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THE INFLUENCE OF CHEMICAL STRUCTURE ON EXOTHERMIC DECOMPOSITION

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Abstract

Exothermic decomposition capability depends on the chemical structure of a substance. There are several functional groups which tend to make a material exhibit exothermic decomposition. We have tried to establish a correlation between decomposition energies and the involved functional groups. The evaluated decomposition energies were found in the literature or come from our own DSC measurements. The result is that many functional groups can be associated with typical decomposition energies.

Functional groups also influence the temperature region of exothermic decomposition, but the dependence of the onset temperature of decomposition with respect to chemical structure cannot be determined as precisely as the corresponding dependence of decomposition energy. Certain functional groups have typical onset temperatures of decomposition which are influenced by other substituents. For nitro compounds in particular, data have been found in temperature regions typical for the various additional substituents.

1. CHEMICAL STRUCTURE AND DECOMPOSITION ENERGY

We define "decomposition energy" as the reaction energy which arises if a substance decomposes under practical (nearly adiabatic) conditions. If the decomposition energy is high, the high temperature achieved will generate an equilibrium composition of reaction products. Low or medium decomposition energies will only produce a small or medium temperature increase, and an equilibrium is not obtained.

We speak here of "reaction energy" and not of "reaction enthalpy", because most of the investigation procedures follow an isochore rather than an isobar pattern. A decomposition under practical conditions is likewise a process which occurs at constant volume.

1.1. Methods of determining decomposition energies

The most important methods for determining decomposition energies are:

- calculation from tabulated thermodynamic data
- calculation from estimated thermodynamic data
- calorimetric bomb
- determination of the adiabatic temperature rise in adiabatic tests
- differential scanning calorimetry

The decomposition energy of explosives is called "heat of explosion". This energy is liberated by achieving chemical equilibrium in the decomposition products after decomposition. The end temperature after decomposition is so high (> 2000 K) that only water vapour, carbon dioxide, carbon monoxide, other simple molecules, radicals, and atoms are formed as reaction products. If the enthalpy of formation of a substance is known, the heat of explosion can be calculated. Heats of formation and other quantities which are necessary for this calculation can be found in well-known thermodynamic handbooks [1 - 4].

Heats of explosion are usually measured by the calorimetric bomb. Nowadays small and medium decomposition energies are mostly determined by DSC methods. By integration of the peak which represents the exothermic decomposition the decompostion energy is determined using a standard substance for calibration.

It is difficult to determine relatively high decomposition energies by DSC because the decomposition occurs here essentially via an isothermal process. The equilibrium which is necessary to obtain the maximum decomposition energy requires high temperatures and is not achieved under the nearly isothermal conditions of the DSC. Yoshida [5] has compared results of DSC and of calorimetric measurements or calculations. He found that the deviation of DSC decomposition energies from results of more precise methods increases with rising decomposition energy.

This paper deals mainly with small or medium decomposition energies. The calculation of these decomposition energies is often difficult or impossible because the reaction products are not in chemical equilibrium. Only if the enthalpies of formation of the substance and of the decomposition products are known, can the decomposition energy be calculated. In most cases, however, the decomposition products are not known.

Up to now products of the exothermic decomposition of substances have only rarely been determined. In the few cases where the decomposition products have been analyzed, a variety of products have been found. Here we see the problem associated with the calculation of decomposition energies. If the decomposition products are known, we do not know all of the heats of formation. But in most cases the decomposition products are not known, and they are frequently polymers of varying composition. We conclude that in most cases it is impossible to calculate small or medium decomposition energies.

Only a few heats of formation of organic compounds are known. For many other compounds the heats of formation can be interpolated from a series of analogous compounds, e.g. hydrocarbons of different chain length [6, 7]. A more general method is the application of the increment method. For each important functional group an incremental value for the heat of formation is determined and tabulated. Using the increments of all functional groups which form a molecule the heat of formation of the molecule is estimated [8, 9].

