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Thermal Stability of Amine Compounds and Dichloromethane

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Dichloromethane is employed as a common solvent in the chemical industry. Due to its low boiling point of 39.7 °C it can be used for the extraction of amine compounds. However, caution is advised while handling and storing amine compounds diluted in dichloromethane, since there were incidents with unexpected reactions between amine compounds and dichloromethane in the past (Bretherick's Handbook of Reactive Chemical Hazards, 2007). For instance, an exothermic reaction occurred during a distillation at 30 °C of a mixture of ethylene diamine and dichloromethane, which subsequently deflagrated (Nolan, 1983). In a later study, the decomposition energy was determined as ΔH_R = -343 kJ/mol (4.04 kJ/g) based on the amount of dichloromethane (Heskey, 1986). Further incidents in the near past are also known among experts, including the reaction of complex molecules with amine functional groups with dichloromethane are also known among experts (Neuenfeld, 2008).

Figure 1: Blown up waste drum with dichloromethane, morpholine, methanol as main components. (Neuenfeld, 2008)

This shows that there is largely unknown potential risk, which requires a more detailed investigation. Therefore the reaction between different amine compounds and dichloromethane was investigated, in order to determine the thermal stability and the reactivity of the amine compounds toward dichloromethane. The thermal stability was investigated by DSC (differential scanning calorimetry). For this purpose, different amine compounds and different molar percentages of amine and dichloromethane were selected. The amine compounds in this study were divided in two categories: aliphatic amines, which also include cyclic amines, and aliphatic-aromatic amines. Two main variables were first compared, the onset of the effect and its decomposition energy.
The investigations show that for aliphatic-aromatic amines, the decomposition energy decreases with the molecular weight of the compound. Cyclic amines show the highest decomposition energy, which is also related with the lowest onset temperature. The results show significant decomposition reactions in ranges of the boiling of dichloromethane. Such reactions were further investigated using different adiabatic calorimetric techniques such as VSP2 (Vent Sizing Package) and Dewar calorimetry.

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1. Thermal Stability via DSC (Differential Scanning Calorimetry)

The reaction between amine compounds and dichloromethane was investigated, in order to determine the thermal stability and the reactivity of the amine compounds toward dichloromethane. The thermal stability was first investigated by DSC (differential scanning calorimetry). For this purpose, a small amount (about 10 mg) of sample was weighed into a crucible. The sample was measured against a crucible of same material filled with aluminium oxide as reference. The crucibles were then placed in the equipment DSC-1 Star DSC of Mettler-Toledo and heated at a rate of 3 K/min to record the thermal trace of the mixture.

Different amine compounds and different molar percentages of amine and dichloromethane were selected. The amine compounds in this study were divided in two categories: aliphatic amines and aliphatic-aromatic amines. Two main variables were first compared, the onset of the effect and its decomposition energy. For comparison of the results the molar percentages are plotted against the decomposition energy for both categories in Figures 2 and 3.

