Journal of Thermal Analysis, Vol. 49 (1997) 1635-1645

ASSESSING THERMAL HAZARDS OF REACTION MIXTURES

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Abstract

A strategy for assessing thermal hazards of chemical manufacturing processes is presented with an emphasis on new developments in the areas of the desired and decomposition reaction research. In the case of the desired reaction, the application of a computer program, CAMEO, for assessing synthetic reaction pathways, and enthalpies, and for evaluating the chemistry of specific failure modes is demonstrated. For the decomposition reaction, an unexpected decomposition destabilization phenomenon in mixtures was observed, which clearly demonstrated the need for chemical/solvent mixture testing to provide reliable thermochemical data for reaction hazard assessment. An application of the reaction mixture hazard evaluation strategy to a chemical process is presented.

Keywords: decomposition, desired reaction, strategy, destabilization

Introduction

When evaluating the hazards of a chemical manufacturing process, all possible exothermic reactions that can occur under both normal and upset conditions should be assessed. These reactions usually include the desired synthetic reaction (if exothermic), any side reactions that can occur, and the undesired decomposition reactions of all thermally unstable reaction mixture components. A hazardous runaway event can develop when an uncontrolled temperature rise from the desired reaction triggers hazardous decomposition reactions, which are accompanied by explosive heat and gas evolution. Careful investigation of the thermochemical properties of the desired and decomposition reactions combined with a thermal hazard evaluation strategy, which considers the worst credible and other credible scenarios, is vital for developing safe processes [1–2].

This paper will concentrate on our recent developments in several areas of hazard evaluation: the desired reaction and possible unintended variations, the decomposition reactions and the changes of decomposition behaviour in mixtures, as well as a strategy for assessing the thermal hazards of reaction mixtures.

Experimental

The TA Instruments Model 2910 Differential Scanning Calorimeter (DSC) was used to conduct the DSC experiments on neat chemicals and mixtures. Mixtures

0368–4466/97/ $ 5.00

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were prepared by inserting specified amounts of a chemical and a solvent in a glass capillary [3], after which the capillary was centrifuged and sealed under nitrogen. The overall sample mass for mixtures as well as for the neat materials was approximately 1 mg. A heating rate of 10°C min^{-1} was employed throughout the experiments. The instrument was calibrated using a dedicated 1 mg indium standard in a glass capillary. The cell constant, onset slope and temperature correction factors are automatically updated by the TA2200 DSC computer. The repeatability of the decomposition energy measured was estimated using data from 21 experiments. The calculated standard deviation was 7.3%. Two measurements would be considered suspects it they differed by more than 20.6%.

Results and discussion

Evaluating the desired reaction

The first step in evaluating the hazards that can arise from a synthetic reaction is estimating its energy potential. The best approach to obtaining the heat of a desired reaction is actual experimental measurements using reaction calorimetry. When, because of time or cost constraints, the experimental determination of reaction heat is not practical, calculation methods for estimating reaction enthalpies from the standard gas phase heats of formation of reactants and products can be applied [4]. The standard gas phase heats of formation can be either found in the literature or, when experimental data is not available, calculated using either a basic bond energy method or Benson group method [4]. Computer programs such as CAMEO (bond energy method) or CHETAH (Benson group) can be used to carry out the calculations. Besides providing the heat of reaction when the reaction products are identified, CAMEO can also predict, using mechanistic logic, primary and

