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Exothermic secondary reactions

Th. Grewer[a], R.L. Rogers[b,*]

[a] *Hoechst AG, 65926 Frankfurt am Main, Germany*
[b] *ZENECA Fine Chemicals Manufacturing Organization, Blackley, Manchester, UK*

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Abstract

Exothermic secondary reactions are often more dangerous than primary reactions because of their relatively high reaction energy. Their hazard can be estimated by comparing the temperature of the process with that at which a secondary reaction occurs on the process scale and by considering the adiabatic temperature increase of both reactions.

The decomposition of reaction components and products are secondary reactions which frequently occur. It is important to recognize that the decomposition in a reaction mixture is often considerably faster than for the pure substance. The effect of solvents or reaction components on thermal stability is discussed. Some substances, for example sulfuric acid, have a large accelerating effect on the decomposition of nitro compounds if they are present in high concentrations. Metals or their salts are catalytically effective in small concentrations of fractions of a percent.

Typical combinations of primary and secondary reactions which often occur are discussed. For every nitration reaction or other reaction of a nitro compound, the decomposition of the nitro compound occurs as a secondary reaction. The reactions of reaction components with one another or with the solvent are further secondary reactions. Some examples of this very extensive type of secondary reactions are discussed.

1. INTRODUCTION

Chemical reactions which are hazardous in production processes can be classified into two classes.

1. The reaction which is the main purpose of the process. This is the reaction that will produce the reaction product for which a plant has been constructed. This reaction is called the "desired reaction" or "primary reaction."

2. Reactions which can occur parallel or successive to the primary reaction but which are not a part of the production process. We call these reactions "secondary reactions". We use the plural form of the word because often more than one secondary reactions are possible in a reactive

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* Corresponding author.

system. Reaction systems are known which contain 4 or 5 possible secondary reactions. We are here interested in secondary reactions only if they are exothermic.

At first sight primary and secondary reactions seem to behave very similarly. Both can — if they are sufficiently exothermic — develop a thermal explosion. The investigation methods applied are also similar, and some methods can be applied to primary reactions as well as to secondary ones.

There are, however, large differences between the two types of reactions. The stability of primary reactions depends on the design of the process which may be continuous or discontinuous. Most reactions in chemical industry are discontinuous reactions. The semi-batch process is a reaction type which occurs very often. If the reaction is not fast enough, an accumulation of reactants is possible which generates the hazard of a thermal explosion.

The thermal explosion which starts if a primary reaction comes out of control is called a "runaway reaction" (in German: durchgehende Reaktion). The simplest case of a runaway reaction is the thermal explosion of a mixture of unreacted substances which are premixed in order to perform a batch reaction. This type of runaway reaction corresponds exactly to the thermal explosion caused by a secondary reaction. But the runaway of semi-batch or continuous reactions is a more complicated process.

Reactions which do not belong to production processes but can occur in distillation processes, during drying, and in other processes of chemical industry, cannot easily be distinguished from secondary reactions. These reactions are usually of the decomposition type. These reactions are particularly important in the storage or transport of products.

There are experimental methods which are only useful for primary reactions, e.g. reaction calorimetry. Other methods, e.g. differential thermal analysis, are useful for exothermic secondary reactions, but normally not for primary reactions. The most important methods for secondary reactions use the principles of thermal analysis or adiabatic self-heating [1].

When an exothermic secondary reaction has been established, it is important to determine the temperature T_S, at which the secondary reaction is observed. This temperature has to be compared with the reaction temperature T_R or the maximum possible temperature $T_{max} = T_R + \Delta T_{ad}$ of the primary reaction (Fig. 1). An estimate of T_S may be obtained by subtracting 100 K from the start of the reaction according to DTA. If the temperature obtained in this way is greater than T_{max}, the secondary reaction will not be initiated by a temperature rise caused by the heat release of the primary reaction [2].

