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Azodicarboxylates: Explosive properties and DSC measurements

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ABSTRACT

A large number of azodicarboxylates and their derivatives are produced and used in the chemical industries. The versatile applications of these azodicarboxylates in research institutes and in the chemical industries for chemical synthesis arouse additional hazards. The intent of this paper is to obtain first knowledge about the structure–response relationship regarding the explosive properties and the thermal hazards of different versatile used azodicarboxylates. The substances are examined with the differential scanning calorimetry (DSC). Furthermore, different laboratory test methods, based on the UN Recommendations on the Transport of Dangerous Goods, are applied to determine the explosive properties of the mentioned substances. On the basis of the obtained results, the known influence of the nitrogen content within the molecule regarding their thermal behaviour could be confirmed. The measured heat of decomposition appeared to be proportional to the nitrogen content within the group of the aliphatic and the aromatic azodicarboxylates. To emphasize this dependency, further investigations should be done. The long term objective of this research is to develop structure–response relationships of the explosive properties and the thermal hazards originating from azodicarboxylates.

1. Introduction

The assessment of the explosive properties and the thermal hazards of energetic substances e.g. azodicarboxylates requires extensive knowledge – in the general application. Therefore, the intent of this paper is to investigate the thermal stability, the decomposition and the explosive properties of 9 different substances (7 azodicarboxylates and two relatives). One thermal analysis method, the differential scanning calorimetry, is used to describe the thermal behaviour. As BAM is the competent authority in Germany for testing, classification and assignment of substances showing explosive properties, tests on selected azodicarboxylates have been performed on the basis of the criteria given in the UN Recommendations on the Transport of Dangerous Goods (UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, 2003).

Diethyl-azodicarboxylate (DEAD) for instance is a very important reagent used in many chemical reactions (Dembinski, 2004; Hillier, Desrosiers, Marcoux, & Grabowski, 2004; Mitsunobu, 1981; Uemura and Chatani, 2005; Vijay, Smitha, Akkattu, & Eringathodi, 2007). On the other hand DEAD represents an explosive hazard. It is shock-sensitive and thermally unstable – it is very sensitive if heated under defined confinement (Urben, 1999). Due to this, the shipment of DEAD as a pure reagent is prohibited in the United States (Sigma–Aldrich). The shipment of DEAD, 40% solution in toluene, is allowed (Sigma–Aldrich). How stable and safe this solution really is, this will be discussed later. To obtain a statement about the structure–response relationship regarding the explosive properties and the thermal stability of azodicarboxylates e.g. DEAD, different derivatives with electron donating and electron-withdrawing groups were selected. Therefore, we have chosen Diisopropyl-azodicarboxylate (DIAD), Di-*tert*-butyl-azodicarboxylate (Di-*tert*-butyl-AD), Bis (2,2,2-trichloroethyl)azodicarboxylate (TCEAD), Dibenzyl-azodicarboxylate (DBAD), Di(4-chlorobenzyl)-azodicarboxylate (Di (4-chlorobenzyl)-AD)), 1,1′-azodicarbonyl)-azodicarboxylate (ADDP) and Ethyldiazoacetate, with 15% dichloromethane (EDA_15% CH_2Cl_2). These substances are also widely used in chemical reactions, e.g. DIAD in Lewis acid or Brønstedt acid catalyzed reactions (Jian-Mei, Zhi-Bin, & Min, 2009) and still for the commonly used Mitsunobu reaction (Mitsunobu, 1981). ADDP, in which the alkoxy group is replaced by a secondary amine such as piperidine has been used in reactions to increase the basicity (Dembinski, 2004; Kosower and Kanetylondner, 1976). DBAD has been used in reactions with phosphanes (Kiankarimi, Lowe, McCarthy, & Whitten, 1999), and Di-*tert*-butyl-AD is gaining popularity as a preferred reagent for the Mitsunobu reaction (Pelletier and Kincaid, 2000). Furthermore, EDA has been used in Cycloaddition reactions (Malisch et al., 1998) and metal-catalyzed reactions (Grohmann, 2007). A study of the 'loss of control' in chemical systems due to decomposition in the case of EDA was examined in the group of Marsanich, Barontini, Cozzani,

