

Decomposition of aromatic diazonium compounds

R. Ullrich *, Th. Grewer

Hoechst AG, 65926 Frankfurt a.M., Germany

(Received 12 November 1992; accepted 18 February 1993)

Abstract

The decomposition of diazonium salts caused an explosion in a peripheral part of a production plant. This incident was initiated by mechanical action and could not be associated with a definite diazonium compound. Therefore we have investigated the impact sensitivity of many of the diazonium chlorides which were produced in the plant.

Aromatic diazonium salts were prepared in small portions of fractions of a gram in the laboratory and were subjected to drop-hammer tests and DTA experiments. The diazonium compounds derived from nitroanilines had a very low critical impact energy of 1–2 J. With increasing molecular mass, the impact energy necessary for an explosion increased until an explosion was no longer observed.

The results show that the hazards connected with diazonium salts can be classified by a drop-weight test. The discussion of the explosion incident shows that hazards must be expected in plants that produce diazonium salts although pure diazonium compounds are not involved in the actual process. Even small deposits in peripheral parts of the plant must be avoided.

1. INTRODUCTION

Aromatic diazonium salts are known to be thermally and mechanically sensitive [1–3]. In practical applications in plants, it is very important to handle only solutions of these compounds or to stabilize the solid products, e.g. by the addition of inorganic compounds or by using big anions.

Diazonium salts with NO_2^- , NO_3^- , ClO_4^- , MnO_4^- , or CrO_4^{2-} anions, or picrates, are particularly unstable or explosive. Anions such as Cl^- , SO_4^{2-} , ZnCl_4^{2-} , BF_4^- and diverse aromatic sulphuric acids stabilize the character of such diazonium salts. Furthermore the kind of substituents on the cation, as well as the position of these substituents, are of great importance for the stability of each diazonium salt. Investigations of thermal stability and combustion properties are published in refs. 4–6.

* Corresponding author.

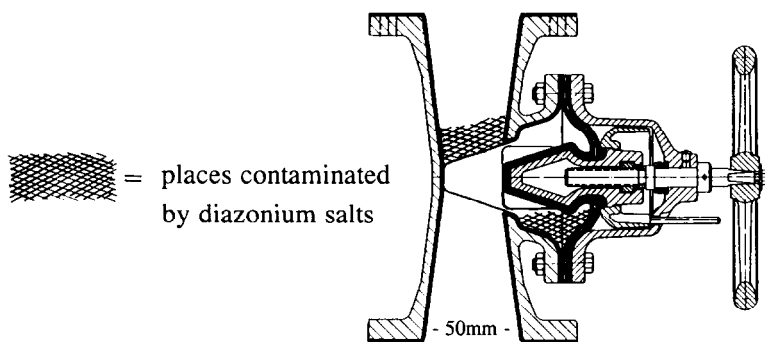


Fig. 1. Cross-section of the valve which exploded due to the decomposition of diazonium salts.

Because most of the diazonium salts are produced in hydrochloric acid solution, we have investigated only diazonium chlorides. Thus the stabilities of diazonium cations can easily be compared. We have investigated these compounds by DTA of the solid salts and of their aqueous solutions, and by testing their mechanical sensitivity using the German drop hammer.

The starting point of our investigations was the explosion of a valve in the vacuum line of a diazonium-salt production plant.

2. REPORT ABOUT AN INCIDENT

Figure 1 shows a cross-section through the valve in which the explosion occurred. The points at which product residues were deposited are hatched. The valve was installed in the vacuum line of a reaction vessel which had previously been used several times for clearing and filtration processes. Apparently, before the incident, spray mist and possibly also foam from the filtered diazonium solution had been deposited in the valve. Thus over a period of several days, it was possible that different diazonium salts dried in the operating vacuum of 200–300 mbar at the given room temperature of 20–25°C and accumulated in the valve.