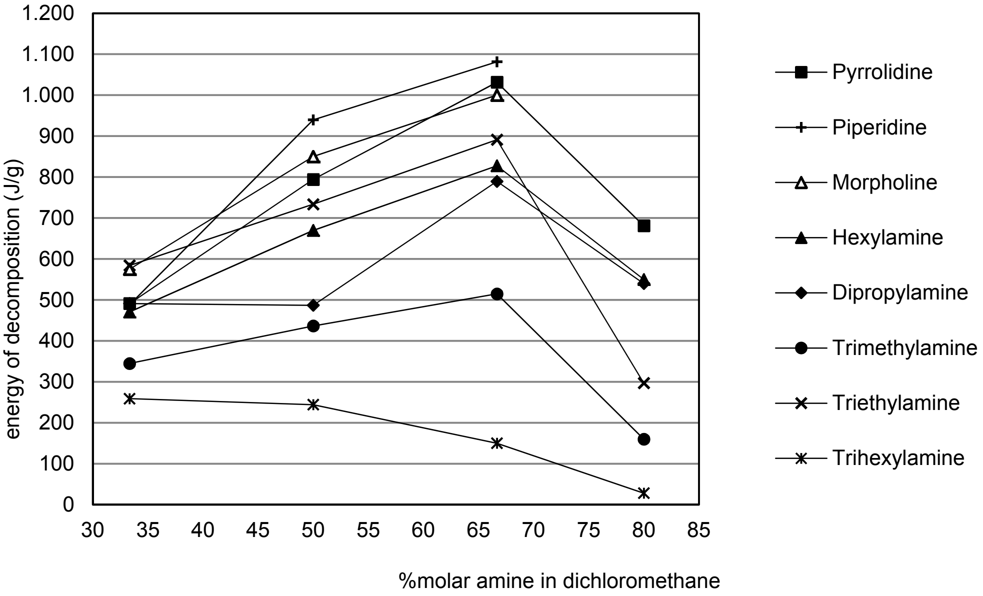

Figure 2: Molar percentages of aliphatic amines in dichloromethane vs energy of the decomposition

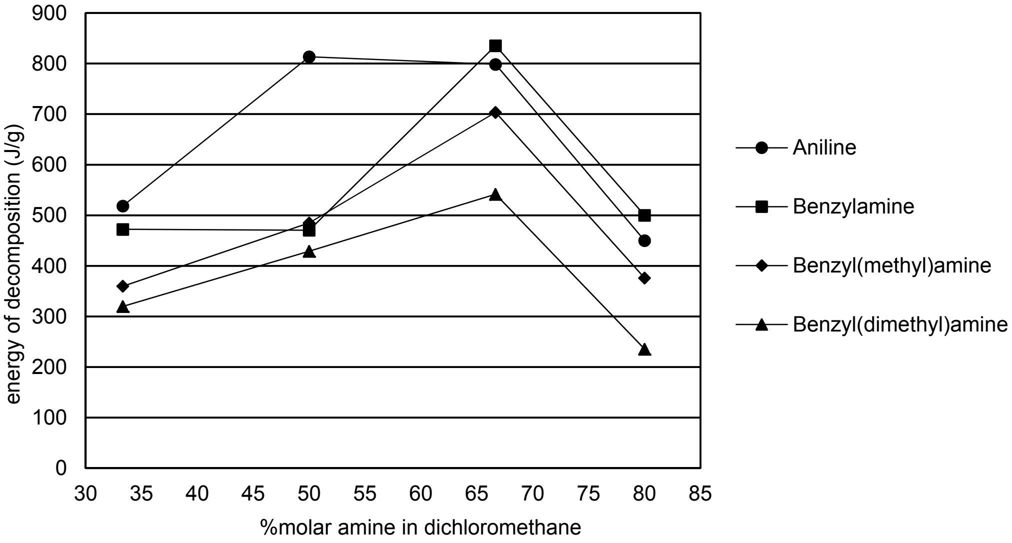

Figure 3: Molar percentages of aliphatic-aromatic amines in dichloromethane vs energy of the decomposition

In addition, all amine compounds and dichloromethane were investigated separately. The raw materials showed no significant thermal effects in the DSC measurements. Due to this result, it can be stated that the observed exothermic effects of the mixtures can be assigned to the reaction between the amine compounds and dichloromethane.

The results show a maximum regarding the decomposition energy for a mixture of amine/dichloromethane with a ratio of 2:1. This statement applies to all cases except for trihexylamine. This compound shows a very low decomposition energy reaching a value of approx. 100 J/g for a 2:1 mixture, which cannot be considered to have any significance. The decomposition energy and onset temperature of the obtained results for a mixture of amine/dichloromethane with a ratio of 2:1 are compared and listed in Table 1 and 2.

Table 1: Energy and onset temperature of the decomposition for aliphatic amines in dichloromethane with ratios of 2:1

Type	Compound	Molecular weight (g/mol)	Energy of decomposition (J/g)	T_{onset} (°C)
Secondary (cyclic)	Pyrrolidine	71.12	1030	40
	Piperidine	85.15	1080	40
	Morpholine	87.10	1000	50
Primary	Hexylamine	101.19	830	110
Secondary	Dipropylamine	101.19	790	130
Tertiary	Trimethylamine	59.11	520	210
	Triethylamine	101.19	890	180
	Trihexylamine	269.51	150	210

Comparing the aliphatic amines, the cyclic amines show the highest decomposition energy, which is also related to the lowest onset temperature. For the non-cyclic aliphatic amines, the decomposition energy decreases with the substitution pattern (primary>secondary>tertiary). The onset temperature of the effect decreases with an increasing decomposition energy.