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Creemers, and Kersten (2004). Di-2-methoxyethyl azodicarboxylate (DMEAD) was newly developed from Sugimura and Hagiya and is now commercially available (Sugimura and Hagiya, 2008). DMEAD has a big advantage in its production process and is also a very good alternative for the potentially explosive and shock-sensitive liquid, DEAD, for the Mitsunobu reaction (Sugimura and Hagiya, 2008). Unfortunately, until now it was not possible to receive the substance DMEAD to investigate its explosive properties and its thermal behaviour in our laboratory. This should be done in the near future.

2. Experimental

To characterize the explosive properties of azodicarboxylates and their derivatives some of the necessary tests have been performed, which are fully described in literature (Method A.14 "Explosive Properties", Annex to Commission Directive 92/69/EEC of 31 July 1992; UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, 2003; Wehrstedt, Wandrey, & Heitkamp, 2005). For better understanding, an overview of these test procedures will be given, briefly. The BAM 50/60 steel tube test (A.1) is used to measure the ability of a substance to propagate a detonation by subjecting it to a cylindrical detonating booster charge under confinement in a steel tube. The ability of a substance to transfer a deflagration is performed with the Deflagration test (C.2). The Koenen test (E.1) and the Dutch pressure vessel test (E.2) are used to determine the sensitivity of a substance to the effect of intense heat under defined confinement. To determine the explosive power of a substance the Trauzl test (F.3) has been used. The 'BAM Fallhammer' (3(a)(ii)) (impact test method) is used to measure the sensitivity of a substance to drop-weight impact. The BAM-Dewar test (H.4) to determine the SADT (self-accelerating decomposition temperature) is a heat accumulation storage test.

Dynamic DSC measurements using different heating rates in the range 0.5–40 K/min were performed using a Perkin Elmer Pyris Diamond Calorimeter. The calibration was carried out at each heating rate for temperature and heat flow, using indium as reference material. For all experiments stainless steel crucibles were used and a 20 ml/min N_2 purge gas was applied. For each substance and heating rate at least two reproducible runs have been done. The sealed stainless steel crucibles, can withstand an inner pressure as high as 15 MPa. According to the standards DIN 51007 and ASTM E 473, a positive deflection in the DSC curve corresponds to an endothermic effect, and a negative deflection corresponds to an exothermic one.

3. Results and discussion

The intent of this study is to obtain knowledge about the structure–response relationship regarding the explosive properties and the thermal behaviour of different azodicarboxylates and two related substances (Table 1). These compounds have been investigated on the basis of the criteria given in the UN Recommendations on the Transport of Dangerous Goods. The appropriate test results are summarized in Table 2 and will be discussed in this section.

3.1. Explosive properties

To characterize the explosive properties of the investigated substances named in this paper some of the necessary test methods have been performed. Unfortunately, due to the lack of a few substances not all test methods could be carried out. Interestingly was the different result for DEAD and DIAD in the Koenen test (UN test E.1), even though both substances differ in only one additional methyl group on each side of the carboxylic group. DEAD showed a limiting diameter of 20 mm, $t_1 = 32$ s, $t_2 = 3$ s, with a fragmentation higher than 9 resulting in a "violent" (Fig. 1). Compared to DIAD, a fragmentation higher than 7 was found, but at a limiting diameter of 1.0 mm resulting in a "low" (Fig. 2). Because of the hazard of DEAD its use has decreased in favour of the more stable substance DIAD (Jian-Mei et al., 2009). The influence of the additional methyl groups in the case of DIAD regarding the explosive properties is obvious. But until now, it cannot be explained whether the different behaviour is caused by the electron donating methyl groups, which could stabilize the 'O–N' bond, or by the corresponding decreasing nitrogen content. Furthermore, the sensitivity to drop-weight impact ("BAM Fallhammer") of DEAD has a limiting value of 4 J. In comparison Trinitrotoluene (TNT) has a limiting diameter of 5 mm and a sensitivity to drop-weight impact of 15 J (Meyer, 1985). The explosive power, which was measured with the Trauzl test, is "not low" (expansion: 33 ml). Therefore, DEAD presents an explosive hazard. It is shock-sensitive and very sensitive if heated under defined confinement (Wehrstedt, 2001).