An attempt to clean the valve mechanically triggered explosive decomposition, which led to the bursting of the valve and, unfortunately, the injury of two workmen. Examination of the valve fragments indicated that a pressure of more than 2000 bar and a temperature of between 2000 and 3000 K had been generated briefly inside the valve.

It is not known exactly which diazonium salts were deposited in the valve. They could have been products from several production series which had been run over a number of weeks, each using various amines. But it is certain that only aromatic amines substituted by chlorine atoms or nitro groups had been used as educts. For this reason we have chosen to

investigate only these and similar compounds from the field of azo chemistry.

3. PREPARATION OF THE DIAZONIUM COMPOUNDS

Diazotations in technical plants are normally carried out using hydrochloric acid. In this study we investigated only diazonium chlorides in order to have a direct comparison with the technical practice. Effects due to varying anions were thus eliminated.

Aromatic amines were diazotized in aqueous solution according to the well-known method using sodium nitrite. The dry diazonium compounds were prepared using the necessary safety precautions in quantities of fractions of a gram. The dilute solutions of the diazonium salts were dried in a vacuum drying oven at 25°C, and simultaneously purified of hydrochloric acid and nitrogen oxides. The drying time that led to the greatest sensitivity to impact was determined for each substance. The normal drying times were 24 or 48 h. Each dried diazonium compound contained 1 mol of NaCl per mole.

4. TEST METHODS

Because the incident was caused by mechanical action, our first procedure was to test the diazonium compounds concerned by a mechanical method. Although there is no international agreement on methods such as the drop hammer, we consider it to be an important method for our particular problem.

Because of the high thermal and mechanical sensitivity of the diazonium compounds, we could only use small samples of less than 1 g. For our own safety, the German drop hammer, which needs 40 mm³ for one test, and differential thermal analysis (DTA) for testing the thermal sensitivity were suitable methods. The test methods we used were as follows.

1. Impact sensitivity. The “Fallhammer” of BAM (Federal Institute of Materials Testing and Research, Berlin) was used as described in the Test Guidelines of the European Community [7]. The impact energy is the product of the falling mass, the height and the gravitational acceleration g . The impact energy is in joules.

2. Exothermic decomposition. Differential thermal analysis was applied using glass ampoules as samples containers. We used the DTA apparatus of Heraeus which is no longer available. Sample sizes of 5–10 mg were used, and the heating rate was generally 10 K min⁻¹. The temperatures of the start of the exothermic decomposition were taken from the DTA diagrams. It is obvious that these temperatures are only useful for comparison of the thermal stability of the samples.

3. Combustibility. A fire train test was applied to some of the diazonium compounds. Classes of combustibility were given according to the terminology of the VDI guideline 2263 [8].

5 DISCUSSION OF THE RESULTS

Forty diazonium salts were tested. The results are compiled in Tables 1–5. The diazo compounds are referred to by their number in the tables.

TABLE 1

Examples of the results of the minimum of impact energy required to start explosion or decomposition

nr 1)	chem. name of the aromatic bases 2)	structure formula of the diazoniumsalts	drying time [h]	drop height [m]										drop weight [kg]		result 4)				
				1,0	0,9	0,8	0,7	0,6	0,5	0,4	0,3	0,2	0,1	3) 5	1	Ex [J]	D [J]			
2	2-nitroaniline		3 6 24 48																	
										2Ex	D	0					x	4	3	
														3Ex			x	1	< 1	
														Ex			x	1	< 1	
3	3-nitroaniline		3 6 24 48															15	5	
										Ex	D			D	0		x	5	2	
														Ex	D		x	2	1	
4	4-nitroaniline		3 6 24 48	6x0													x			
										Ex	D	D	6x0				x		30	20
												2Ex	D			3D	x		20	5
												2Ex	D			3D		x	4	1
13	2-chloroaniline		3 6 24 48																10	5
										2Ex	D							x	9	3
												2Ex	D			2D	6x0	x	6	2
														2Ex	D	D		x	3	1
14	3-chloroaniline		3 6 6 24 48																15	10
														2Ex	2D	6x0	x		15	5
										3D	1D	6x0		3Ex	3D	1D			7	
										2Ex	D			3D	2D	6x0		x	8	3
														2Ex	6D		x	4	1	
15	4-chloroaniline		3 6 24 48																	
														2Ex	1Ex	D	D	x		
										Ex	D				D			x	8	3
												3Ex	2Ex	D	D	D	6x0	x	5	2
32	4,4'-diaminodi- phenylamine		3 6 6 24 24 48 48																	
														3Ex	1Ex	D	D	x	15	5
																			10	5
														2Ex	D			x		7
														2Ex	1Ex	D		x	10	
															2D			x		5
															2Ex	D		x		
															D	0				8