Many incidents which have happened in production reaction systems

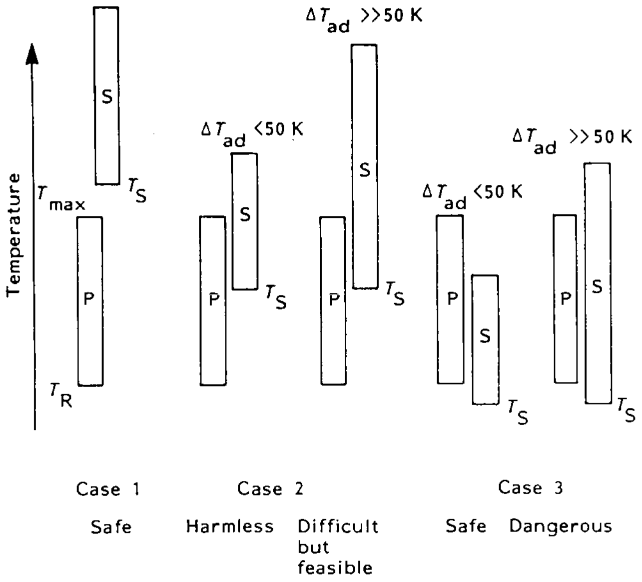

Fig. 1. Ratio of secondary reaction (S) to primary reaction (P).

have originated from secondary reactions. Secondary reactions often have heats of reaction which surpass the primary reaction considerably. An example is the nitration of an aromatic compound. The secondary reaction associated with this primary reaction is the decomposition of the nitro compound. The reaction enthalpies are about $-150\,\mathrm{kJ\,mol^{-1}}$ for the primary and $-400\,\mathrm{kJ\,mol^{-1}}$ for the secondary reaction.

The reaction energy of a secondary reaction, which can be obtained by integration of the DTA peaks, provides information on the danger of a secondary reaction. It should be referred to the total mass of the reaction mixture. This heat of reaction ΔU can be used to calculate the maximum adiabatic temperature rise ΔT_{ad}

$$\Delta T_{ad} = -\Delta U / c_p$$

The specific heat c_p for organic substances (at room temperature) is 1.5–2.0. Therefore, ΔT_{ad} is, to a first approximation, proportional to the heat of reaction.

A small reaction energy of $-\Delta U < 100\text{–}200\,\mathrm{J\,g^{-1}}$ or an adiabatic temperature rise of less than 50 K signifies that the secondary reaction can ususally be disregarded for safety reasons. If no clear conclusions can be drawn from the DTA studies, a more precise determination of T_S is needed. This is obtained from adiabatic tests such as ADT_{24} of the secondary reaction — the temperature which pertains to an induction time for 24 h [2].

The diagram in Fig. 1 is used for the evaluation of secondary reactions in connection with a primary reaction. If $T_S > T_{max}$, no hazard exists and the tests on the secondary reactions can be terminated. If T_S lies between T_R and T_{max}, a considerable hazard may exist. Nevertheless, the reaction can be carried out safely if the reaction conditions are designed to prevent T_S being attained during the primary reaction. If this cannot be guaranteed, safety devices, e.g. venting, reaction inhibition, or emergency cooling, should be considered.

When the temperature T_S of a highly exothermic secondary reaction is more or less the same as T_R or lower, it is rarely possible to run the primary reaction safely. It should be recognized that the above only apply to a secondary reaction in conjunction with the primary reaction. In many cases, two or more exothermic secondary reactions occur. Analogous observations can then be made. A precise rule cannot be laid down for these cases.

2. EXOTHERMIC DECOMPOSITION OF MIXTURES

Exothermic secondary reactions include decomposition or polymerization reactions of the reaction components, reaction products, or the solvent. Other secondary reactions are reactions of reaction components or products with the solvent. We first consider exothermic decomposition reactions of reaction mixtures.

The exothermic decomposition of pure substances is not the subject of this paper. Here, we discuss decomposition reactions in mixtures, considering the influence of components of the mixture on the thermal stability of substances which are capable of exothermic decomposition in a pure state.

Usually, the decomposition reaction is promoted by admixed substances. This can be demonstrated by considering nitrobenzene which as a pure substance is relatively stable. In Table 1, the onset temperatures of the decomposition in DTA is given for mixtures of nitrobenzene with some substances [1]. The table begins with pure nitrobenzene. A solution of nitrobenzene in acetic acid has a thermal stability approximately the same

TABLE 1

Exothermic reactions of nitrobenzene mixed with some substances

Substance added	Mass proportion/%	DTA onset temperature of decomposition ($10\ K\ min^{-1}$)/°C
–	–	380
Acetic acid	50	360
Sulfuric acid	50	220
Chlorosulfonic acid	50	200
Sodium hydroxide	50	130
$FeCl_3$	10	220
$AlCl_3$	20	220