DEAD is currently only available in solution (e.g. 40% in toluene). Due to the lower concentration, the expansion of the lead block is only 5 ml and the sensitivity to drop-weight impact is >40 J. But even for a 40% solution the Dutch pressure vessel test (UN test E.2) shows a "violent" result (limiting diameter ≥ 24.0 mm, $t_1 = 29$ s, $t_2 = 73$ s). Also the Koenen test (UN test E.1) shows an explosion at a limiting diameter of 1.0 mm (result: "low"). These results could be explained by the evaporation of toluene based on its special test procedure. Thus, the toluene seems to be unsuitable to completely suppress the explosive properties of DEAD.

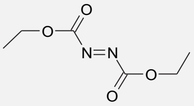
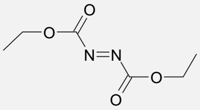
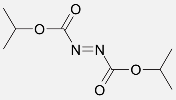
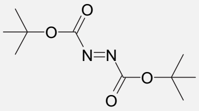
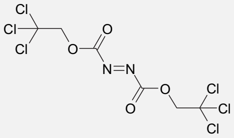
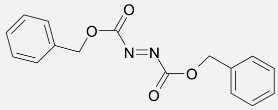
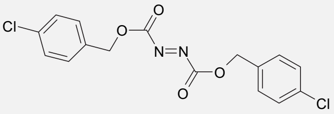
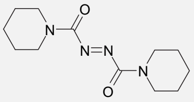
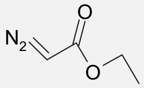
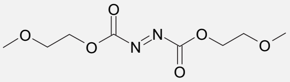
As aforementioned, because of the additional methyl groups, DIAD is more stable than DEAD. Hence, Di-*tert*-butyl-AD should be more thermally stable; this was confirmed by the Koenen and the Trauzl tests. An explosive power could not be observed for Di-*tert*-butyl-AD. The reason for this behaviour could be explained by the electron donating effect of the two additional methyl groups on each side of the carboxylic group. Due to considerable delocalisation of charge (through –N=N– double bonds) the insensitivity to impact and a high level of thermal stability may be accounted, caused by different resonating structures (Sikder, Maddala, Agrawal, & Singh, 2001).

In the case of Bis(2,2,2-trichloroethyl)-AD (TCEAD), three hydrogen atoms are substituted by chlorine atoms (electron-withdrawing effect) on each ethyl azocarboxylate group. The "BAM Fallhammer" test showed no effect (>40 J). But the expansion of the lead block (Trauzl test) with 39 ml was higher ("not low"), than the expansion of pure DEAD with 33 ml. Therefore, the electron-withdrawing influence of the chlorine atoms on the stability of the molecule seems to be obvious. We could not perform other tests on TCEAD because of the small amount available in our lab. To relate to a tendency of the electron-withdrawing influence of the chlorine atoms in TCEAD regarding its hazards more tests have to been done.

Having an aromatic benzyl group on each site of the azodicarboxylate groups, as in the case of DBAD, the thermal behaviour is similar to the thermal behaviour of DIAD and Di-*tert*-butyl-AD. Both the Koenen and the Trauzl tests result a "no". In the case of Di (4-chlorobenzyl)-AD, with the electron-withdrawing chlorine atom in para-position, there appeared a small difference in the Trauzl test ("low"). The value for the expansion of the lead block is with 13 ml higher than the value of DBAD ("no", 8.5 ml). No explosive power could be observed for the azodicarboxylates with the aromatic functional groups.

ADDP, having two piperidine groups instead of the two alkoxy groups in the molecular structure, showed no explosive power. In spite of its highest total nitrogen content of 22%, compared to the other eight examined substances, ADDP pointed to be a stable molecule.

Table 1
Data of the substances.