Table 2: Energy and onset temperature of the decomposition of aliphatic-aromatic amines in dichloromethane with ratios of 2:1

Type	Compound	Molecular weight (g/mol)	Energy of decomposition (J/g)	T_{onset} (°C)
Primary	Aniline	93.13	800	130
	Benzylamine	107.15	840	100
Secondary	Benzyl(methyl)amine	121.18	700	80
Tertiary	Benzyl(dimethyl)amine	135.21	540	130

For the aliphatic-aromatic amines, it can be observed that the energy of the exothermic effect decreases with the molecular weight of the compound and also decreases with the substitution pattern.

The decomposition of morpholine in dichloromethane was further investigated by S. Neuenfeld in 2008. Figure 4 shows an FTIR analysis of the starting materials and the reaction product, showing that variety of products is formed during the decomposition.

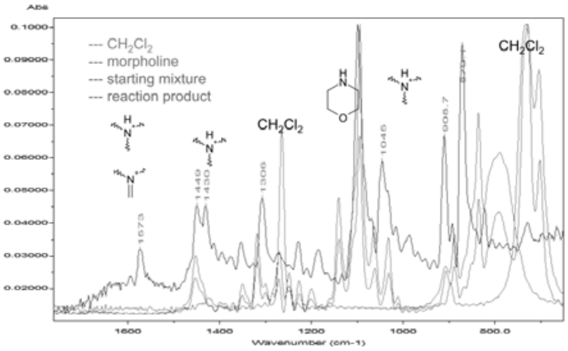

Figure 4: FTIR analysis of the starting materials and reaction product of morphopline in dichloromethane (Neuenfeld, 2008)

This leads to the assumption of a multiple reaction system. An example of possible reaction mechanisms is shown in Figure 5 (Neuenfeld, 2008), which are followed by further decomposition steps.

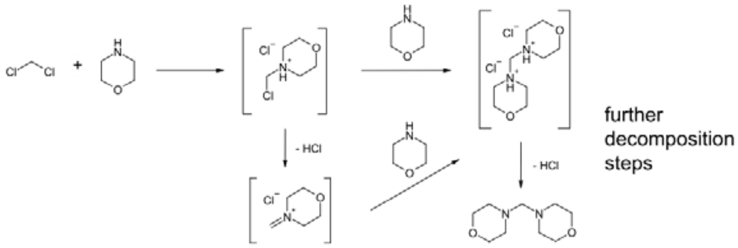

Figure 5: Possible reaction mechanisms for the reaction of morpholine and dichloromethane (Neuenfeld, 2008)

2. Adiabatic Calorimetry

On the basis of the results of the DSC measurements, two different amine compounds were investigated using two different adiabatic calorimetry techniques: Dewar calorimetry and VSP2 (Vent Sizing Package).

2.1. Dewar Calorimetry of Dipropylamine and Dichloromethane

For the investigation of the reactivity of dipropylamine toward dichloromethane (ratio 2:1) the investigation was performed by using Dewar calorimetry. For this purpose, about 95 g of the mixture were filled into a Dewar vessel, which was placed in a high pressure autoclave with a volume of 0.75 L. This autoclave was closed and put into an aluminium oven. The sample was heated up to storage temperature of 55 °C. Since no significant exothermic effect was observed within 24 h, the temperature was increased stepwise until a runaway reaction could be detected. During the run away reaction, the temperature of the aluminium oven was adjusted to the temperature of the sample. The course of the temperature and pressure were recorded during the whole test.

Figure 6 shows the course of the temperature and pressure during the test. An exothermic reaction was detected starting at a temperature of about 70 °C. The reaction reaches a maximum temperature of 216 °C after 170 hours.

