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ORIGINAL RESEARCH

Relative energy of organic compounds II. Halides, nitrogen, and sulfur compounds

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Abstract The energies of the following types of compounds are characterized by their calculated relative enthalpies: alkyl, alkenyl, and aryl halides; carboxylic acid halides; carbonyl halides; amines; carboxylic acid amides; hydrazine derivatives; nitriles; heteroaromatic compounds; nitro-compounds; organic nitrites and nitrates; organic sulfides; thiols; disulfides; sulfoxides; sulfones; organic sulfites and sulfates; and selected inorganic compounds. Stabilization energy of pyrrol and thiophene has been estimated.

Keywords Heat of formation · Relative energy · Relative enthalpy · Stabilization energy · Education

Abbreviations

Bu	Butyl
Et	Ethyl
Me	Methyl
Ph	Phenyl
Pr	Propyl
X	Halogen

Introduction

This article is devoted to demonstrate the relative energies of organic halogen, nitrogen, and sulfur compounds using the relative enthalpies introduced earlier [1, 2]. The relative enthalpies express the energies of substances relative to those of properly selected reference compounds. By definition, the relative enthalpies of the reference compounds are zero or near zero. The reference compounds are gas phase non-branched alkanes containing at least two carbon atoms and their following derivatives:

R–F	R–Cl	R–Br	R–I
R–O–R	R–S–R	R_3N	

In order to demonstrate the effects determined entirely by the structures, only the relative enthalpies of gas phase compounds are used. Most of the relative enthalpies are calculated from heats of formation taken from compilations of Cox and Pilcher [3] and Stull et al. [4] by correcting them with the relative enthalpies of the constituent elements of compounds.

C: −22.85	H: 21.73	O: 125.83	N: −89.31	S: −41.62
F: 198.06	Cl: 47.11	Br: 4.08	I: −53.82	

All relative enthalpies (H^0_{rel}s) are expressed in kJ/mol. The relative enthalpy of methyl chloride (3.1 kJ/mol), for example, is calculated by adding to its heat of formation (−86.3 kJ/mol) the relative enthalpy of carbon (−22.85 kJ/mol) and three times the relative enthalpy of hydrogen (3 × 21.73 kJ/mol) and that of chlorine (47.11 kJ/mol).

Halides

The constituent elements of alkyl halides and their relative enthalpies are listed in Table 1. In accordance with experience, and as reflected by the relative enthalpies, fluorine

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Table 1 Relative enthalpies of halogens, hydrogen halides, and reference alkyl halides

Element	H^0_{rel} (kJ mol^{-1})	ΔH^0_{f} (kJ mol^{-1})	Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_{f} (kJ mol^{-1})
C (s)	−22.85	0	H_2	43.46	0
F_2	396.12	0	HF	−51.3	−271.1
Cl_2	94.22	0	HCl	−23.5	−92.3
Br_2 (l)	8.16	0	HBr	−10.4	−36.1
I_2 (s)	−107.64	0	HI	−5.7	26.4
Et–F	−0.5	−261.5	Et–Br	3.0	−64.0
Et–Cl	−1.6	−111.7	Et–I	0.8	−8.4
Pr–F	0.5	−281.2	Pr–Br	−0.2	−87.9
Pr–Cl	0.6	−130.1	Pr–I	−0.8	−30.5
Bu–Cl	4.0	−147.3	Bu–Br	1.0	−107.3

is a very high energy substance. The energies of chlorine, bromine, and iodine are gradually decreasing. The H^0_{rel}s of hydrogen halides are also gradually changing in opposite direction. The lowest H^0_{rel} belongs to hydrogen fluoride.

The relative enthalpies of the reference alkyl halides are close to zero. The possible reasons for the deviations are, at least in part, the potential experimental errors.