This method has been refined by Benson [10, 11] and further developed by the working group E27 of ASTM [12 - 14]. The familiar CHETAH program has originated from this work. The application to the calculation of high decomposition energies is obvious. For small or medium decomposition energies the same difficulties arise as in the calculation from measured data. The unknown reaction products prevent the computation.

Most of the data used in this discussion are decomposition energies which have been directly measured. These experimental data were found in the literature or were measured in the author's laboratory.

1.2. Inorganic compounds

We want to begin the survey with inorganic compounds. The heats of decomposition are tabulated in Table 1. A systematic discussion of the connection to chemical structure can not be given. Some substances which are known as oxidizers show an exothermic decomposition as pure substances, e.g. $NaClO_2$ or $KMnO_4$. Peroxides of metals usually do not decompose exothermically. Salts of ammonium with oxygen containing acids are known to have large decomposition energies. Heavy metal azides, fulminates, and hydrazine salts are known as explosives.

1.3. Organic compounds

The number of organic compounds which are capable of exothermic decomposition is very large. With these substances a systematic discussion is possible and necessary. For this discussion we start by applying the increment method.

In order to estimate the decomposition energies of substances of low or medium decomposition energies by the increment method, the heats of formation of the substance and its decomposition products must be computed. If, however, the decomposition of related substances (substances which have the same characteristic functional group) are considered, the simplest assumption is that the decomposition follows the same scheme. We conclude therefore that the estimation of the decomposition energy according to the increment method will yield the same decomposition energy for all substances having the same characteristic group.

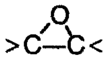
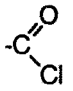
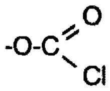
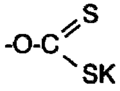
Table 1
Decomposition Energies of Inorganic Compounds -Δ U (kJ/mol)

		Reference
ammonium dichromate	306	[16]
ammonium iodate	176	[18]
ammonium nitrate	128	[15]
ammonium perchlorate	131	[15]
ammonium peroxodisulfate	74	[18]
hydrazine (liquid)	112	+
hydrazinium sulfate	90	[18]
hydrazine nitrate	368	[17]
hydrazine perchlorate	433	[17]
hydrogen azide	264	*
hydrogen peroxide	98	*
hydroxylammonium chloride	132	[19]
hydroxylammonium sulfate	263	[18]
lead azide	485	*
mercury fulminate	423	[15]
potassium permanganate	14	[18]
potassium peroxydisulfate	78	[18]
sodium azide	54	[18]
sodium chlorite	135	[18]
sodium dithionate	94	[18]
sodium hypophosphite	36	[18]
sodium peroxydisulfate	86	[18]

* calculated (decomposition into elements)
\+ calculated (decomposition into N_2 and NH_3)

Functional groups which are responsible for strong exothermic decomposition and explosibility are tabulated in the handbook of Bretherick [20]. Some typical groups which characterize compounds with low or medium decomposition energies are shown in Table 2.

Table 2
Groups of medium or low decomposition energies

$>C=C<$			
$-N=C=O$	$-C\equiv N$	$>C=N-$	$>N-N<$
$>S=O$	$-SO_2Cl$	$-SO_2NH_2$	
$P(OR)_2$	$P(OR)_3$		

We must also consider substances whose exothermic decomposition cannot be attributed to one molecular group but depend on the presence of two substituents in the same molecule. A well-known example is an amino compound which additionally contains a chlorine or bromine atom. Table 3 lists functional groups which may cause exothermic decomposition in combination.

Table 3
Groups which cause exothermic decomposition in combination

Group 1	Group 2
$-NH_2$	-Cl, -Br
$-NH_2$	$-OCH_3$
-NH-	$-SO_2Cl$
-OK, ONa	-Cl
-COOK, COONa	-Cl

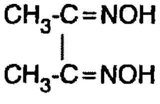
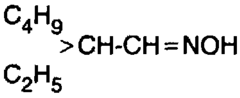
For our empirical treatment of decomposition energies we will use groups for which these data are known for a number of substances. We compare these decomposition energies, and when we find an agreement of the data we are able to assign a typical decomposition energy to the functional group.