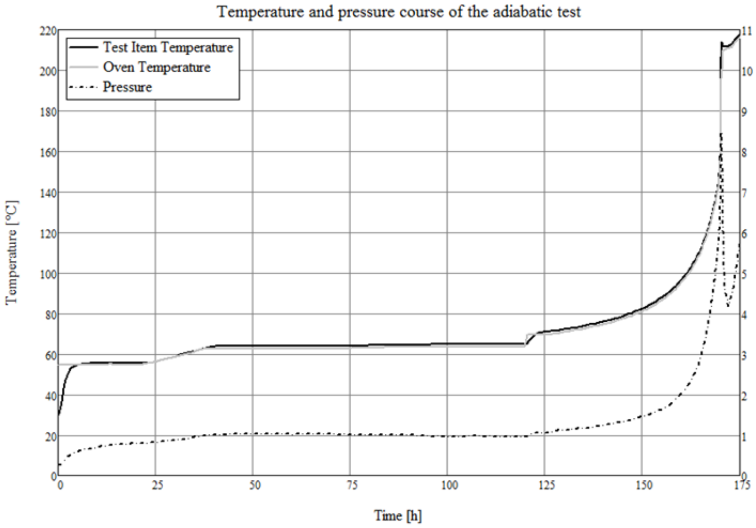

Figure 6: Temperature and pressure course of dipropylamine and dichloromethane (ratio 2:1)

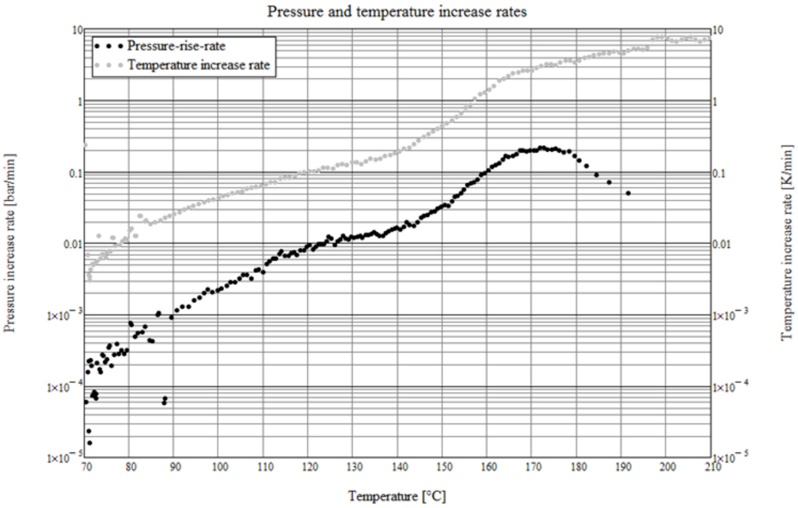

Figure 7: Temperature and pressure increase rate of dipropylamine and dichloromethane (ratio 2:1)

The pressure increase the pressure increase rate shown in Figure 7 can be derived from the first derivative of the time resolved course of t. This rate includes the pressure increase caused by other effects, like vapour pressure increase and thermal expansion of the liquid. The maximum pressure increase rate of the mixture of about 0.2 bar/min was observed in the temperature range from 165 to 180 °C. From the course of the temperature trace, the temperature increase rate can be derived, which is also shown in Figure 4. The temperature rise rate reaches its maximum of 8 K/min at temperature of about 210 °C.

2.2. Adiabatic Test with the VSP2 with Piperidine and Dichloromethane

For the investigation of the reactivity of piperidine toward dichloromethane (ratio 2:1), the investigation was performed using the adiabatic calorimeter VSP2 (Fauske & Associates, LLC). For this purpose, about 35 g of the mixture were filled into a thin walled steel test cell with a volume of 110 mL. The test cell was placed into a heater assembly, which was installed into 4 L pressure vessel. The pressure vessel was closed and the test was started at ambient temperature. A slow exothermic reaction was detected at ambient temperature and the sample temperature was followed by the heater of the VSP2. The temperature increase led to a runaway reaction within a time period of about 210 min. To avoid a bursting of the test cell due to pressure increase inside the test cell, the pressure inside the 4 L pressure vessel was adjusted slightly below the pressure of the test cell. The course of the temperature and pressure were recorded during the whole test.

