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Identification of a safe diazotransfer reagent ☆

Linda D. Tuma

Merck Research Laboratories, P.O. Box 2000, Rahway, NJ 07065, USA

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Abstract

Eight effective diazotransfer reagents have been evaluated for their thermal stability using DSC analysis and impact sensitivity testing. *p*-Dodecylbenzenesulfonyl azide was the least hazardous reagent of those tested. The results of contamination studies and detonation velocity tests are also reported for *p*-dodecylbenzenesulfonyl azide.

Keywords: Contamination; Diazotransfer; DSC; Detonation; Explosive; Impact velocity

1. Introduction

Diazotransfer reagents and reactions are increasingly being used as the most convenient method of achieving certain preparative chemistry steps, but their explosive potential needs to be given consideration before their use in large scale operations as several serious accidents have been reported [1,2]. Faced with the need to develop a large scale diazotransfer reaction, eight effective diazotransfer reagents (Fig. 1) were evaluated for their thermal stability using differential scanning calorimetry analysis and impact sensitivity testing. *p*-Dodecylbenzenesulfonyl azide, the reagent of choice, was then subjected to additional studies, including contamination and detonation velocity testing.

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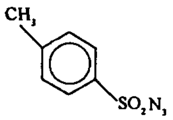
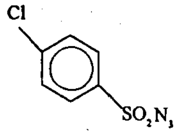
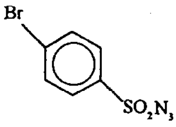
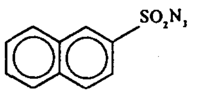
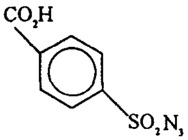
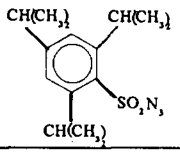
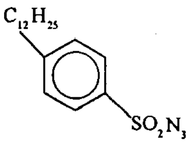
	-	p-Toluenesulfonyl azide
	-	p-Chlorobenzene azide
	-	p-Bromobenzene azide
	-	Napthalene-2-sulfonyl azide
	-	p-Carboxybenzenesulfonyl azide
	-	2,4,6-Triisopropylbenzenesulfonyl azide
	-	p-Dodecylbenzenesulfonyl azide

Fig. 1. Diazotransfer reagents evaluated in this study.

2. Experimental

2.1. Differential scanning calorimetry analysis

The specific heat of decomposition, initiation temperature and the relative rate of heat release were determined using a TA 1090 thermal analyzer system (TA

Instruments, New Castle, DE, USA), utilizing a high pressure differential scanning calorimetry cell (800 lbf in^{-2} nitrogen). A constant sample mass (8.7 mg) and heating rate (10°C min^{-1}) were used. The relative rate of decomposition is taken as the maximum slope of the line connecting the exothermic initiation point to the maximum decomposition curve height. The values obtained were then compared to that of *p*-toluenesulfonyl azide, whose value was arbitrarily set at 1.0.

2.2. *Impact sensitivity testing*

Impact sensitivity testing was measured on a Technoproducts Drop Weight tester (Technoproducts Inc., Saratoga, CA, USA). A constant sample mass/volume (20 mg (solids), 30 μl (liquids)) was subjected to decreasing impact weights, dropped from a constant height of 50 cm, until there was no indication of impact sensitivity. The sensitivity value (kg cm) for a given sample is the potential energy value (wt. × ht.) at which positive results are obtained. Positive impact sensitivity is indicated by any of the following: change in sample color, smoke, audible pop, deformation of sample pan, flash, spark, puncture of the steel diaphragm, etc.

2.3. *Contamination studies*

A solution of *p*-dodecylbenzenesulfonyl azide in hexane (350 mg ml^{-1}) was contaminated with various metals and metal salts to determine what effects these contaminants have on the initiation temperatures and rate of heat release. A constant mass of *p*-dodecylbenzenesulfonyl azide, with 10% by mass of the contaminant added, was used in these studies. The changes in initiation temperature and rate of heat release were determined using the TA 1090 thermal analyzer, utilizing a high pressure differential scanning calorimetry cell (800 lbf in^{-2} nitrogen). The results of the contaminated samples were compared to those of the uncontaminated solution of *p*-dodecylbenzenesulfonyl azide in hexane.

