouring agents by means of SD code [11]. Heats of explosion (Q_v), detonation velocities (D) at density $\rho = 1.2 \text{ d/cm}^3$, and volumes of gaseous products are collected in Table 2. The results of calculation are thought to be logical ones. Azo-dye Violet 4K (No. 7 in all Tables) is dinitrocompound, and has the greatest heat of explosion. Azo-dye Yellow 3 (No. 8 in all Tables) does not contain nitro groups, and has the least heat of explosion. Azo-dye Scarlet G (No. 1 in all Tables) is mononitrocompound, and it mediates.

Chemical structures of substances under investigation (Table 2) are similar. Compounds include azo group with that two benzene rings connect, rings gave several substituents. In some cases one or two nitro-groups are combined with benzene ring.

Burning of organic nitrocompounds was investigated in detail [12]. It was shown that heat instability of burning [13, 14] is characteristic feature for many, even saturated by nitro-groups, explosives (for example, for PETN). Burning of aromatic mono- and di- nitrocompounds in inert atmosphere can propagate only at high pressure [4], i.e. heat instability of burning [13, 14] become apparent for them still more. Heat of explosion of azo-dyes is not high value and propagation of detonation processes requires great diameter or massive confinement.

However some incidents with mononitrotoluene [15] and colouring agents [16] took place and were described in literature in such conditions when temperature of their treatment was close to extreme level. This implies that estimation of ability to heat explosion of such substances is especially important one.

Calculation of the critical temperature at that exponential increasing of decomposition rate begins was carried out according equation that is consequence of solution of task about heat explosion at convection heat transfer with environment (Semenov's task) [17]:

$$T_* = \frac{E}{R \ln \frac{e V d B E Q}{S Nu \kappa R T_*^2 c_v}}$$

Where T_* is critical temperature, E – activation energy, R – gas constant, e – base of natural logarithm (the critical value of Semenov's criterion), V – volume of vessel in that heat explosion takes place (vessel is sphere $d = 1.5$ cm), B – preexponential factor, Q – heat of reaction decomposition (it is supposed that $Q = 0.5 Q_v$), S – surface of heat exchange, Nu – Nusselt's criterion, κ – coefficient of thermal diffusivity, ($\kappa = 10^{-3}$ cm²/s for organic nitrocompounds), c_v – heat capacity at constant volume ($c_v = 1.255$ J/g K s for organic nitrocompounds).

Table 1. Melting points (T_f) and kinetic parameters of decomposition reactions azo-dyes under investigation

No.	Trade mark (translation from Russian)	Chemical name and gross formula	T_f , °C	Kinetic parameters [9]	
				E, KJ/mol	LgB, s ⁻¹
1	Scarlet G	4'-nitro-4-(ethyl- β -oxyethyl) aminoazobenzene, C ₁₆ H ₁₈ N ₄ O ₃	158-159	86.7	4.8
2	Vinous C	2'-chlor, 4'-nitro-4-(ethyl- β -oxyethyl)aminoazobenzene, C ₁₆ H ₁₇ N ₄ O ₃ Cl	133-134	96.0	5.9
3	Red-brown	2',6'-dichlor, 4'-nitro-4-(ethyl- β -oxyethyl)aminoazobenzene, C ₁₆ H ₁₆ N ₄ O ₃ Cl ₂	139-140	117.8	8.0
4	Orange p/e	4'-nitro-4-(ethyl- β -cyanethyl) aminoazobenzene, C ₁₇ H ₁₇ N ₅ O ₂	160-161	123.6	7.8
5	Scarlet p/e	2'-chlor, 4'-nitro-4-(ethyl- β -cyanethyl)aminoazobenzene, C ₁₇ H ₁₆ N ₅ O ₂ Cl	136-137	155.0	10.8
6	Yellow-brown	1',6'-dichlor, 4'-nitro-4-(ethyl- β -cyanethyl)aminoazobenzene, C ₁₇ H ₁₅ N ₅ O ₂ Cl ₂	142-143	158.4	11.9
7	Violet 4K	2',4'-dinitro, 2-methyl, 4-liethanoleamineazobenzene, C ₁₇ H ₁₆ N ₅ O ₆	186-187	105.6	7.8
8	Yellow 3	4'-acetoamino, 2-oxy, 5-methyl-azobenzene, C ₁₅ H ₁₅ N ₃ O ₂	194-195	142.9	10.5
9	Yellow-strong 2K	2',4'-dinitro, 4-oxy-diphenylamine, C ₁₂ H ₉ N ₃ O ₅	193-194	164.2	12.5