Alkyl, alkenyl, and aryl halides

Data of Table 2 demonstrate the H^0_{rel}s of the four methyl halides. It has long been observed that in the stepwise fluorination of methane the heats of reactions are increasing step-by-step. This allows concluding that in these reactions gradually lower energy compounds are formed. The same effect is clearly observed by directly comparing to each other the H^0_{rel}s of the fluorinated derivatives of methane listed in Table 2. This reflects the special feature of fluorine since in contrast to this, in the case of the other three halides the H^0_{rel}s are gradually increasing with the degree of substitution. In this respect fluorine resembles oxygen. As described in Part I, the multiple attachment of alkoxy groups to the same carbon atom is energetically favorable.

The large stabilization is also observed with other compounds containing multi-fluorinated carbon atoms. The H^0_{rel}s of 1,1-difluoro ethane and 1,1,1-trifluoro ethane, for example, are also low.

Data of Table 2 also show that if one fluorine atom in CF_4 is replaced by one Cl, Br, or I, stabilization of the molecule decreases by about the same value.

Table 3 shows the effects of halogen substitution on secondary and tertiary carbon atoms relative to methyl substitution on the same atoms. If the substitution occurs on secondary carbon the effect of halogens, except chlorine, is about the same as that of the methyl group. In the case of tertiary carbon, however, the stabilization effects of all halogen substitutions are larger and increase from iodine to fluorine.

The data listed in Table 4 can be used to show whether or not the halogen atoms are interacting with the double bond of ethylene or with the aromatic ring of benzene to bring about stabilization. The stabilization effects are compared to that of a methyl group. The H^0_{rel} of vinyl

Table 2 Relative enthalpies of halogen derivatives of methane and ethane

Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_{f} (kJ mol^{-1})	Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_{f} (kJ mol^{-1})
CH_3F	6.5	−233.9	CH_3Br	6.7	−37.7
CH_2F_2	−36.1	−452.9	CH_2Br_2	24.6	−4.2
CHF_3	−104.4	−697.5	$CHBr_3$	36.2	25.1
CF_4	−163.6	−933.0	CBr_4	43.7	50.2
CH_3Cl	3.1	−86.3	CH_3I	2.5	14.0
CH_2Cl_2	19.5	−95.4	CH_2I_2	31.0	118.0
$CHCl_3$	39.0	−101.3	CHI_3	48.3	210.9
CCl_4	65.2	−100.4	CI_4	29.8	267.9 [5]
CH_3–CHF_2	−56.4	−493.7	CH_3–CF_3	−131.9	−745.6
CF_3Cl	−75.1	−694.5	CF_3Br	−73.5	−648.9
CF_3I	−72.4	−689.9			

Table 3 Relative enthalpies of secondary and tertiary alkyl halides

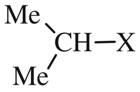
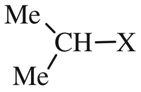
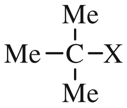
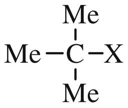
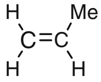
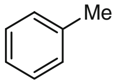
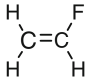
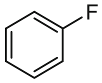
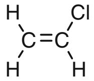
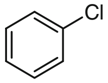
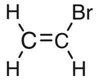
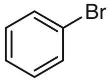
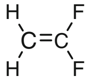
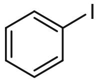
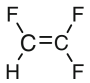
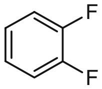
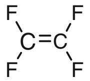
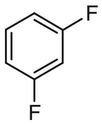
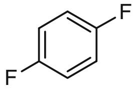
X	 H^{o}_{rel} (kJ mol^{-1})	 ΔH^{o}_{f} (kJ mol^{-1})	 H^{o}_{rel} (kJ mol^{-1})	 ΔH^{o}_{f} (kJ mol^{-1})
Me	−8.6	−134.5	−19.5	−166.0
F	−33.9	−315.5 [6]	−57.6	−359.8[6]
Cl	−15.7	−146.4	−32.0	−183.3
Br	−9.4	−97.1	−25.6	−133.3
I	−12.1	−41.8	−23.3	−73.6