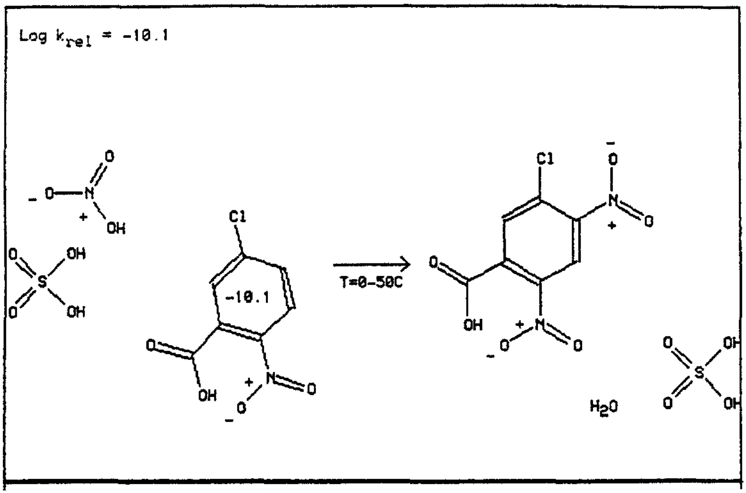


Fig. 1 Simulation of a nitration reaction using CAMEO

secondary reaction pathways given the starting materials and conditions [5]. This is illustrated in Fig. 1 where CAMEO predicted the reaction products and the estimated heat of nitration in a mixture of nitric and sulfuric acids.

An important failure scenario that might be overlooked during process development is the introduction of an incorrect chemical or amount of a chemical into the reaction media or a failure to introduce a necessary component (reactant, catalyst, etc.) into the mixture. Assessment of all possible mischarges experimentally is generally too time consuming. CAMEO can be used as a screening tool for evaluating reactivity and energy potential in these situations.

Evaluating the decomposition reaction

The decomposition hazards of a reaction mixture can be characterized by observing decomposition of individual chemical species during a standardized test, such as DSC. Historically, this information on neat chemical decomposition was generally considered sufficient, or even conservative, for reaction mixture hazard evaluation, because diluting a chemical with solvent was assumed to reduce the heat evolved per unit mass of mixture and the heat generation rate. More recently, emphasis has been placed on the necessity of also studying the decomposition of chemicals in the solvent mixtures present during processing [6]. This approach recognizes the possibility that the decomposition of a chemical can be altered in a mixture.

Significant activation of decomposition of nitrobenzene derivatives in mixtures with various solvents, resulting in lower decomposition onset temperatures (T_0) and/or increased rates of energy release has been documented [6]. The influence of the solvent type and concentration on the decomposition behaviour of several nitrobenzenes can be observed in the attached DSC overlay plots (Figs 2–6). The curves clearly show the decreased stability of the chemicals in solvents and the significant

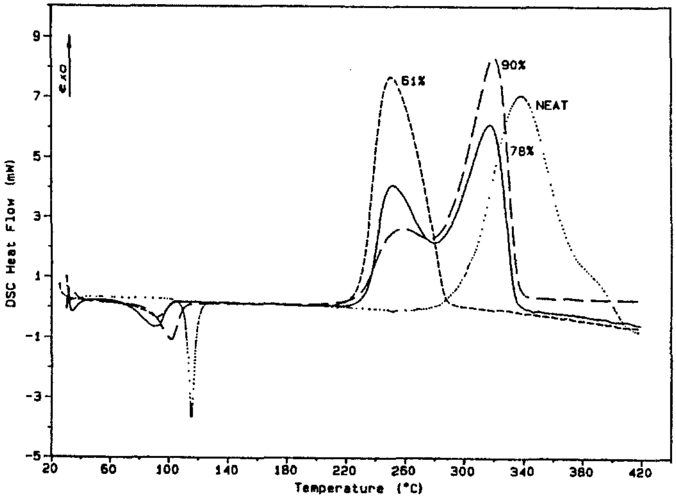


Fig. 2 DSC curves of *p*-nitrophenol, neat and in mixtures with methanesulfonic acid

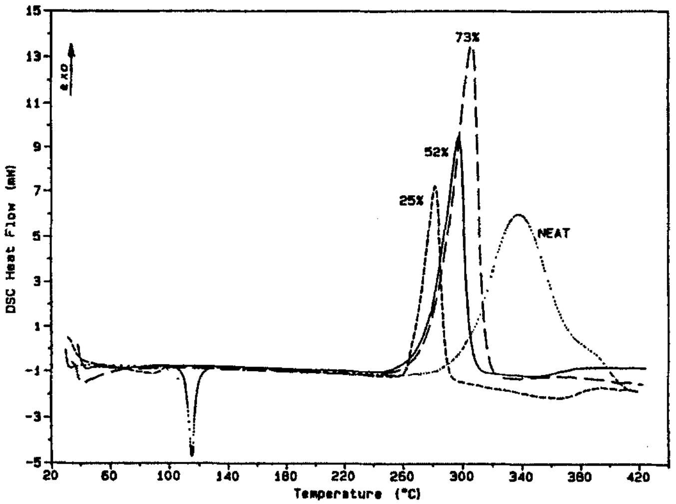


Fig. 3 DSC curves of *p*-nitrophenol, neat and in mixtures with 5% solution of sodium hydroxide