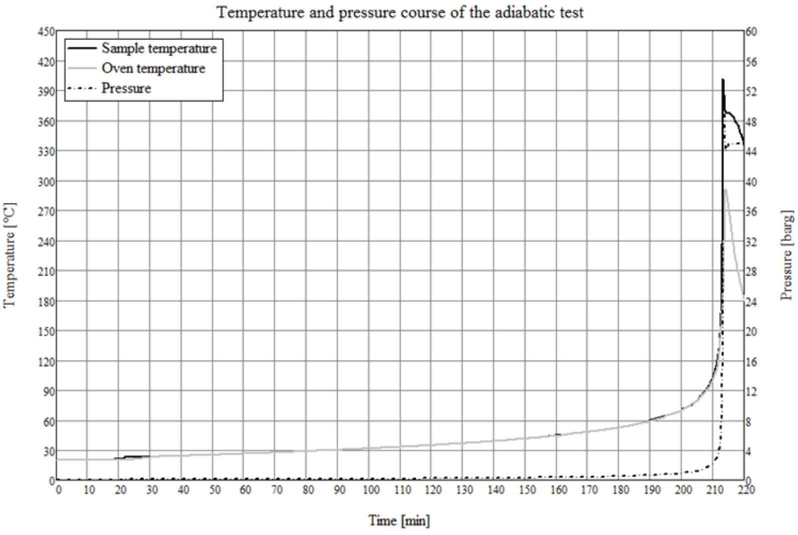

Figure 8: Temperature and pressure course of piperidine and dichloromethane (ratio 2:1)

Figure 8 shows the course of the temperature and pressure during the test. The reaction starts at ambient temperature reaching a maximum reaction temperature of 400 °C after a time period of 213 min. A maximum pressure of 53 bar_g was detected at this point. Using a thermal inertia of φ=1.3 and the observed temperature increase of 374 K (temperature increase from 27 °C to 401 °C) an adiabatic temperature rise of ΔT_{ad} = 490 K was observed.

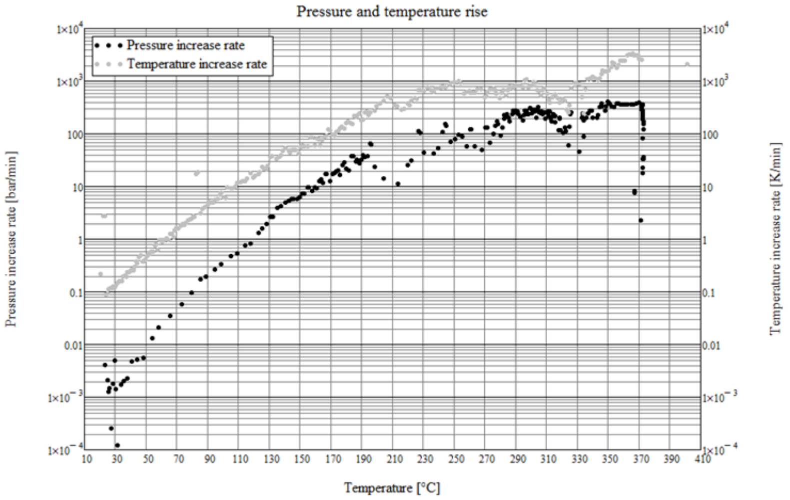

Figure 9: Temperature and pressure increase rate of piperidine and dichloromethane (ratio 2:1)

The pressure increase rate shown in Figure 9 can be derived from the first derivative of the time resolved course of the pressure increase. This rate includes the pressure increase caused by other effects, like vapour pressure increase and thermal expansion of the liquid. The maximum pressure increase rate of the mixture of about 400 bar/min was observed in the temperature range from 350 to 370 °C. From the course of the temperature trace, the temperature increase rate can be derived. The maximum temperature increase rate was found to be 3300 K/min observed at a temperature of approx. 365 °C.
After the test and cooling down to approx. 20 °C, the residual pressure in the autoclave was about 14,5 bar_g, which is caused by the formation of a permanent, gaseous compound.

3. Conclusions

The investigations via DSC and other adiabatic calorimetric techniques of the reaction behaviour of different amine compounds with dichloromethane show a great reaction potential for some mixtures. For aliphatic-aromatic amines, the decomposition energy decreases with the molecular weight of the compound. Cyclic amines show the highest decomposition energy, which is also accompanied by the lowest onset temperatures. In addition, it was proven that the reactivity decreases with the number of substitutions of the amine compounds. In the adiabatic tests, a hazardous reaction behaviour in regards of the onset temperatures and the temperature / pressure rise rates was observed. This should be considered while handling and storing amine compounds diluted in dichloromethane in closed systems. There is a great risk of over-pressurization due to the high vapour pressure caused by exceeding the boiling point of dichloromethane and the formation of permanent gas during the decomposition, as seen in the blown up waste drum filled with dichloromethane and morpholine (Neuenfeld, 2008).

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