1) Continuous number of the tested substances.

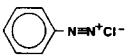
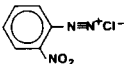
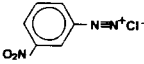
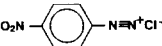
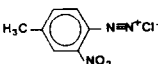
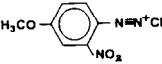
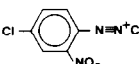
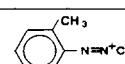
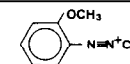
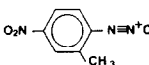
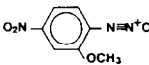
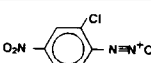
2) Nomenclature according to the International Union of Pure and Applied Chemistry (IUPAC).

3) Ex, explosion; D, decomposition (carbonizing or burning without an explosion).

4) J, Joule ($9.81 \times \text{mkp}$).

TABLE 2

Stability tests of differently substituted nitrobenzene diazonium chlorides

tested substances			drop hammer			exoth. decomposition	
nr. 1)	chem. name of the aromatic bases 2)	structure formula of the diazonium salts	result 3)	impact- energy [J] 4)	drying time [h] 5)	dried salt [°C] 6)	dissolved salt [°C] 6)
1	aniline		Ex D	3 1	24	40	50
2	2-nitroaniline		Ex	1	24	60	70
3	3-nitroaniline		Ex D	2 1	48	90 (20°C/min)	90
4	4-nitroaniline		Ex D	4 1	48	80 (20°C/min)	90
5	2-nitro-p-toluidine		Ex D	10 5	48	60	70
6	2-nitro-anisidine		Ex D	2 1	48	60 (20°C/min)	120
7	2-nitro-4-chloraniline		Ex D	2 1	48	60 (20°C/min)	80
8	5-nitro-o-toluidine		Ex D	20 5	48	80 (20°C/min)	80
9	5-nitro-o-anisidine		Ex D	2 1	48	120 (20°C/min)	100
10	4-nitro-o-toluidine		Ex D	4 1	48	60 (20°C/min)	80
11	4-nitro-o-anisidine			2 1	24 48	70 (20°C/min)	100
12	2-chloro-4-nitroaniline		Ex D	10 7	48	50 (20°C/min)	50

1) Continuous number of the tested substances.

2) Nomenclature according to IUPAC (NH₂, 1 position).

3) Ex, explosion; D, decomposition (carbonizing or burning without explosion).

4) J, Joule (9.81 × mJ).

5) The shortest drying time at which the highest impact sensitivity was reached.

6) DTA heating rate, 10 K min⁻¹ except where indicated.

TABLE 3

Stability tests of differently substituted mono- and dichlorobenzene diazonium chlorides and of sulphonamide- and carbonamide-substituted benzene diazonium chlorides