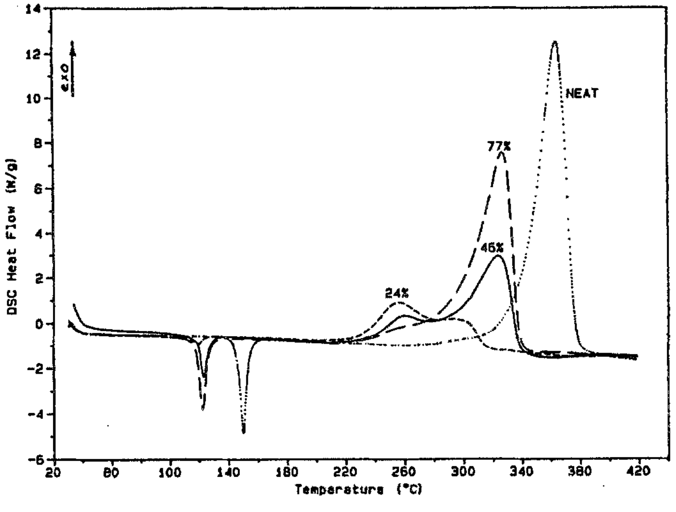


Fig. 4 DSC curves of *p*-nitroaniline, neat and in mixtures with 5% solution of hydrochloric acid

effect of the mixture concentrations on stability. For example, analyzing the behaviour of *p*-nitrophenol in a strongly acidic solvent at different concentrations (Fig. 2), it is apparent that at a small concentration of the solvent (90% *p*-nitrophenol) a new exothermic peak appears beginning at about 200°C (compared with 270°C for the neat chemical). With rising solvent concentration, the new peak increases while the original peak becomes smaller and moves to lower temperature.

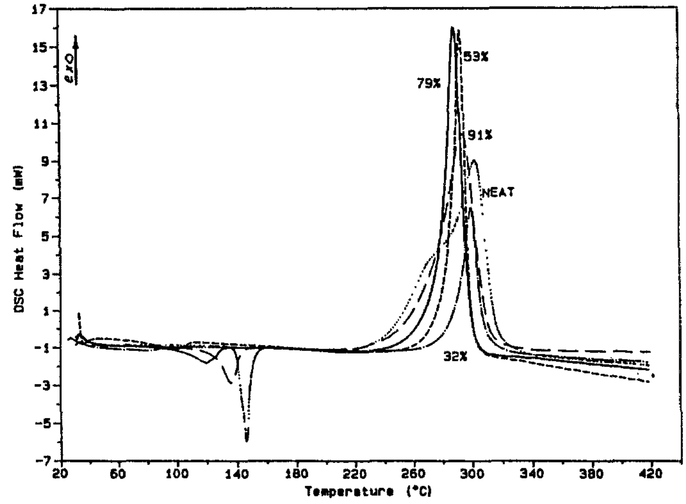


Fig. 5 DSC curves of 4-hydroxy-3-nitrobenzaldehyde, neat and in mixtures with acetone

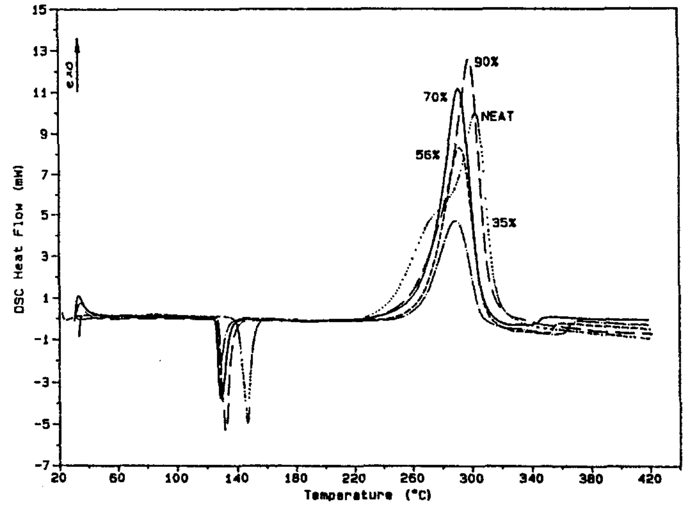


Fig. 6 DSC curves of 4-hydroxy-3-nitrobenzaldehyde, neat and in mixtures with water

When the solvent concentration reaches about 40% (61% *p*-nitrophenol), the original decomposition peak of the neat material disappears completely.