Table 4 Relative enthalpies of halogen derivatives of ethylene and benzene

Compound	H^{o}_{rel} (kJ mol^{-1})	ΔH^{o}_{f} (kJ mol^{-1})	Compound	H^{o}_{rel} (kJ mol^{-1})	ΔH^{o}_{f} (kJ mol^{-1})
	82.3	20.4		64.0	50.0
	81.5	−136.0 [7]		53.2	−116.6
	101.6	35.1		70.6	51.8
	102.0	78.4		80.8	105.0
	48.7	−345.2		80.4	162.5
	74.5	−495.8		51.5	−294.5
	88.0	−658.6		36.1	−310.0
	76.3	82.9		38.8	−307.2

fluoride is about the same as that of propene but in the case of chloride and bromide a considerable destabilization can be observed. A second substitution by fluorine on the same carbon atom results in a large (−33 kJ/mol) stabilization. Introduction of a third and fourth fluorine into the molecule brings about destabilization.

Replacing the methyl group of benzene by fluorine shows −11 kJ/mol stabilization relative to toluene. The

Table 5 Relative enthalpies of carboxylic acid halides

Compound	H_{rel}^{0} (kJ mol^{-1})	$\Delta H_{\mathrm{f}}^{0}$ (kJ mol^{-1})	Compound	H_{rel}^{0} (kJ mol^{-1})	$\Delta H_{\mathrm{f}}^{0}$ (kJ mol^{-1})
Me–CO–Me	−29.9	−217.6	Ph–CO–Cl	12.6	109.2
Me–CO–F	−101.8	−445.2	Ph–CO–Br	30.2	−48.5
Me–CO–Cl	−51.9	−244.3	Ph–CO–I	31.3	10.5
Me–CO–Br	−41.4	−190.8	CH_2Cl–CO–Cl	−27.7	−245.6
Me–CO–I	−34.9	−125.9	$CHCl_2$–CO–Cl	1.8	241.4
Me–COO–Me	−96.1	−409.6	CCl_3–CO–Cl	31.8	−236.8
		50.0	Cl–CO–CO–Cl	−26.1	−326.4

Table 6 Relative enthalpies of carbonyl halides

Compound	H_{rel}^{0} (kJ mol^{-1})	$\Delta H_{\mathrm{f}}^{0}$ (kJ mol^{-1})	Compound	H_{rel}^{0} (kJ mol^{-1})	$\Delta H_{\mathrm{f}}^{0}$ (kJ mol^{-1})
F–CO–F	−140.8	−639.9	Br–CO–Br	27.1	−84.1
Cl–CO–Cl	−21.6	−218.8			

stabilization effect of chlorine is less than that of the methyl group. Bromine and iodine substitution show destabilization. A second substitution by fluorine in fluorobenzene brings about a considerable further stabilization if the two substituents occupy 1,3 or 1,4 position in the ring.

Carboxylic acid halides

Carboxylic acid halides are known as very reactive compounds. They contain a halogen atom bonded to a carbonyl carbon. For this reason their relative energy can be compared to those of ketones and carboxylic acid esters. The H_{rel}^{0} of acetyl fluoride in Table 5 indicates the stabilization effect of the fluorine atom that is much larger that that of the methyl group in acetone. In fact the stabilization effect of the fluorine atom is in the range of that of an OMe group in methyl acetate (Part I). In other words the relative energies of thee carboxylic acid fluorides are about the same as the relative energies of esters.

The data of Table 5 also demonstrate that the stabilization effect of the chlorine atom in the acid halides is about half of that of fluorine and a further gradual reduction is observed toward bromides and iodides. Thus the relative energy of acetyl iodide is about the same as that of acetone.

The H_{rel}^{0}s of the benzoyl halides are compared to those of the corresponding acetyl halides. As expected the presence of the aromatic ring in the molecules increases the energy. The energy differences, however, are only 64–71 kJ/mol, somewhat smaller than the H_{rel}^{0} of benzene (76.3 kJ/mol).

Table 5 also demonstrates that replacing by chlorine of hydrogen atoms on the α carbon atom of acetyl chloride its stabilization is reduced and the relative energy is gradually increased.