2.4. *Detonation velocity testing*

The object of this testing was to determine if a condensed phase of the sample is capable of propagating a detonation when subjected to a high intensity shock wave under conditions of high confinement.

Detonation velocity testing of solutions of *p*-dodecylbenzenesulfonyl azide in hexane was performed by Hazards Research Corporation (Rockaway, NJ, USA). The sample container was fabricated from 8 in long stainless steel pipe, of diameter 2 in. The bottom of the tube was sealed with a thin non-reactive plastic diaphragm. A high energy donor charge (160 g RDX (Cylonite)) was placed directly below the diaphragm and acted as an initiator. A cold rolled steel plate 4 in × 4 in × 0.375 in was placed on top of the fixture and served as a witness plate. The propagation velocity was measured and used, along with the condition of the witness plate, to determine whether a detonation had occurred.

3. Results

3.1. *Differential scanning calorimetry and impact sensitivity testing*

Table 1 summarizes the test results obtained with the eight diazotransfer reagents tested. Methanesulfonyl azide, the most hazardous azide, exhibited the highest specific heat of decomposition, relative rate of decomposition and shock sensitivity. *p*-Toluenesulfonyl azide is a close second to methanesulfonyl azide in impact sensitivity, but shows a lower relative rate of decomposition and heat of decomposition. The isomeric mixture of *p*-dodecylbenzenesulfonyl azide showed the lowest heat of decomposition with no indications of impact sensitivity. A comparison of the DSC traces obtained for *p*-toluenesulfonyl azide and *p*-dodecylbenzenesulfonyl azide is shown in Fig. 2.

3.2. *Contamination studies*

Table 2 summarizes the results of the contamination studies of a solution of *p*-dodecylbenzenesulfonyl azide in hexane (350 mg ml^{-1}). Carbon steel, Hastelloy B, Hastelloy C, tantalum, manganese (ionic state), cobalt (ionic state) and chromium (ionic state) contamination cause an increase in the relative rate of decomposition, but have no effect upon the initiation temperature of the exotherm.

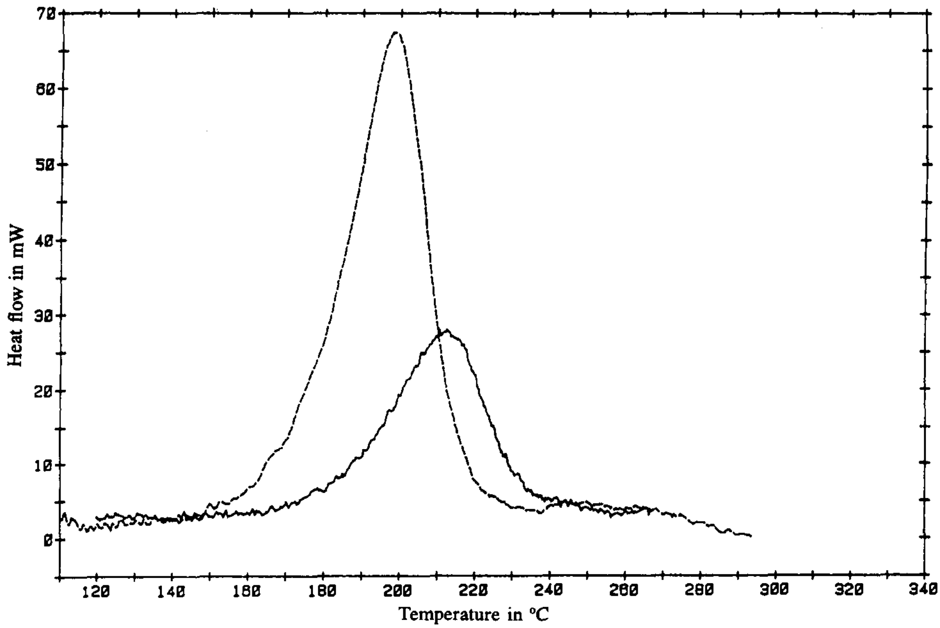


Fig. 2. DSC traces obtained for *p*-dodecylbenzenesulfonyl azide (——) and *p*-toluenesulfonyl azide. (- - -).