Table 1, columns 3 and 4, provides a comparison of the energy evolved by each of several neat chemicals to that of their respective mixtures after correction for concentration. It can be seen that the total energy release per gram of decomposing species remained about the same regardless of concentration. The standard deviations of the energies measured varied between 2 and 8% for all chemicals, which can be attributed to the experimental error of the test presented above.

Table 1 Decomposition energies in mixtures

Mixture	Conc./%	Energy				
		mixture/ J g^{-1}	decomposing species/J g^{-1}	average	standard deviation	standard deviation/%
p-Nitrophenol	100	2420	2420	2531	134	5.28
in CH_3SO_3H	90	2142	2380			
	78	2052	2631			
	61	1643	2693			
p-Nitrophenol	100	2420	2420	2484	136	5.48
in 5% NaOH	73	1784	2444			
	52	1227	2360			
	25	678.5	2714			
p-Nitroaniline	100	2232	2232	2442	204	8.37
in 5% HCl	79	1773	2244			
	46	1225	2663			
	24	631	2629			
4-Hydroxy-	100	2158	2158	2265	52	2.28
3-nitro-	91	2113	2322			
benzaldehyde	79	1804	2284			
in CH_3COCH_3	69	1557	2257			
	53	1213	2289			
	32	730	2281			
4-Hydroxy-	100	2158	2158	2356	104	4.39
3-nitro-	90	2190	2433			
benzaldehyde	70	1676	2394			
in H_2O	56	1366	2439			
	35	824	2354			

For the *p*-nitrophenol in acid, one explanation for the shifting energy levels and curve shapes is the formation of an intermediate or a complex between the chemical and the solvent that is more prone to decomposition than the original chemical. At low solvent concentrations, when there is not enough solvent to form the intermediate/complex with the entire amount of the chemical, two peaks appear on the DSC curve; the first one representing the decomposition of the complex, the second one – decomposition of the residual chemical. When the amount of solvent added is sufficient to form a complex with the entire amount of the chemical, only decomposition of the complex can be observed. If we analyze the behaviour of the same chemical in a strongly basic solvent (Fig. 3), a different phenomenon is observed.

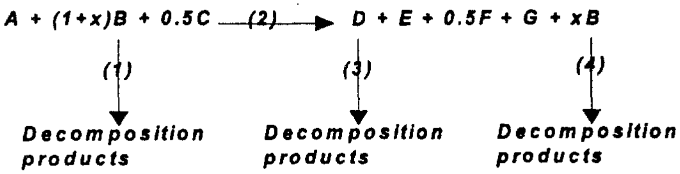
The entire decomposition peak is shifted to lower temperatures with a significant increase in the rate of heat evolution. In this case the nature of the destabilization effect is apparently different, but the practical outcome is the same – increased thermal hazards in the mixture. When acetone and water are used as solvents (Figs 5–6), even though the decomposition onset temperatures do not change significantly, there is a significant increase in the rate of heat evolution by the mixtures (the peak height) compared to that of the neat chemical. This will have a dramatic impact on the safety of the process, especially considering that the presence of a solvent would usually tend to decrease the rate of heat evolution. It is critical that the phenomenon is discovered and taking into account when safety recommendations are developed.

Overall, the presented experimental results clearly show the dramatic and sometimes unexpected change in decomposition of a chemical when mixed with a solvent. These results identify the limitations of defining the decomposition hazards of synthetic chemical reactions using only neat chemical test data.