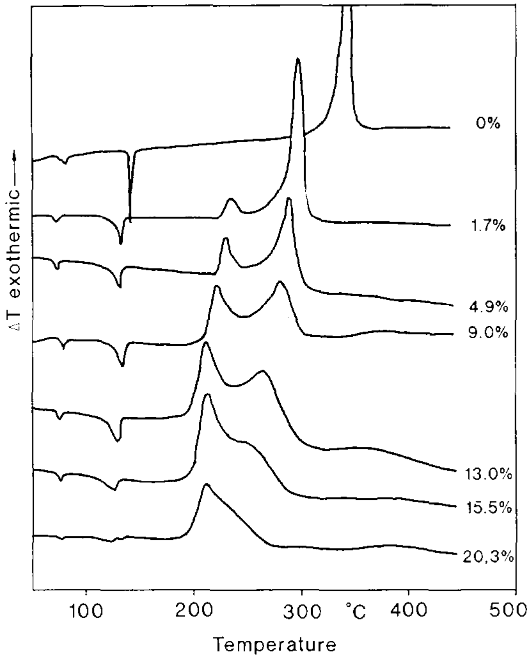

Fig. 2. DTA diagrams of 3-nitrobenzoic acid with sulfuric acid in different concentrations.

as pure nitrobenzene. The stabilities of the solutions in sulfuric acid and chlorosulfonic acid, are, however, much lower. The decomposition begins at temperatures about 150 K lower than for nitrobenzene alone. This effect is very important for the nitration of aromatic compounds in sulfuric acid. The reaction mixtures decompose under practical conditions at temperatures around 150°C.

Figure 2 shows DTA diagrams of 3-nitrobenzoic acid with increasing levels of concentrated sulfuric acid. With small amounts of sulfuric acid, an additional exothermic peak appears beginning at about 200°C. With rising H_2SO_4 content, the peak at 200°C increases whereas the normal peak of 3-nitrobenzoic acid becomes smaller and moves to lower temperatures. With high H_2SO_4 content, only the peak at 200°C remains. If more than 10% H_2SO_4 is present in the solution, the first peak is larger than the second. A higher proportion of sulfuric acid has no further influence on the practical onset temperature of the decomposition.

The quantitative displacement of the temperature region of decomposition to lower temperatures is demonstrated in the best possible way by the results of adiabatic tests. Results of this kind are represented in Fig. 3 for pure 4-nitrobenzoic acid and with added H_2SO_4, in the well-known diagram of $\log \tau_{ad}$ versus $1/T$. The displacement is 130 K to lower temperatures, even with an H_2SO_4 content of only 4% (by mass).

Chlorosulfonic acid has an influence on the exothermic decomposition

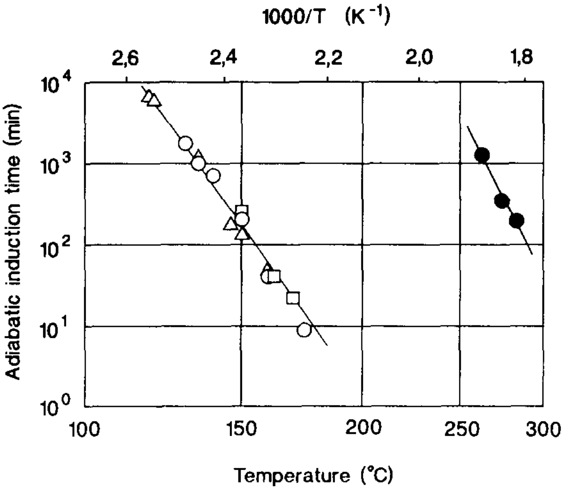

Fig. 3. Dependence of τ_{ad} on temperature for pure 4-nitrobenzoic acid and with admixtures of sulfuric acid: ●, pure; □, 4% H_2SO_4; ○, 9% H_2SO_4; △, 16% H_2SO_4.

of nitro compounds that is very similar to that of sulfuric acid. Figure 4 shows DTA diagrams of nitrobenzene containing different amounts of chlorosulfonic acid. With small quantities of $ClSO_3H$, two exothermic peaks are observed. With high $ClSO_3H$ proportions, the peak at high temperature vanishes and only the peak at about 200°C remains.