tested substances			drop hammer			exoth. decomposition	
nr.	chem. name of the aromatic bases	structure formula of the diazonium salts	result	impact energy [J]	drying time [h]	dried salt [°C]	dissolved salt [°C]
1)	2)		3)	4)	5)	6)	6)
13	2-chloroaniline		Ex D	3 1	48	120	120
14	3-chloroaniline		Ex D	4 1	48	90	70
15	4-chloroaniline		Ex D	5 2	48	80 (20°C/min)	90
16	2,5-dichloroaniline		Ex D	8 5	48	120 (20°C/min)	120
17	2-chloro-5-trifluoromethylaniline		Ex D	9 2	48	110 (20°C/min)	120
18	4-chloro-o-toluidine		Ex D	10 7	48	60	70
19	5-chloro-o-anisidine		Ex D	15 5	48	90 (20°C/min)	110
20	3-amino-4-methoxybenzamide		Ex D	20 10	48	100	120
21	3-amino-4-methoxybenzene-N,N-diethylsulfonamide		Ex D	10 5	48	80 (20°C/min)	70
22	3-amino-4-methoxybenzene-N-n-butylsulfonamide		Ex D	15 5	48	70	110
23	2-amino-4,4'-dichlorodiphenylether		Ex D	15 5	48	80	80
24	2,6-dichloro-4-nitroaniline		Ex D	25 20	48	60 (20°C/min)	50

1) Continuous number of the tested substances.

2) Nomenclature according to IUPAC (NH₂, 1 position).

3) Ex, explosion; D, decomposition (carbonizing or burning without explosion).

4) J, Joule (9.81 × mkg).

5) The shortest drying time at which the highest impact sensitivity was reached.

6) DTA heating rate, 10 K min⁻¹ except where indicated.

TABLE 4

Stability tests of different *N*-benzoylated or *N*-arylated benzene diazonium chlorides and of special tetrazonium chlorides

tested substances			drop hammer			exoth. decomposition	
nr. 1)	chem. name of the aromatic bases 2)	structure formula of the diazonium salts	result 3)	impact- energy [J] 4)	drying time [h] 5)	dried salt [°C] 6)	dissolved salt [°C] 6)
25	5'-amino-2',4'-di methoxy-benzanilide		no Ex D	50 5	48	100	130
26	4'-amino-2'-methyl- 5'-methoxybenz- anilide		no Ex D	50	48	125 (20°C/min)	100
27	4'-amino-2',5'- diethyloxi- benzanilide		no Ex D	50	48	100 (20°C/min)	60
28	4-amino-diphenyl- amine		Ex D	40 9	48	95 ⁸⁾	100 ⁷⁾ weak exoth. D
29	4-amino-3-methoxy- diphenylamine		no Ex D	100 4	48	95 ⁸⁾	no exoth. D
30	4-amino-4'-methoxy- diphenylamine		no Ex D	100 20	48	90 ⁸⁾	100
31	3,3'-dimethoxy- benzidine		Ex D	20 7	48	130 (20°C/min)	120
32	4,4'-diamino- diphenylamine		Ex D	10 2	24	50 100 145	80
33	4-amino-2-methyl-5- ethoxy-4'-(4'-amino- phenyl-amino)-azo benzene		Ex D	35 30	48	80 (20°C/min)	80

1) Continuous number of the tested substances.

2) Nomenclature according to IUPAC (NH₂, 1 position).

3) Ex, explosion; D, decomposition (carbonizing or burning without explosion).

4) J, Joule (9.81 × mkg).

5) The shortest drying time at which the highest impact sensitivity was reached.

6) DTA heating rate, 10 K min⁻¹ except where indicated.

7) Effect too weak on account of too low a concentration in the reaction solution.

8) Results by Dr. Duch, APh Hoechst; rate of heating; 1.5 K min⁻¹.

Table 1 shows detailed results for some typical diazonium salts. They are listed in order of decreasing sensitivity to impact. The results demonstrate that the sensitivity to impact of the chlorobenzene diazonium chlorides, as well as that of the nitrobenzene diazonium chlorides, decreases from ortho through meta, to para-substitution, and that the nitro group imparts greater sensitivity to impact than the chlorine substituent. This may be attributed