Strategy for assessing thermal hazards of reaction mixtures and its application

The strategy for assessing thermal hazards of reaction mixtures formed at different stages of a chemical manufacturing process is summarized in Fig. 7. The information about the desired reaction (using CAMEO), the decomposition of neat chemicals, as well as chemicals in solvents and in process reaction mixtures, combined with the process and equipment information, and a failure mode assumption is input into a calculation program. The calculation results enable the evaluation of the thermal hazards and recommendations for process safety. Application of this strategy to a specific process is described below. The results of the analysis are summarized in Table 2.

The following scheme represents the reactions that can occur in the reaction mixture. The reactant B, which is in excess during the synthesis, also functions as a solvent for the mixture. No additional solvents were used.



The heat of the desired reaction was evaluated using CAMEO.

The thermal stability of the neat chemical was tested using DSC. Only two components, reactant B and product D, appeared to be thermally unstable and showed exothermic activity during DSC experiments (Fig. 8). Testing of the thermally unstable components in a solvent was not applicable because no solvent was used during the synthetic reaction. Instead, the entire reaction mixture containing all three reactants was tested in the DSC apparatus. The DSC curves of the neat chemicals and the reaction mixture are overlaid in Fig. 8. The low temperature (100–200°C)

Table 2 Thermal hazard analysis of a synthetic chemical reaction

Components	Mol. weight	Energy		Reaction mixture composition			Energy mixture/ J g^{-1}	Energy release in competing reactions/J g^{-1}		T_{ab}/°C assumes c=2	T_{max}/°C	T_0/°C
		exp./ J g^{-1}	calc./ kJ mol^{-1}	mass/ g	mass/ %	moles		reaction (1)	reaction (2)(3)(4)			
Reactants:												
A	114			0.75	44.12	0.0066						
B	50	2776		0.50	29.41	0.0100	816	816	0	408		206
C	138			0.45	26.47	0.0033						
Solvent:												
Catalyst:												
Products:												
D	109	947		0.72	42.36	0.0066	401	0	401	200		280
E	76			0.50	29.31	0.0066						
F	62			0.20	12.04	0.0033						
G	18			0.12	6.99	0.0066						
B	50	2776		0.17	10.00	0.0034	278	0	278	139		206
Reactions:(2)			143			0.0066	555	0	555	278	378	T_p=100
What if reaction mixture		2134						816	1234			

T_{ab} – adiabatic temperature rise, °C; T_p – process temperature, °C; c – heat capacity of the reaction mixture, J g^{-1} °C^{-1}.
T_{max} – maximum temperature that can be reached by the synthetic reaction if adiabatic conditions occur; $T_{max}=T_p+T_{ab}$, °C.

exothermic activity in the mixture is attributed to the heat of the desired reaction. The shift of the entire DSC curve of the mixture to lower temperatures, in comparison with the decomposition curves of the neat chemicals, again demonstrates the decomposition destabilization phenomenon in mixtures.

The overall amount of energy that can be released in the mixture as a result of the competing pathways (1 or 2+3+4) was calculated and can be found in Table 2. The maximum energy release of the reaction mixture as calculated from neat chemical DSC results was 1234 J g^{-1}. This was significantly lower than that of the