In Tables 4 to 8 decomposition energies of several series of organic compounds containing typical functional groups are tabulated. We begin with organic hydrazo compounds in Table 4. The decomposition energies were determined by DSC. Considering the relatively large error in DSC measurements the agreement is very good. We conclude from Table 4 that the decomposition energy of organic hydrazo compounds is -80 +/- 10 kJ/ mol.

Table 4
Decomposition energies -Δ U (kJ/mol) of hydrazo compounds

1.1-dimethyl hydrazine	69
phenyl hydrazine	71
phenyl hydrazine hydrochloride	87
1.2-diphenyl hydrazine	81
acetic acid hydrazide	76
maleic acid hydrazide	66
1.2.4-triazole	76

Table 5
Decomposition energies -Δ U (kJ/mol) of hydroxylamine and oximes

$(NH_2OH)\ HCl$	263 =2.132
$(NH_2OH)_2\ H_2SO_4$	132
acetone oxime	110
benzaldoxime	144
 $CH_3\text{-}C{=}NOH$ $CH_3\text{-}C{=}NOH$	230 = 2.115
 $(C_4H_9)(C_2H_5){>}CH\text{-}CH{=}NOH$	140

The next series of compounds are oximes which are prepared from aldehydes or ketones and hydroxylamine. For that reason we include hydroxylammonium salts in the same table. All the data in Table 5 were determined by DSC. The table shows that oximes have an approximate decomposition energy of -110 to -140 kJ/ mole.

Table 6 contains substances with a double bond. The "decomposition" of these substances is really a polymerization. The heats of polymerization were taken from a table of thermodynamics of polymerization [21]. The heat of polymerization of substances with a double bond is -80 +/- 10 kJ/mol. A heat of reaction of the same order of magnitude arises by decomposition reactions, e.g.

$$C_nH_{2n+1}\text{-}CH{=}CH_2\ (lq)\ \text{----->}\ C_{n+1}H_{2n+4}\ (g)\ +\ C \qquad (1)$$

for α-olefins [22]. DSC investigations of many olefins have also yielded decomposition energies in the region of -70 to -90 kJ/ mol.

Table 6
Decomposition energies -Δ U (kJ/mol) of compounds with double bonds

acrolein	80
acrylic acid	67
acryl nitrile	77
1- butene	87
styrene	73
vinyl acetate	88
vinyl chloride	71

Nitro compounds are substances which are used very frequently in the Chemical Industry. They have a relatively large decomposition energy which is liberated only if high temperatures and thermodynamic equilibrium are obtained. In DSC experiments only a part of the decomposition energy is set free [5, 23]. The decomposition energies represented in Table 7 are "heats of explosion" which have been determined using a calorimetric bomb [15]. The heat of explosion of the nitro compounds (divided by the number of nitro groups in the molecule) is rather exactly -400 kJ/mol. This value was proved from measurements of many nitro compounds.

Table 7
Decomposition energies -Δ U of aromatic nitro compounds [15]
(kJ/mol Nitro group)

1.3-dinitrobenzene	387
2.4-dinitrotoluene	402
dinitroorthocresol	387
trinitroaniline	379
trinitro benzoic acid	387
trinitrotoluene	383
trinitrophenol	384

In Table 8 decomposition energies of organic peroxides are presented. The exothermic decomposition of a peroxide consists of at least two steps: 1. the elimination of oxygen, 2. the oxidative action of the formed oxygen on the organic molecule. These two steps can be separated in the decomposition of H_2O_2: Whereas the decomposition energy of H_2O_2 is about -100 kJ/mol, in the presence of an organic substance nearly a threefold energy is observed. Correspondingly the decomposition energy of a peroxide is -300 +/- 50 kJ/mol. The largest energies (350 - 360 kJ/mol) have been measured for diacyl peroxides.