Name	Structure	Abbreviation	Molecular formula	Aggregate state (color)
Diethyl-azodicarboxylate		DEAD	$C_6H_{10}N_2O_4$	Liquid (yellow)
Diethyl-azodicarboxylate, 40% in toluene		DEAD 40%_Tol	$C_6H_{10}N_2O_4$	Liquid (orange)
Diisopropyl-azodicarboxylate		DIAD	$C_8H_{14}NO_4$	Liquid (orange)
Di-*tert*-butyl-azodicarboxylate		Di-*tert*-butyl-AD	$C_{10}H_{18}N_2O_4$	Solid (yellow)
Bis(2,2,2-trichloroethyl) azodicarboxylate		TCEAD	$C_6H_4N_2O_4Cl_6$	Solid (yellow)
Dibenzyl-azodicarboxylate		DBAD	$C_{16}H_{14}N_2O_4$	Solid (yellow)
Di(4-chlorobenzyl)-azodicarboxylate		Di(4-chlorobenzyl)-AD	$C_{16}H_{12}N_2O_4Cl_2$	Solid (orange)
1,1′-(Azodicarbonyl)-dipiperidine		ADDP	$C_{12}H_{20}N_4O_2$	Solid (yellow)
Ethyldiazoacetate with 15% CH_2Cl_2		EDA_15%CH_2Cl_2	$C_4H_6N_2O_2$	Liquid (yellow)
Di-2-methoxyethyl-azodicarboxylate		DMEAD	$C_8H_{14}N_2O_6$	Solid

In comparison to the just mentioned substances, EDA_15% CH_2Cl_2, the ‘half’ molecule of DEAD, shows an explosion at a limiting diameter of 1.0 mm (“low”) in the Koenen test. The expansion of the lead block in the Trauzl test is 29 ml (“not low”). And a limiting diameter of 2.0 mm (“low”) was found in the Dutch pressure vessel test. The “BAM Fallhammer” test shows a limiting impact value of 20 J. After storing of EDA_15% CH_2Cl_2 for 7 days initially 75 °C, the sample gained over 100 °C (H.4 test). These results confirm the instability and high reactivity of EDA, which is also described by Clark, Shah, Peterson, Grogan, and Camden (1999)

Table 2
Test data.

UN test								
Test name	Nitrogen content [%]		Deflagration test [C.2]	Koenen test [E.1]	Dutch pressure vessel test [E.2]	Trauzl test [F.3]	“BAM Fallhammer” test [3(a)(ii)]	BAM-Dewar test [H.4]
	Relating to N═N	Total						
DEAD	16.09	16.09	–	Violent F(>9) (∅ 20.0 mm)	–	Not low (33 ml)	4 J	–
DIAD	13.85	13.85	–	Low, F(7) (∅ 1.0 mm)	–	No (8.5 ml)	>40 J	–
Di-*tert*-butyl-AD	12.17	12.17	–	No (<1.0 mm)	–	No (7.0 ml)	>40 J	–
TCEAD	7.36	7.36	–	–	–	Not low (39 ml)	>40 J	–
DEAD 40%_Tol	<6.44	<6.44	No	Low, F(2) (∅ 1.0 mm)	Violent (∅ ≥ 24 mm)	No (5 ml)	>40 J	Stable
DBAD	9.39	9.39	–	No (<2.0 mm)	–	No (8.5 ml)	>40 J	–
Di(4-chlorobenzyl)-AD	7.63	7.63	–	No (<1.0 mm)	–	Low (13 ml)	>40 J	–
ADDP	*11.10*	22.21	–	No (<1.0 mm)	–	No (6.5 ml)	>40 J	–
EDA_15% CH_2Cl_2	<24.55	<24.55	No	Low, F(>9) (∅ 1.0 mm)	Low (∅ 2.0 mm)	Not low (29 ml)	20 J	>100 °C

“–”: not performed (lack of substance); *F*: number of fragments.
BAM-Dewar test: the substance was stored for 7 days at 75 °C.
BAM 50/60 steel tube test: DEAD (result: “no detonation”).