Table 1
DSC and impact sensitivity test results

Sulfonyl azide	m.p./°C	ΔH_D/ kcal mol^{-1}	ΔH_D/ cal g^{-1}	Approximate initiation temperature/°C	Relative rate of decomposition	Impact sensitivity/ kg cm
Methane/sulfonyl azide	20 [3]	−67.4	−557	125	1.96	50
p-Toluene/sulfonyl azide	19–20 [4]	−79.9	−405	120	1.00	50
p-Chlorobenzene/sulfonyl azide	39 [5]	−78.15	−360	139	0.14	300 [a]
p-Bromobenzene/sulfonyl azide	54.5–55.5 [6]	−74.2	−283.5	127	0.24	300 [b]
Naphthalene-2-sulfonyl azide	41–43 [7]	−64.5	−277	146	0.96	300 [c]
p-Carboxybenzene/sulfonyl azide	184–186 [8]	−53.6 [e]	−236 [e]	163	2.29 [f]	300 [d]
2,4,6-Triisopropylbenzene/sulfonyl azide	39–40 [9]	−62.4	−202	136	0.52	Negative to 300
p-Dodecylbenzene/sulfonyl azide (mixture) [g]	Liq. [h]	−58.9	−168	151	0.36	Negative to 150

The conversion factor from calories to joules is 1 cal = 4.186 J. The number of test samples showing discoloration on impact is [a] 4 of 6; [b] 6 of 6; [c] 5 of 6; [d] 3 of 6. [e] Uncorrected for the latent heat of fusion. [f] Decomposes faster but at a higher initiation temperature than *p*-toluenesulfonyl azide. [g] Isomeric mixture. [h] Isomerically pure *p*-dodecylbenzenesulfonyl amide, m.p. 97.5° [9].

Table 2
Thermal stability of metal contaminated *p*-dodecylbenzenesulfonyl axide in hexane

Contaminant added	Exothermic initiation Temp./°C	R/mW °C^{-1}	R^X/R^T [c]
None	128	0.81 [a]	–
Copper	136	0.64 [b]	0.79
Hast B	144	0.90 [b]	1.11
Tant	135	0.92 [b]	1.14
Tant – 24 h age	144	1.25 [b]	1.54
Hast C	136	0.87 [b]	1.07
Hast C – 24 h age	129	0.84 [b]	1.04
316L	140	0.72 [b]	0.89
316L – 24 h age	142	0.73 [b]	0.91
Carbon steel	146	0.95 [b]	1.17
Carbon steel – 24 h age	140	1.00 [b]	1.24
Rust	135	0.81 [b]	1.00
$MnCl_2$	132	1.06 [b]	1.31
$MnCl_2$ – 48 h age	138	0.84 [b]	1.04
$CoCl_2$	128	1.05 [b]	1.30
$SnCl_2$	140	0.63 [b]	0.78
$FeCl_3$	102	3.68 [b]	4.29
$FeCl_3$ – 17 h age	111	3.47 [b]	4.28
$CuCl_2$	120	1.50 [b]	1.84
$CrCl_2$	129	0.93 [b]	1.15

The various contaminants had very little effect upon the size of the exothermic decomposition of *p*-dodecylbenzenesulfonyl azide/hexane solutions. [a] Relative rate of decomposition of uncontaminated solution, R^T. [b] Relative rate of decomposition of contaminated solution, R^X. [c] Ratio of relative rates of decomposition, ideally ≤ 1.0.

Contamination with copper (ionic state) and iron (ionic state) cause a decrease in the exotherm initiation temperature and an increase in the relative rate of decomposition.

3.3. Detonation velocity testing

Detonation velocity testing of solutions of *p*-dodecylbenzenesulfonyl in hexane, at concentrations not exceeding 350 mg of azide per ml of hexane, exhibited a decaying velocity. It is characteristic of detonations that the propagation velocity is constant and supersonic. The lack of a constant velocity in the tests indicated that the tested concentration of *p*-dodecylbenzenesulfonyl azide in hexane did not sustain a detonation.

4. Conclusions

The results of differential scanning calorimetry, impact sensitivity, contamination and detonation velocity testing show that *p*-dodecylbenzenesulfonyl azide is the least hazardous diazotransfer reagent of those tested.

p-Dodecylbenzenesulfonyl azide, as a solution in hexane/toluene, has been used as a diazotransfer reagent in large scale operations for over 9 years at Merck without incident.

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