Exothermic reactions of nitrobenzene with sodium hydroxide, aluminium chloride, or iron chloride have to be expected if nitrobenzene or other nitro compounds are used as solvents for organic reactions. The strong influence of alkali hydroxide on the decomposition of nitro compounds

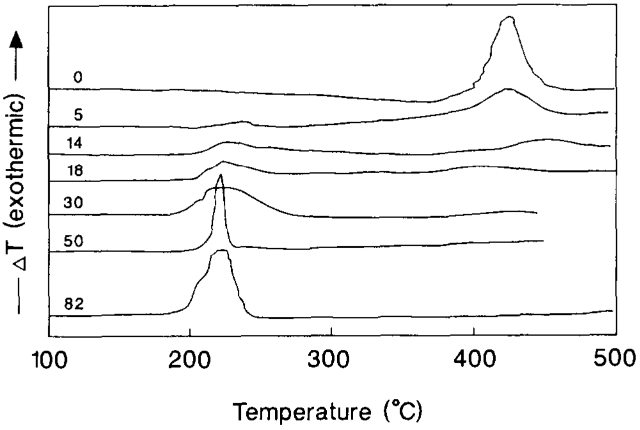

Fig. 4. DTA diagrams (3 K min^{-1}) of nitrobenzene with different amounts of chlorosulfonic acid. The numbers are mol.% of chlorosulfonic acid.

may be regarded more as a reaction with alkali. It is evident that it cannot always be stated whether added materials catalyze the decomposition reaction or whether a real reaction with the added substance occurs.

3. CATALYSIS OF EXOTHERMIC DECOMPOSITION

A well-known example a compound whose exothermic decomposition is subject to strong catalytic effects is hydrogen peroxide. Salts of many heavy metals are catalysts for this decomposition. In particular, alkali hydroxides are efficient catalysts, i.e. the decomposition is dependent on pH: the reaction rate rises with increasing pH [3]. In the plot of log τ_{ad} versus $1/T$ shown in Fig. 5, different pH values result in different straight lines.

There are some substances which as pure products are not capable of exothermic decomposition (in the temperature range up to 500°C), but show an exothermic effect under the influence of catalysts. Benzyl chloride and some other aromatic halogen compounds belong to this group of

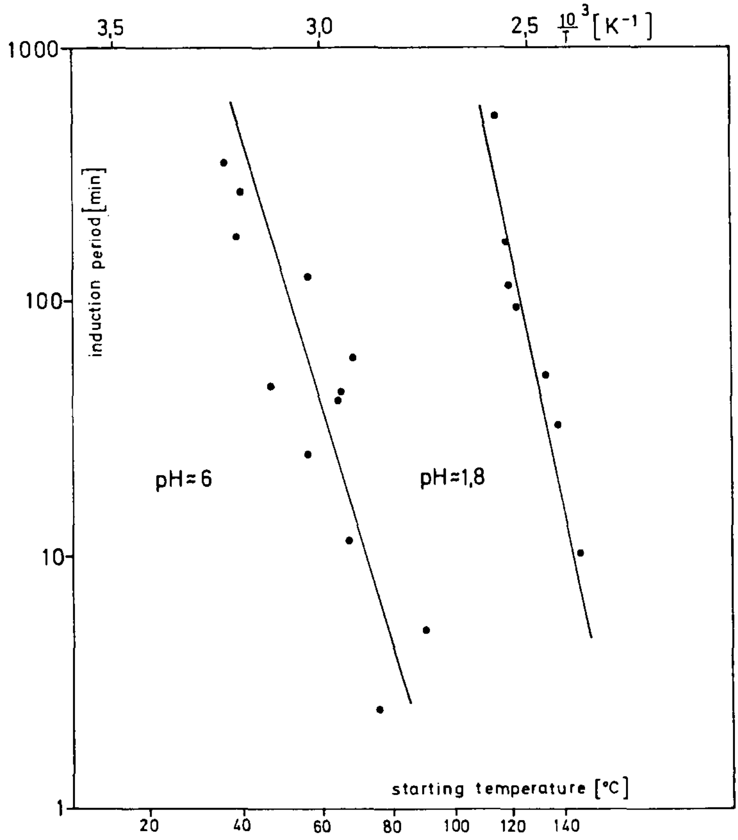

Fig. 5. The catalytic action of OH^- on the decomposition of H_2O_2 (50%). Adiabatic induction times at different pH values [2].

substances. The "decomposition" of benzyl chloride is really a polymerization reaction in which the side chain of the molecule is involved. It is catalized, e.g. by iron salts or acids, and pyridine is reported to be stabilizer.