Fig. 1. Koenen test on DEAD at 20.0 mm (fragments > 9).

and Clark et al. (2002). They investigated three different solutions of EDA in toluene, ranging from 11 to 97 wt %. On the basis of the experiments by ARC (accelerating rate calorimetry) and by DSC they ascertained that the heat of decomposition is proportional to the concentration of EDA. Marsanich et al. investigated also EDA in toluene (12, 17, 21 and 30% by weight of EDA), concerning the ‘loss of control’ in chemical systems (Marsanich et al., 2004). In our opinion, based on the results of our experiments, the use of dichloromethane as a diluent for EDA poses a potential safety risk.

Fig. 2. Koenen test on DIAD at 1 mm (fragments > 7).

3.2. Thermal behaviour

Differential scanning calorimetry was used to describe the thermal behaviour of the azodicarboxylates. For each substance, at least two reproducible runs at different heating rates from 0.5 to 40 K/min were recorded. To measure the heats of decomposition effectively, we used closed pressure-tight stainless steel crucibles. Typical sample weights of 2–5 mg were employed. The DSC measurement of DEAD at 5 K/min shows a broad shoulder with three peaks among them (Fig. 3). Until now we have no information about the exact mechanism of the decomposition of this substance. Therefore, the total area was integrated and gave an exothermic decomposition energy of −1466 J/g (Wehrstedt, 2001).

The DSC parameters of the azodicarboxylates at 5 K/min are summarized in Table 3. The measured heat of decomposition appears to be proportional to the total nitrogen content within the group of the azodicarboxylates. In this known behaviour there seems to be no significant difference between the groups of the azodicarboxylates with the aliphatic or aromatic functional groups. As an exception, ADDP with the highest total nitrogen content of about 22% does not show the highest value of the heat of decomposition of these nine examined samples. This leads to following statement that the value of the decomposition energy mainly

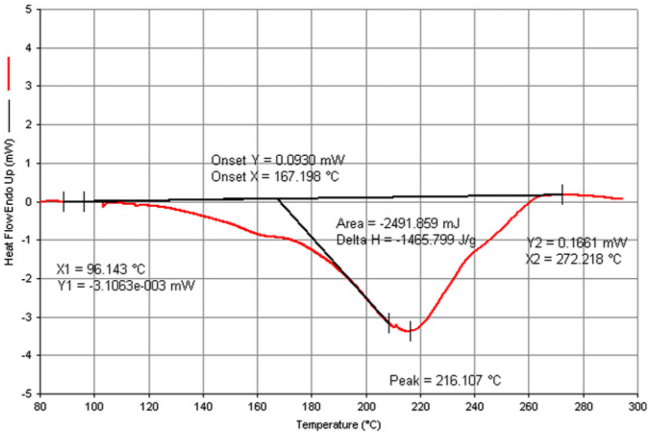


Fig. 3. DSC curve of DEAD, 5 K/min.

Table 3
DSC data.

Heating rate: 5 K/min				
	Total nitrogen content [%]	Heat of decomposition [J/g]	Start of decomposition [°C]	Extrapolated onset temperature [°C]
DEAD	16.09	−1466	96	167
DIAD	13.85	−778	186	212
Di-*tert*-butyl-AD	12.17	−740	113	129
TCEAD	7.36	−456	194	206
DEAD 40%_Tol	<6.44	−355	217	219
DBAD	9.39	−676	169	195
Di(4-chlorobenzyl)-AD	7.63	−545	180	207
ADDP	22.21	−739	151	173
EDA_15% CH_2Cl_2	<24.55	−1762	50	79

Table 4
DSC data.