Table 2. Results of elemental analysis of azo-dyes

No. *)	Substance	Calculation, %		Experiment, %	
		C	H	C	H
1	Scarlet G	61.13	5.78	61.18	5.70
7	Violet 4K	52.43	4.93	52.14	4.95
8	Yellow 3	56.89	5.63	55.82	5.76

*) Here and later: numbers of azo-dyes are the same that in Table 1.

Table 3. Experimental enthalpies of formation in solid state (ΔH_f^S) and calculated detonation velocity (D at density $\rho = 1.2 \text{ g/cm}^3$), heat of explosion (Q_v) and volume of gaseous products of explosion (V)

No.	Substance	ΔH_f^S , kJ/mol	D, m/s	Q_v , kJ/kg	V, m ³ /kg
1	Scarlet G	-230.5	4340	2290	0.575
7	Violet 4K	-328.4	5166	3158	0.601
8	Yellow 3	-247.0	4142	1672	0.519

Calculation T^* according to foregoing transcendental equation was carried out on PC by means of cut-and-try method with applying simple program that was written in application Mathcad.

Heat sink is taken into account. In the case of melting high explosives decomposition is accompanied by intensive formation of gas bubbles, that mixes thoroughly liquid melt, and Nusselt's criterion is recommended to assign $Nu = 30$, for non-fusible explosives $Nu = 5$ [13]. Azo-dyes mediate. Decomposition of them proceeds more smooth than high explosives, mixing of liquid melt in this case is less intensive, heat explosion of them propagates in degenerated mode. Nusselt's criterion is assigned $Nu = 15$.

Mainly E and B exert influence on T^* , $Q -$ heat of reaction decomposition affects much less. It would be noted that reaction of decomposition at slow heating proceeds in condensed explosive, final products of explosion do not form, so it is assigned that $Q = 0.5 Q_v$ [13]. The most of azo-dyes (Table 1) are mononitrocompounds and heat of explosion of them are assumed the same as calculated Q_v value of azo-dye Scarlet-G (No. 1 in all Tables). Azo-dye Yellow-strong 2K (No. 9 in Table 1) is dinitrocompound, and heat of explosion of it is assumed the same as calculated Q_v value of azo-dye Violet 4K (No. 7 in all Tables).

The comparison of calculated and experimental critical temperature at that exponential increasing of decomposition rate begins is given in Table 4.

Table 4. Comparison of calculated and experimental temperatures of exponential growth of decomposition rate

No.	Azo-dye	T*, °C		Deviation, %
		Calculation	Experiment [10]	
1	Scarlet G	287	268	+7.1
2	Venous C	268	256	+4.7
3	Red-brown	266	262	+1.5
4	Orange p/e	302	295	+2.4
5	Scarlet p/e	293	266	+10.1
6	Yellow-brown	263	258	+1.9
7	Violet 4K	209	218	-4.1
8	Yellow 3	265	274	-3.3
9	Yellow-strong 2K	260	274	-5.1

Conclusion

Deviations of calculated T* from experimental one are several percents for most of all colouring agents under investigation and in one case runs up to 10%. Averaged difference between calculated and experimental T* values is $\pm 4.5\%$. In that way it was shown that regularities of classic Theory of heat explosion of high explosives are applied for calculation of azo-dyes temperature heat explosion.

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