The exothermic decomposition of substances with double bonds is also, in reality, a polymerization. This reaction is usually strongly influenced by catalysts. Substances with double bonds are often supplied with inhibitors which are added to prevent the polymerization. The monomers containing these inhibiting additives can often only be polymerized with difficulty. This is a reason why the investigation of monomers on decomposition or spontaneous polymerization is difficult and often not reproducible.

An interesting problem is whether metal salts which may come from the surface of containers in which products are handled can catalyze exothermic decompositions. This problem was studied with some nitro compounds which were exposed to systematically varied metal salts [4]. It was found that most metals and their salts did not influence exothermic decomposition. Iron salts, however, had a catalytic effect, and they were surpassed by molybdenum and vanadium salts.

The nitro compounds tested were 4-nitrophenol, 3-nitrobenzoic acid and 4-chloronitrobenzene. Figure 6 shows the DTA diagrams of 3-nitrobenzoic acid to which about 1% of different compounds was added. The effectiveness of the additives is shown by the displacement of the exothermic peak to lower temperatures, compared with the peak of the pure substance. The effect of some metal salts is demonstrated in Table 2.

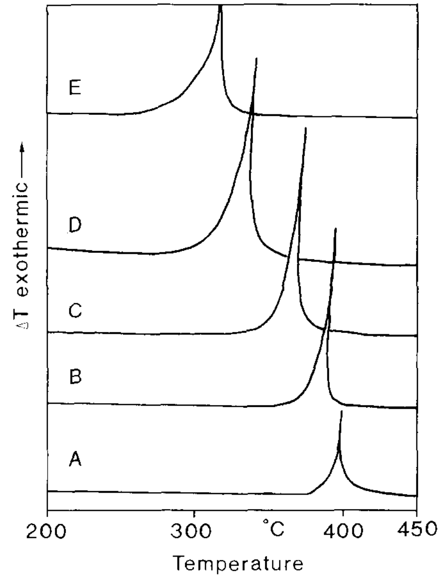

Fig. 6. DTA diagrams of pure 3-nitrobenzoic acid and with addition of some metal salts: A, pure substance; B, 1.6% NaCl; C, 1.3% $FeCl_3$; D, 1.5% VCl_3; E, 1.6% $MoCl_5$.

TABLE 2

Influence of additives on the exothermic decomposition of 3-nitrobenzoic acid; DTA onset and peak temperatures (10 K min^{-1})

Substance added	Concentration/ mass%	DTA onset temperature/°C	DTA peak temperature/°C
–	–	360	400
NaCl	1.6	340	390
Hg_2Cl_2	0.8	340	400
$CrCl_3$	2.0	320	390
$SbCl_3$	2.1	320	390
$NiCl_2$	1.4	310	390
CuCl	1.5	310	360
$ZnCl_3$	1.9	300	380
$FeCl_3$	1.5	290	370
H_2SO_4	2.2	270[a]	370
$SnCl_2$	1.4	260	370
H_2SeO_3	2.3	260	380
VCl_3	1.5	250	330
$MoCl_5$	1.6	240	320

From Fig. 6 as well as from Table 2, the relatively strong effect of molybdenum and vanadium salts can be observed.

The catalytic effect of these additives is relatively strong if the pure nitro compound investigated decomposes at relatively high temperatures. 4-Chloronitrobenzene is such a substance. The adiabatic induction time τ_{ad} of the decomposition of this compound, pure and with added molybdenum and vanadium salts, was measured at different temperatures. The diagram of log τ_{ad} versus $1/T$ given in Fig. 7 shows a displacement of about 120 K to lower temperatures as the result of the catalytic effect.