TABLE 5

Stability tests of differently substituted substituted azobenzenediazonium chlorides

tested substances			drop hammer			exoth. decomposition	
nr. 1)	chem. name of the aromatic bases 2)	structure formula of the diazonium salts	result 3)	impact- energy [J] 4)	drying time [h] 5)	dried salt [°C] 6)	dissolved salt [°C] 6)
34	4-amino-2,4'-di- methyl-5-methoxy-2- nitro-azobenzene		Ex D	25 15	48	70	110
35	4-amino-2,5-di- methoxy-4'-nitro- azobenzene		Ex D	20 3	48	100	7)
36	4-amino-2,5-di- methoxy-2',6'-di- chloro-4'-nitro- azobenzene		no Ex only D	40 4	48	90	7)
37	4-amino-3-chloro- 4'-nitro- azobenzene		Ex D	15 2	48	100	80
38	2-amino-4-methoxy- 5-methyl-2'-methyl- sulfonyl-4'-nitro- azobenzene		no Ex	40	48	90 (20°C/min)	70
39	2-amino-4-methoxy- 5-methyl-2'-chloro- 4'-nitro- azobenzene		no Ex D	40 10	48	70 (110) (120)	60
40	α-(4'-amino-2',5'-di- methoxyphenyl-azo)- acetoacetanilide		no Ex D	40 10	48	110	ab 100

1) Continuous number of the tested substances.

2) Nomenclature according to IUPAC (NH₂, 1 position).

3) Ex, explosion; D, decomposition (carbonizing or burning without explosion).

4) J, Joule (9.81 × mkg).

5) The shortest drying time at which the highest impact sensitivity was reached.

6) DTA heating rate, 10°C min⁻¹ except where indicated.

7) Effect too weak on account of too low a concentration in the reaction solution.

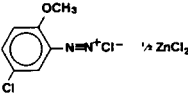
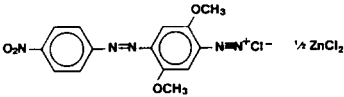
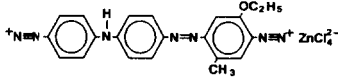
8) Results by Dr. Duch, APH Hoechst; rate of heating; 1.5 K min⁻¹.

to the intramolecular oxygen supply by the nitro group [8]. In contrast, the tetra-azo compound 32 is relatively stable under the influence of imino isomerism in spite of its two diazo groups.

Table 2 lists the variously substituted nitrobenzene diazonium chlorides. For comparison, unsubstituted benzene diazonium chloride is also included. Generally speaking, nearly all these substances exhibit high sensitivity to impact. Marked desensitization due to substitution occurred only in the case of substances 5, 8 and 12.

TABLE 6

Examples of stabilization by thinning of diazonium chlorozincates with inorganic salts

nr.	name of the starting base and structure formula of the derivated diazonium salts	stage of preparation	concentration weight %	rel. to mole	class
19	5-chloro-o-anisidine 	concentrated dried	95	273,3	6
		dilution I	56		3
		dilution II	30		1
		standard ware	27		1
35	4-amino-2,5-dimethoxy-2',6'-dichloro-4'-nitroazobenzene 	concentrated dried	97	417,7	6
		dilution I	45		5
		dilution II	33		3
		standard ware	30		2
33	4-amino-2-methyl-5-ethoxy-4'-(4''-amino-phenyl-amino)-azobenzene 	concentrated dried	85	592,4	6
		dilution I	48		5
		dilution II	40 / 40,5		4 3
		standard ware	33 / 33,6		1 2

Definition of the combustibility classes and examples of combustibility behaviour at room temperature (VDI 2263 page 1/Part 1 [9]).

type of reaction		class	reference product
No spreading of fire	no ignition	1	table salt
	brief ignition and rapid extinction	2	tartaric acid
	localized combustion or glowing with practically no spreading	3	d(+)-lactose
Fire spreads	glowing without sparks (smoldering) or slow decomposition without flame	4	H - acid; (1-amino-8-naphthol-3,6-disulfonic acid), tobacco
	burning with flame or spark generation	5	sulfur
	very rapid combustion with flame propagation or rapid decomposition without flame	6	black powder

Table 3 presents variously substituted mono- and dichlorobenzene diazonium chlorides, and also sulphonamide- and carbonamide-substituted benzene diazonium chlorides. The double-halogenated diazonium com-

pounds 16 and 17 exhibited a somewhat lower sensitivity to impact than the mono-substituted ones. The same is valid for the nitro compound 24.