The author has compiled some additional tables of this type. Some of them contain only a small number of compounds, e.g. 3 to 5 substances. All functional groups which have been found to exhibit decomposition energies of the same order of magnitude in different molecules are shown in Table 9. Not all functional groups, which may produce exothermic decomposition, fit into this table. For instance -C≡N compounds often have large decomposition energies, e.g. ethylene cyanide. Others like e.g. acetonitrile do not show any exothermic effect.

Table 8
Decomposition energies -Δ U (kJ/mol) of organic peroxides

		Reference
tert-butyl peroxybenzoat	330	[25]
tert-butyl peroxy-2-ethylhexanoat	330	[24]
tert-butyl peroxypivalat	250	[26]
cumol hydroperoxide	265	[27]
dicumyl peroxide	340	[24]
dibenzoyl peroxide	340	[24]
dioctanoyl peroxide	370	[24]
diisononayl peroxide	360	[24]

In Table 9 exact values of decomposition energies are not specified. Only a range of data is given for each functional group. The number of substances taken into consideration is indicated. If this number is small the tabulated decomposition energy can not be considered as precise. For safety applications the larger value of the range given in the table should always be used.

There are compounds for which an exothermic decomposition is possible on the basis of thermodynamic data, but has never been observed. Examples are

$$CH_3OH \longrightarrow .5\ CH_4 + H_2O_g + .5\ C \qquad \Delta_R H = -40\ \mathrm{kJ/mol} \qquad (2)$$

and

$$C_6H_6 \longrightarrow 1.5\ CH_4 + 4.5\ C \qquad \Delta_R H = -195\ \mathrm{kJ/mol} \qquad (3)$$

$$\text{or} \qquad 6\ C + 3\ H_2 \qquad \Delta_R H = -83\ \mathrm{kJ/mol} \qquad (4)$$

The exothermic decomposition of benzene does not occur as a separate reaction, but it is part of the decomposition of aromatic nitro compounds. The high temperatures achieved by these decomposition reactions promotes the destruction (or in reality polymerization) of the benzene nucleus.

Table 9
Assignment of decomposition energies to molecular groups

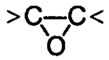
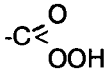
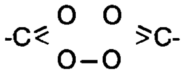
Group	-Δ U (kJ/mol)	Reference	Number of substances
$>C=C<$	40 ... 90		10
$-C\equiv C-$	120 ... 170		3
	70 ... 100		5
$>COOH$	230 ... 280	[24]	3
 $-C\genfrac{}{}{0pt}{}{O}{OOH}$	240 ... 290	[24]	5
 $-C\genfrac{}{}{0pt}{}{O}{O}-\genfrac{}{}{0pt}{}{O}{O}C-$	230 ... 360	[24]	4
$>S=O$	40 ... 70	[29]	3
-NH-NH-	70 ... 110		8
$-N=N-$	100 ... 180		5
$-N_2^+$	160 ... 190		7
$>C=N\equiv N$	170 ... 190		4
$-N_3$	200 ... 240		4
$>C=NOH$	110 ... 140		7
$>N-OH$	180 ... 240		3
$>N-O$	100 ... 130		4
$>C-N=O$	150 ... 290		3
$-N=C=O$	50 ... 75		6
$>C-NO_2$	380 ... 410	[15]	20
$>N-NO_2$	390 ... 450	[15]	4
$-O-NO_2$	440 ... 480	[15]	14
$-NH_2 \bullet HNO_3$	330 ... 360	[15]	7

Table 9 refers to types of compounds whose exothermic decompositions have long been known. The exothermic reaction is localized in certain groups located in the molecule. There are, however, some other classes of substances capable of exothermic decomposition in which a single functional group responsible for the reaction can not be specified. Some types have been tabulated in Table 3.