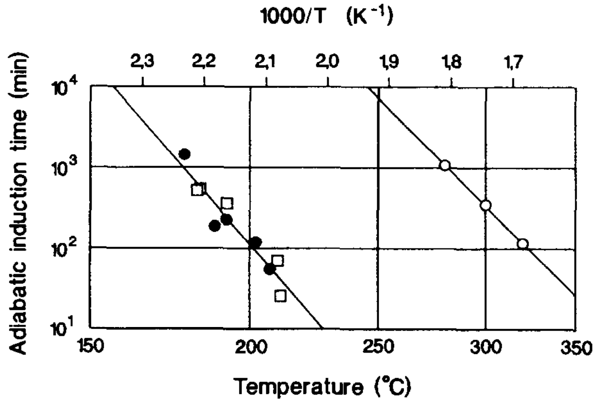

Fig. 7. Log τ_{ad}–$1/T$ diagram of the adiabatic induction times of pure 4-chloronitrobenzene pure and with additions of metal salt; ○, pure; ●, with 1% VCl_3; □, with 1% $MOCl_5$.

The catalytic effect of the construction materials on decomposition reactions is illustrated by an incident which occurred during the distillation of chloro-alkylanilines. Thermal stability tests had been carried out in the presence of stainless steel. The distillation was, however, carried out in a mild steel still. Following the incident, it was found that the decomposition and temperature was 70 K lower in the presence of mild steel. The initial slow decomposition reaction generated hydrochloric acid which further reacted with the mild steel of the still body to give ferrous chloride. The decomposition reaction was accelerated by the autocatalytic effect of the hydrochloric acid/ferrous chloride and ultimately led to a runaway and explosion.

4. TYPICAL EXOTHERMIC SECONDARY REACTIONS

If the safe management of a technical reaction is to be discussed, all the exothermic reactions that can participate have to be determined. Examples of primary reactions with their associated exothermic secondary reactions are listed in Table 3. Typical reaction enthalpies of the reactions are specific in order to give a survey of the hazards of the reactions.

The typical secondary reactions given in Table 3 are associated with definite primary reactions. Each diazotization reaction has N_2 elimination as the secondary reaction; each nitration has the decomposition associated with the $-NO_2$ group. In these cases the primary reactions are often so fast that only the secondary reactions are relevant in safety discussions. It can

TABLE 3

Examples of primary reactions with their associated exothermic secondary reactions

Primary reaction	$\Delta_R H$/kJ mol^{-1}	Secondary reaction	$\Delta_R H$/kJ mol^{-1}
Simple diazotization, e.g. of an aniline	150	Elimination of nitrogen	160
Diazotization of a nitro compound	150	Elimination of nitrogen	160
Sulfonation of a nitro compound	60	NO_2 decomposition[a]	400
Chlorosulfonation of a nitro compound	60	NO_2 decomposition[a]	400
Amination of a chloro nitro compound	120	NO_2 decomposition[a]	400
Nitration of an aromatic compound	150	NO_2 decomposition[a]	400

[a] Indicates the complicated set of reactions associated with the decomposition of nitro compounds.

be seen that the secondary reactions are usually more exothermic than the primary reaction.

All other reactions involving, for example, nitro, azo or epoxy compounds, have as possible secondary reactions the decomposition related to these groups, if these functional groups are not destroyed by the primary reaction.

The nitration of aromatic compounds using mixtures of nitric and sulfuric acid is often accompanied by an additional exothermic secondary reaction if an excess of nitric acid is applied. This secondary reaction occurs in the temperature region of 70–120°C, whereas the nitration reaction itself is carried out at room temperature. An example is the nitration of dimethylterephthalate. If an excess of nitric acid is used, the DTA diagram of the reaction mixture shows an exothermic peak before the decomposition peak.

This type of secondary reaction is typical for nitration reactions where the introduction of a second nitro group is very slow or impossible because of steric or other hindrances. The secondary reaction is either a second nitration step which is rather slow and begins at a higher temperature, or an oxidation by the surplus nitric acid. In the example of dimethylterephthalate, the introduction of a second nitro group is hindered by three substituents present in the molecule. With an excess of nitric acid methyl nitrate is formed by hydrolyzing an ester group. The first exothermic peak is probably caused by the decomposition of methyl nitrate.

Bretherick [5] has pointed out that alcohols in mixtures with nitric acid react vigorously, even at rather low temperatures. Nitric acid is used preferably in nitration reactions. Consequently, the very exothermic oxidation reactions with nitric acid represent a particular hazard in these reactions. They typically occur in mixtures which have a too high a concentration of nitric acid — caused either in order to achieve a larger yield or by erroneously overdosing nitric acid.