The shock sensitivity decreases with increasing molecular mass because of the diminishing specific energy of the decomposition. Thus, most of the compounds starting from number 25 onwards are distinctly less shock-sensitive. The tetrazonium chlorides 31–33 have two diazonium groups in their molecules and, consequently, are quite shock-sensitive in spite of their relatively large molecular mass.

A correlation between shock sensitivity and thermal stability was not found.

6. DESENSITIZATION BY DILUTION

The desensitization (stabilization) of solid diazonium salts by dilution with inorganic salts is a method that is frequently used in chemical production. Table 6 shows the effect of dilution in correlation with the class of combustibility [9] on three different diazonium chlorozincates. Experience has shown that the sensitivity to impact is affected in the same way as the combustion number, both being reduced by dilution.

In this connection, the considerable influence of water must be mentioned, e.g. as residual moisture in a diazo salt or as the water of crystallization of an added inert salt. Because of its high heat capacity and high heat of vaporization, water is an ideal energy absorber for the exothermic decomposition of diazo compounds. Hydrate water can be introduced into a mixture of diazo salts, e.g. in the form of aluminium sulphate hexahydrate or higher hydrates of aluminium sulphate.

7. CONCLUSION

Although certain rules relating to stability can be derived from the molecular structure of the test materials, it is scarcely possible to make a reliable prediction in each individual case. Even though the chemical structures of the substances in question are of decisive importance, the great variety of substituent effects which interact in complex ways, as well as the size and type of the crystals, and also the degree of contamination with foreign substances, prevent a reliable estimate of their shock and thermal stabilities.

On the basis of extensive test material, it was shown that the BAM drop-hammer test yields impact sensitivities which correlate well with the chemical structure of the substances. We conclude that the BAM-type drop hammer is very useful for classifying the diazonium salts according to the hazard they represent.

From the incident described above and from our test results, we can conclude that neither the aqueous solution in which the diazonium salts are produced nor the stabilized final products present a hazard. Nevertheless,

hazards can arise during the production process in parts of the plant where solid diazonium salts are deposited. For safe working, it is necessary to check the whole plant for places where these deposits can be formed and to take care to avoid such deposits or to remove them at regular time intervals.

ACKNOWLEDGEMENTS

The authors thank K. Habermeier and H. Rippert for the preparation and testing of the diazonium compounds, and Dr. R. Driscoll and D. Terry for their assistance in preparing the English manuscript.

REFERENCES

- 1 K. Holzach, *Die Aromatischen Diazoverbindungen*, F. Enke, Stuttgart, 1947.
- 2 H. Zollinger, *Chemie der Azofarbstoffe*, Birkhäuser, Basel, Stuttgart, 1958.
- 3 H. Hertel, in *Ullmanns Encyclopädie der technischen Chemie*, Vol. 10, Verlag Chemie, Weinheim, 4th edn., 1975 p. 109.
- 4 D.F. DeTar and A.R. Ballantine, *J. Am. Chem. Soc.*, 78, (1956) 3916.
- 5 A.E. Fogelzang, V.Ya. Adzheman and B.S. Svetlov, *Fiz. Goreniya Vzryva*, 10 (1974) 449.
- 6 P.D. Storey, *Runaway Reactions*, *Inst. Chem. Eng. Symp. Ser.*, 68 (1981) 3/P:1.
- 7 Test Methods 84/499/EEC, *Official Journal of the European Communities* L251, 27 A.14, 1984.
- 8 T. Grewer, *Thermochim. Acta*, 187 (1991) 133.
- 9 Test Methods for the Determination of the Safety Characteristics of Dusts, VDI 2263, Part 1, Verein Deutscher Ingenieure, Düsseldorf, 1990.