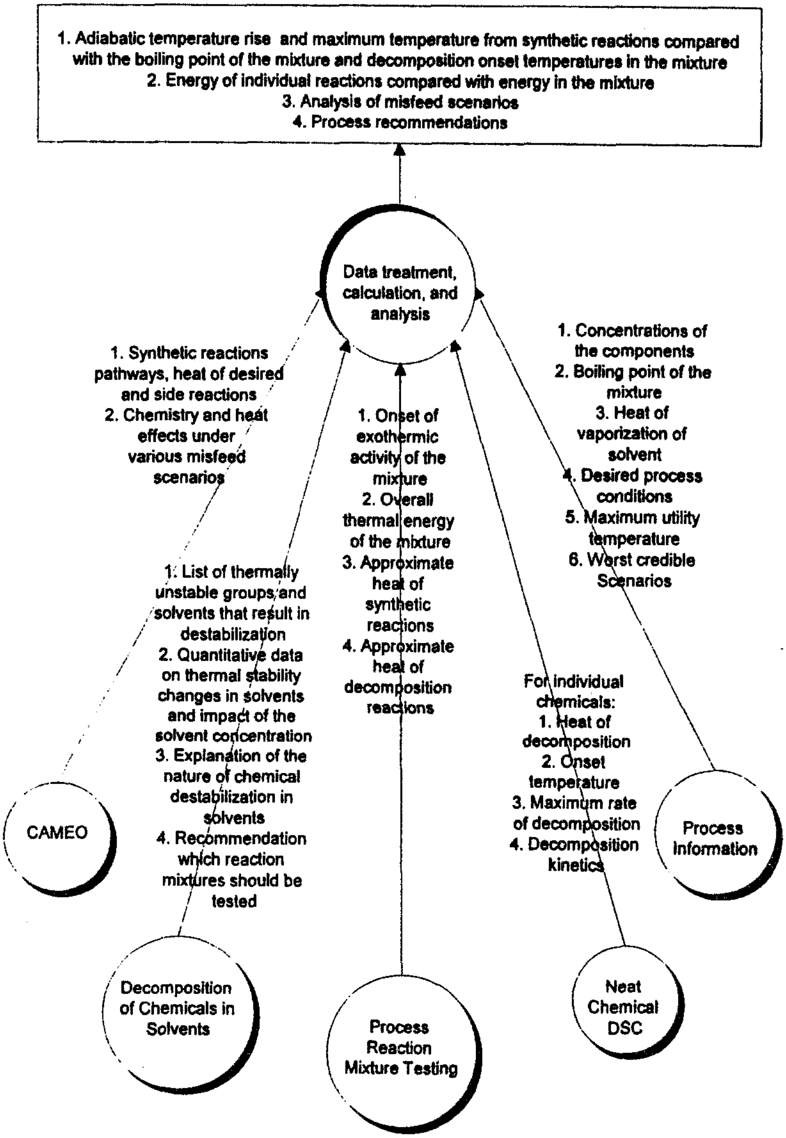


Fig. 7 Strategy for assessing thermal hazards of reaction mixtures

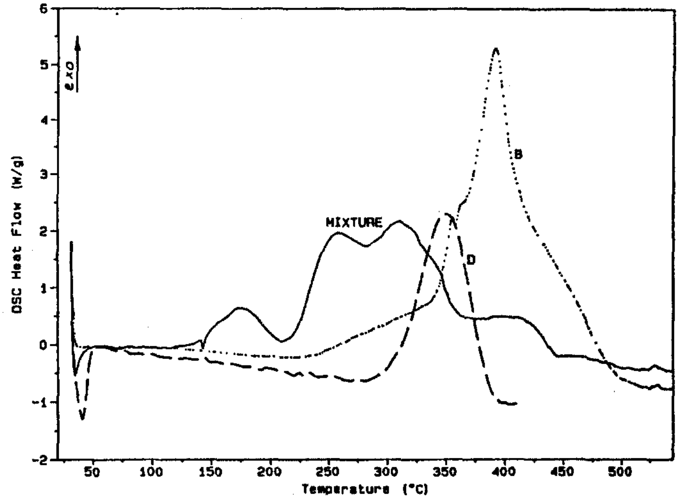


Fig. 8 DSC curves of reactant B, product D, and reaction mixture for the process under assessment

reaction mixture as measured by DSC, which indicates that other exothermic side reactions must have occurred in the reaction mixture. The calculated maximum temperature that can be reached by the synthetic reaction if adiabatic conditions occur (T_{max}) was significantly higher than the onset temperatures of the decomposition reactions (Table 2). This indicates that if insufficient heat removal occurs during the desired reaction (a failure scenario), the potential exists for a thermal runaway.

Conclusion

A program for process hazard assessment of chemical manufacturing processes can have different levels of sophistication and complexity. At one end of the spectrum is complete characterization of the kinetics and thermodynamics of the chemistry coupled with full analysis of the normal process and anticipated potential maloperations. The trade off is the increased time and cost for this type of analysis *vs.* the incremental value provided to the safety analysis. The use of modelling techniques such as CAMEO, and of analytical tools such as that presented in Table 2 can enhance the development of a safe process with minimum additional cost. The evaluation of the decomposition hazards of process mixtures in addition to those of the individual chemicals is a necessary element of the hazard assessment program.

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The authors would like to thank P. R. Kingsley for carrying out the experimental work necessary to complete this project. The authors also wish to acknowledge the support of Eastman Kodak Company in the preparation of this study.

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