Many combinations of primary and secondary reactions are possible. The authors have investigated many reaction systems of this kind. Some special reaction systems which have been the cause of incidents are as follows.

(i) *The Seveso reaction* [6, 7], *the hydrolysis of 1,2,4,5-tetrachlorobenzene in ethylene glycol as the solvent*

Primary reaction: the formation of the sodium salt of 2,4,5-trichlorophenol.

First exothermic secondary reaction: the formation of adducts of trichlorophenol with ethylene glycol.

Second exothermic secondary reaction: the combination of two molecules of 2,4,5-trichlorophenol. By elimination of hydrogen chloride the highly toxic substance tetrachlorodioxydibenzodioxin is formed.

(ii) *The reaction of 3-nitro-4-methoxybenzoic acid with thionyl chloride* [8].

Primary reaction: the formation of the acid chloride.

Exothermic secondary reaction: polycondensation of the acid chloride formed with synchronous elimination of methyl chloride.

Second exothermic secondary reaction: NO_2 decomposition.

5. VARIOUS EXOTHERMIC SECONDARY REACTIONS

In addition to decomposition reactions, between components of the reaction system belong to the class of exothermic secondary reactions. Reactions of a reaction component with the solvent, for example, belong to this class of reactions. The variety of these reactions is very large, and only a few of them are reported in the literature. Bretherick [5] lists a large number of possible secondary reactions.

Secondary reactions which frequently occur are reactions of organic compounds with strong oxidizers, e.g. HNO_3, CrO_3, $KMnO_4$, or H_2O_2. Particular attention should be paid to mixtures of organic substances with nitric acid. Many organic compounds can be mixed with nitric acid in arbitrary proportions. These mixtures are often capable of deflagration and — in specified concentration region — of detonation [9]. Gustin has investigated the concentration limits of detonation in the system adiptic acid–nitric acid–water [10].

As a consequence many nitration reactions with concentrated nitric acid or oxidation reactions with HNO_3 are very hazardous.

Some oxidizing agents, such as H_2O_2 or $NaClO_2$, decompose exothermically themselves and generate a second exothermic reaction by oxidation with the eliminated oxygen. For example, H_2O_2 has a decomposition energy of $-100\,kJ\,mol^{-1}$. The "decomposition energy" of mixtures of H_2O_2 with organic substances is increased by oxidation by the oxygen eliminated from the H_2O_2 and is about $-300\,kJ\,mol^{-1}$.

Further exothermic secondary reactions which commonly occur are the reactions of reactive solvents like dimethyl formamide and dimethyl sulfoxide with substances that contain chlorine, e.g. CCl_4, $SOCl_2$ or $POCl_3$. In addition, exothermic reactions of halogenated hydrocarbons can occur, for example, that of CCl_4 with acetone under the influence of alkali.

Many apparently stable substances react vigorously with strong alkali. The reaction of nitro compounds with alkali has already been mentioned. This reaction produces azoxybenzene derivatives among the products. The decomposition of the azoxy-type compound will carry on the exothermic reaction. Mixtures of nitro compounds with alkali are often capable of deflagration.

The exothermic reaction of epoxides with alkali is usually not a decomposition but a polymerization. The initiation of the polymerization of ethylene oxide by, for example, sodium hydroxide is a well-known procedure for the polymerization of ethylene oxide. For that reason an explosion must be considered if, in error, ethylene oxide is brought into contact with sodium hydroxide or another alkali. The polymerization of ethylene oxide has about the same heat of reaction as the decomposition which produces CO, CH_4, carbon, etc. The strong adiabatic temperature rise caused by the polymerization can possibly lead to the decomposition reaction.

In addition to the above exothermic reactions caused by the introduction of foreign substances, the influence of water on many substances or mixtures should be noted. Water used as a cooling or heating medium surrounds many reactions containers filled with reaction mixtures that can react vigorously with water. Mixtures containing sulfuric acid, chlorosulfonic acid, sulfur trioxide or thionyl chloride are typical. But organic products such as acid halogenides, metallo-organic compounds, etc. can also react exothermically with water.

6. CONCLUSION

It has been shown that exothermic reactions can occur in many situations either as simple decomposition reactions or true secondary reactions. The wide variety of circumstances under which they can occur reinforces the need for every chemical process to be systematically investigated in order to identify potential hazards that may occur in plant operation.

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