Heat of decomposition [J/g]						
Heating rate	0.5 K/min	1 K/min	5 K/min	10 K/min	20 K/min	40 K/min
DEAD	–	–	−1466	–	–	–
DIAD	–	−807	−778	−871	−905	−809
Di-*tert*-butyl-AD	−629	−714	−740	−718	−715	−746
TCEAD	–	–	−456	−417	−422	−448
DEAD 40%_Tol	–	−390	−355	−449	−419	−448
DBAD	–	−647	−676	−707	−684	−709
Di-(4-chlorobenzyl)-AD	−446	−436	−545	−544	−491	−483
ADDP	−644	−557	−739	−752	−677	−686
EDA_15%CH_2Cl_2	–	−1963	−1762	−1725	−1631	−1659

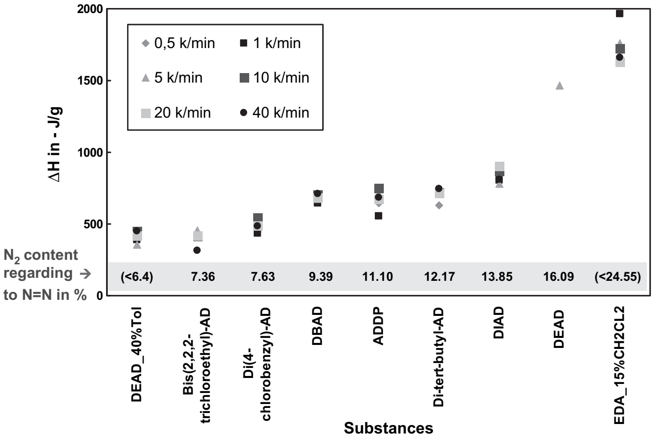


Fig. 4. Dependence of ΔH [−J/g] of different azodicarboxylates on different heating rates.

Table 5
DSC data.

Extrapolated onset [°C]						
Heating rate	0,5 K/min	1 K/min	5 K/min	10 K/min	20 K/min	40 K/min
DEAD	–	–	168	–	–	–
DIAD	–	190	212	224	231	241
Di-*tert*-butyl-AD	124	118	129	142	146	158
TCEAD	–	–	206	214	231	249
DEAD 40%_Tol	–	208	219	234	236	246
DBAD	–	172	195	205	218	240
Di-(4-chlorobenzyl)-AD	176	183	207	214	227	235
ADDP	149	158	173	179	187	197
EDA_15%CH_2Cl_2	–	77	79	127	140	142

depends on the —N═N— bonding fewer than on the presence of single-bonded N groups. Therefore, only the azodicarboxylates of the same structure should be compared to each other to receive a structure–response relationship regarding the thermal behaviour. In the case of DEAD and DEAD 40%_Tol there is also an expected correlation between the heat of decomposition and the onset temperatures vs. the concentration of DEAD in toluene. A higher concentration of DEAD in toluene corresponds to a higher instability of the solution. This behaviour was also found for different concentrations of EDA in toluene (Clark et al., 2002). Their DSC data ranges for the heat of decomposition from 300 to 600 J/g at concentrations of 20 and 40 wt.% EDA, respectively. In comparison to these values, the DSC data for EDA_15% CH_2Cl_2 at the same heating rate are significantly higher (−1762 J/g). Because of its high volatility dichloromethane as a diluent for EDA poses a potential safety risk.

The dependency of the heat of decomposition for the examined substances at six different heating rates is summarized in Table 4 and shown in Fig. 4. The above-mentioned proportional correlation between the heat of decomposition and the nitrogen content regarding to —N═N— is almost independent from the heating rate.

The dependence on the extrapolated onset temperature for the nine samples at six different heating rates is summarized in Table 5 and shown in Fig. 5. It is well known that the extrapolated onset temperature in DSC experiments increases with increasing heating rate. The analysis of the DSC data shows that the onset temperatures range mostly from 150 to 250 °C, except for DEAD, Di-*tert*-butyl-AD and EDA_15% CH_2Cl_2, where the extrapolated onset temperatures are between 80 and 150 °C.