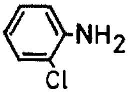
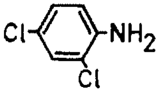
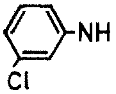
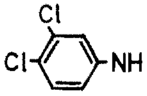
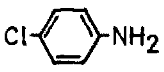
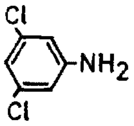
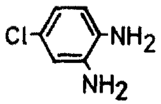
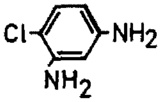
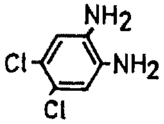
Organic compounds that contain only the elements C, H, and O constitute another class of compounds of this type. Table 10 summarizes the energies of decomposition of some C-H-O compounds. From this table it is apparent that such compounds can exhibit considerable exothermic effects. Carbohydrates belong to this class. Their exothermic decomposition has, however, long been known. The carbonization of wood is a well-known exothermic process [30] and is important for the production of charcoal. On the other hand, there are no signs that the exothermic decomposition of carbohydrates can be dangerous.

Table 10
Decomposition energies of C-H-O compounds, determined by DSC

Substance	Decomposition energy -Δ U	
	kJ/mol	J/g
1.4-dioxane	17	165
glucose	73	406
galactose	54	300
sucrose	165	480
cornstarch		460
cellulose		330
polyvinylalcohol		540
pyruvic acid	48	540

For C-H-O compounds there is no apparent systematic relationship between structure and exothermic decomposition. For these compounds the energy-generating process may be the conversion of O-C bonds to O-H bonds. At most 40 to 50 kJ/mol can be released because of the higher binding energy of the O-H bond. In Table 10 the energy of decomposition per mole cannot be related to any particular group. Because of the widely varied molecular masses the reaction energy referred to the mass unit is a more realistic value.

Table 11
Decomposition Energies -Δ U (kJ/mol) of chlorinated amino benzenes

	52		42
	0		42
	81		0
	111		
	161		175

In Table 3 pairs of molecular groups were tabulated which together cause exothermic decomposition. Investigation of the decomposition energies of these compounds did not reveal any quantitative agreement. We illustrate this using the example of chloro-amino derivatives of benzene. The decomposition energies given in Table 11 exhibit a strong dependence between the decomposition energy and the mutual arrangement of the chlorine atom and the NH$_2$ group. In the para and ortho positions different decomposition energies were found whereas the meta position does not produce an exothermic effect.

2. CHEMICAL STRUCTURE AND DECOMPOSITION KINETICS

Typical functional groups also exhibit an influence on the kinetics of exothermic decomposition which determines the temperature region where the decomposition occurs. The onset temperature of decomposition is not generally defined in the existing literature. It can, however, be deduced from the most important experimental methods:

- From temperature-programmed methods like DTA or DSC an on set temperature of decomposition can be interpreted as the temperature where the exothermic peak begins.

- From adiabatic measurements like the Dewar test or ARC a temperature can be found which belongs to a definite induction period or time to maximum rate. The temperature attributed to an induction period of 24 hours is called ADT_{24}.

An onset temperature of exothermic decomposition can often be attributed to a functional group if no other substituents are present in the molecule. Other substituents in the molecule generally diminish the thermal stability of the substance, i.e. the ADT_{24} is reduced. In Table 12 typical onset temperatures of exothermic decomposition are given for some substances.

Table 12
Typical onset temperatures of decomposition (°C) for some molecular groups

Group	onset temperature of decomposition in DTA (10 K/min)	ADT_{24} from Dewar tests
$-NO_2$	360	280
$=NOH$	200	110
-NO	150	80
-C-O-O-	130	80
$-N_2^+$	150	80
$-NH-NH_2$	250	220
$-N_3$	130	80

Whereas the data concerning decomposition energies are rather reliable, this is not true for data concerning temperatures of decomposition as shown in Table 12. These temperature data should not be used for safety applications. Table 13 shows to what degree the temperature of decomposition of nitro compounds of benzene depends on a further substituent in the molecule. The table refers to nitrobenzene which has a second substituent in the para position.

Using results from additional substances, we would like to show that the dependence on additional substituents in nitro compounds can be considered as a more general correlation. Chloro-nitro compounds are more stable than chloro-amino compounds, and these have a greater stability than nitrophenols. The results we would like to show are adiabatic induction times which we have plotted in three graphs in logarithmic scale versus reciprocal absolute temperatures (Figure 1 to 3) [18].