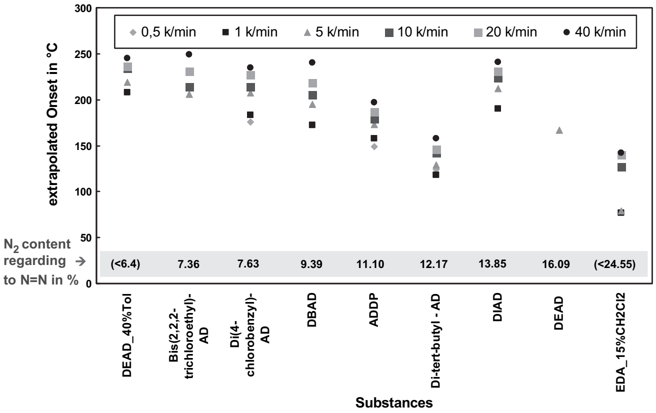


Fig. 5. Dependence of the extrapolated onset temperatures of different azodicarboxylates on different heating rates.

4. Conclusions

Thermal stability tests on various azodicarboxylates and two relatives of them were performed to study their thermal hazards. The samples were examined with DSC at six different heating rates, to determine the heat of decomposition and the onset temperatures. Furthermore, different laboratory test methods, based on the UN Recommendations on the Transport of Dangerous Goods, were applied to determine the explosive properties of the mentioned substances. The intent of this study is to obtain an indication for the structure–response relationship regarding the explosive properties and the thermal behaviour of azodicarboxylates that are used. In long term on the basis of our results combined with the results of further investigations the aim is to assess and predict the thermal behaviour of different types of azodicarboxylates. The test data in this paper show, that the investigated azodicarboxylates with the aliphatic functional groups have a higher explosive potential than the two azodicarboxylates with the aromatic functional groups. Primarily, the reason for this seems to be the already known influence of the total nitrogen content particularly the nitrogen content relating to the $-N{=}N-$ group of each substance. The intense reaction of the examined substances in the Trauzl test was found for TCEAD (Table 2). Although the total nitrogen content of TCEAD was only half of the value of DEAD. This could be caused by the influence of the electron-withdrawing chlorine substituents in TCEAD. Unfortunately, because of the lack of the substance TCEAD only two tests could be performed. For a better assessment of the influence on the chlorine substituents on the thermal stability further experiments have to be done.

The DSC experiments also confirmed the known proportional correlation between the total nitrogen content and the value of the heat of decomposition within the group of azodicarboxylates. The heat of decomposition increases with increasing nitrogen content.

In our opinion, according to information which we received by the DSC data and the test data of the azodicarboxylates, it is important to measure not only the heat of decomposition but also to carry out some significant tests to determine explosive properties. DSC measurements can only provide a first indication of thermal behaviour. But for the assessment of explosive properties and thermal hazards, BAM recommends additional tests on the basis of the UN Manual. Looking at the shown dependency of the hazard of azodicarboxylates on the nitrogen content it can be assumed that the new alternative for the Mitsunobu reaction, DMEAD (nitrogen content: 11.96%), should have thermal behaviour and explosive properties comparable with Di-*tert*-butyl-AD. But to be sure special tests and thermal analytical investigation have to be done to assess the explosive properties and the thermal stability of this substance.

References

Clark, J. D., Shah, A. S., Peterson, J. C., Grogan, F. M., & Camden, S. K. (1999). Application of reaction calorimetry toward understanding the large scale chemistry of ethyl diazoacetate. In *27th North-American-Thermal-Analysis-Society conference*. Savannah, Georgia: Elsevier Science Bv.

Clark, J. D., Shah, A. S., Peterson, J. C., Patelis, L., Kersten, R. J. A., Heemskerk, A. H., et al. (2002). The thermal stability of ethyl diazoacetate. *Thermochimica Acta, 386*(1), 65–72.

Dembinski, R. (2004). Recent advances in the Mitsunobu reaction: modified reagents and the quest for chromatography-free separation. *European Journal of Inorganic Chemistry, 13*, 2763–2772.

Grohmann, M. (2007). *Zweikernige Ruthenium (I, I)- und Rhodium (II, II)-Komplexe als Katalysatoren für Lactam-Synthesen durch intramolekulare carbenoide C–H Insertionen von α-Diazoacetamiden*. Vol. dissertation, Universität Ulms, Ulm.

Hillier, M. C., Desrosiers, J. N., Marcoux, J. F., & Grabowski, E. J. J. (2004). Stereoselective carbon–carbon bond formation via the Mitsunobu displacement of chiral secondary benzylic alcohols. *Organic Letters, 6*(4), 573–576.

Jian-Mei, L., Zhi-Bin, Z., & Min, S. (2009). Lewis acid or Brønsted acid catalyzed reactions of vinylidene cyclopropanes with activated carbon–nitrogen, nitrogen–nitrogen, and iodine–nitrogen double-bond-containing compounds. *Chemistry – A European Journal, 15*(4), 963–971.

Kiankarimi, M., Lowe, R., McCarthy, J. R., & Whitten, J. P. (1999). Diphenyl 2-pyridylphosphine and di-*tert*-butyl azodicarboxylate: convenient reagents for the Mitsunobu reaction. *Tetrahedron Letters, 40*(24), 4497–4500.

Kosower, E. M., & Kanetylondner, H. (1976). Glutathione. 13. Mechanism of thiol oxidation by diazenedicarboxylic acid-derivatives. *Journal of the American Chemical Society, 98*(10), 3001–3007.

Malisch, W., Grün, K., Fried, A., Reich, W., Pfister, H., Hutter, G., Zsolnai, L., et al. (1998). Cycloaddition reactions of molybdenum and tungsten phosphenium complexes with diazoethyl acetate: synthesis and structural characterization of 3-membered and 5-membered phosphametallacycles Phosphenium complexes. 39. *Journal of Organometallic Chemistry, 566*(1–2), 271–276.

Marsanich, K., Barontini, F., Cozzani, V., Creemers, A., & Kersten, R. (2004). Different scale experimental techniques to approach the problem of substances generated in the loss of control of chemical systems: a study on ethyl diazoacetate decomposition. *Journal of Loss Prevention in the Process Industries, 17*(1), 9–22.

Method A.14. (1992). Explosive properties. Annex to Commission Directive 92/69/EEC of 31 July 1992. *Official Journal of the European Communities, 35*, 87–97.

Meyer, R. (1985). *Explosivstoffe*. Weinheim: VCH.

Mitsunobu, O. (1981). The use of diethyl azodicarboxylate and triphenylphosphine in synthesis and transformation of natural products. *Synthesis, 1*, 1–28.

Pelletier, J. C., & Kincaid, S. (2000). Mitsunobu reaction modifications allowing product isolation without chromatography: application to a small parallel library. *Tetrahedron Letters, 41*(6), 797–800.

Sigma–Aldrich, from http://www.sigma-aldrich.com.

Sikder, A. K., Maddala, G., Agrawal, J. P., & Singh, H. (2001). Important aspects of behaviour of organic energetic compounds: a review. *Journal of Hazardous Materials, 84*(1), 1–26.

Sugimura, T., & Hagiya, K. (2008). DMEAD – a separation-friendly reagent for the Mitsunobu reaction. *SYNFORM*.

Uemura, T., & Chatani, N. (2005). Copper salt catalyzed addition of arylboronic acids to azodicarboxylates. *Journal of Organic Chemistry, 70*(21), 8631–8634.

UN recommendations on the transport of dangerous goods, manual of tests and criteria. (2003). New York and Geneva: United Nations.

Urben, P. G. (Ed.). (1999). *Bretherick's handbook of reactive chemical hazards*. Oxford: Butterworth-Heinemann.

Vijay, N., Smitha, C. M., Akkattu, T. B., & Eringathodi, S. A. (2007). Novel reaction of the "Huisgen zwitterion" with chalcones and dienones: an efficient strategy for the synthesis of pyrazoline and pyrazolopyridazine derivatives. *Angewandte Chemie International Edition, 46*(12), 2070–2073.

Wehrstedt, K.-D. (2001). Diethylazodicarboxylate, 35% in toluene, and technically pure. In *IGUS EOS meeting*. Washington.

Wehrstedt, K. D., Wandrey, P. A., & Heitkamp, D. (2005). Explosive properties of 1-hydroxybenzotriazoles. *Journal of Hazardous Materials, 126*(1–3), 1–7.