In Figure 1 the results of compounds which contain only nitro groups and chlorine atoms are plotted. Figures 2 and 3, respectively, show the results of nitroanilines and nitrophenols. Each figure contains a series of straight lines which show that similar compounds have similar thermal stability relationships. The shift to lower temperatures can clearly be seen for the nitroanilines relative to the chloro-nitro benzenes and for the nitrophenols relative to the nitroanilines.

Table 13

Onset temperatures of decomposition (°C) of 4-nitrocompounds of benzene

substituent	onset temperature of decomposition in DTA (10 K/min)	ADT_{24} from Dewar tests
-H	360	280
-Cl	360	260
-COOH	340	250
$-CH_3$	300	230
$-NH_2$	270	220
-OH	260	180
-CHO	230	170

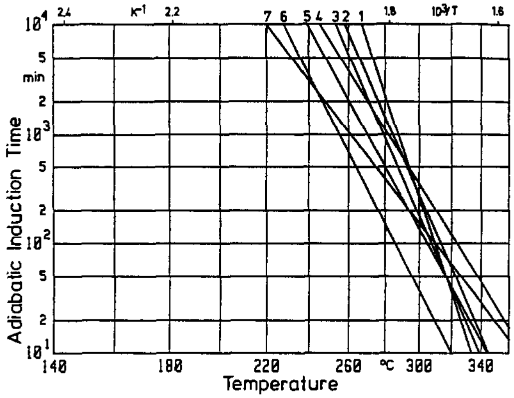


Figure 1. Induction time-temperature diagrams of compounds containing nitro groups and halogen atoms

1) 1.3-dinitrobenzene
2) nitrobenzene
3) 4-fluoro-3-chloro-nitrobenzene
4) 4-chloro-nitrobenzene
5) 2-chloro-nitrobenzene
6) 2.4-dinitro-chloro-benzene
7) 1.2-dinitro-chloro-benzene

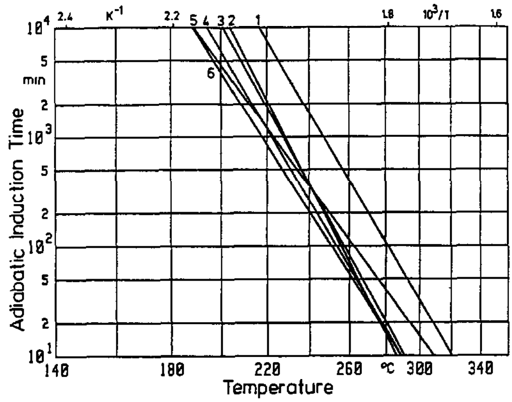


Figure 2. Induction time-temperature diagrams of compounds containing nitro and amino groups

1) 4.4'-dinitro-diphenylamine
2) 6-chloro-2.4-dinitro-aniline
3) 2-nitroaniline
4) 4-nitroaniline
5) 2.4-dinitroaniline
6) 3-nitroaniline

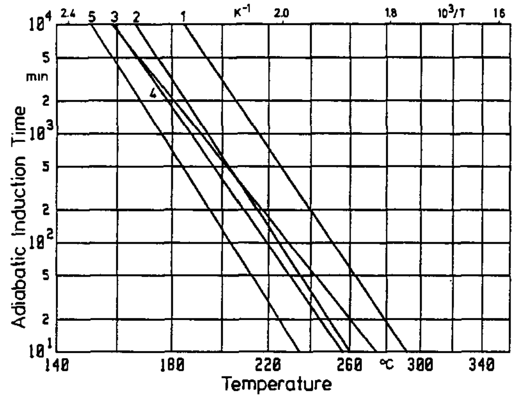


Figure 3. Induction time-temperature diagrams of compounds containing nitro and oxy groups

1) 3-nitrophenol
2) 2.4-dinitrophenol
3) 4-nitrophenol
4) 2-nitrophenol
5) 2.6-dichloro-4-nitrophenol

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