Among the gas phase heats of formation of dicarboxylic acid chlorides only that of oxalyl chloride is available. Its H_{rel}^{0} suggests that direct bonding of the two carbonyl groups is unfavorable since in the case of a compound containing two isolated –CO–Cl groups a H_{rel}^{0} of about −100 kJ/mol would be expected.

Carbonyl halides

In Table 6 H_{rel}^{0}s of three carbonyl halides are listed. Comparison of the H_{rel}^{0} of carbonyl fluoride to that of acetyl fluoride (Table 5) shows that replacing of the methyl group in acetyl fluoride by a second fluorine atom further reduces the energy by about 40 kJ/mol. Replacement of one of the two methyl groups of acetone to give acetyl fluoride results in a larger, 70 kJ/mol reduction. The H_{rel}^{0}s of carbonyl chloride and of carbonyl iodide indicate that replacing of the methyl group of the corresponding acetyl halide by bromine or iodine brings about an increase in the relative energy.

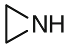
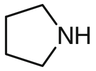
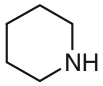
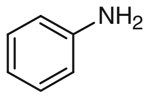
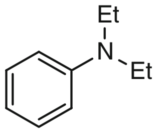
Nitrogen compounds

As expressed by its H_{rel}^{0} in Table 7 nitrogen is a very low energy element. The reference compound of the nitrogen containing organic compounds is triethyl amine. The H_{rel}^{0} of this compound is fixed to zero.

Amines

Amines are derived from ammonia. In ammonia all bonds of nitrogen are formed with hydrogen. While the H_{rel}^{0} of the reference compound, triethyl amine is zero, that of ammonia is a large negative value (Table 7).

Table 7 Relative enthalpies of amines

Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_{f} (kJ mol^{-1})	Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_{f} (kJ mol^{-1})
N_2	−178.62	0	Et_3N	0.0	−99.6
NH_3	−69.8	−45.7	Pr_3N	0.6	160.8 [8]
Me–NH_2	−26.5	−23.0	$(C_8H_{17})_3N$	−4.3	474.8 [9]
Et–NH_2	−28.9	−46.0	iPr-NH_2	−45.1	−83.8
Pr–NH_2	−34.7	−72.4	tBu-NH_2	−61.5	−119.9
Bu–NH_2	−33.7	−92.0		97.1	123.4
Me_2NH	−1.7	−18.8		11.3	−3.6
Et_2NH	−14.1	−72.4		−13.5	−49.0
Me_3N	13.8	−23.8		12.7	86.9
				48.5	40.2

The H^0_{rel}s of the primary, secondary, and tertiary amines are gradually increasing, showing that bonding of nitrogen to hydrogen is more favorable than bonding to carbon. This behavior is similar to that of oxygen. H^0_{rel}s of 2-amino-propane and 2-methyl-2 amino-propane demonstrate that bonding of the amino group to a higher order carbon atom results in decreasing of energy.

The cyclic amines are secondary amines and so their H^0_{rel}s are expected to be lower by about 14 kJ/mol than those of the cyclic alkanes. This is the case when the H^0_{rel}s of piperidine and cyclohexane (0.6 kJ/mol) and H^0_{rel}s of pyrrolidine and cyclopentane (25.9 kJ/mol) are compared to each other. The difference between the H^0_{rel} of aziridine and cyclopropane (115.2) is not much different: 18 kJ/mol.

The data of Table 7 help to see whether or not there is an energy reducing interaction between the aromatic ring of benzene and the amino group. Replacing a methyl group of propane (1.5 kJ/mol) by an amino group reduces the H^0_{rel} by 30 kJ/mol. By replacing a methyl group of toluene (64.0 kJ/mol) by the same group the H^0_{rel} decreases by a much larger value: 51 kJ/mol. This indicates a −21 kJ/mol extra stabilization. An extra stabilization can be deduced in the case of diethylamino benzene too.

Carboxylic acid amides

The H^0_{rel}s listed in Table 8 show that carboxylic acid amides are low energy compounds and in this respect resemble the esters. The H^0_{rel} of *N*,*N*-dimethyl formamide, for example, is somewhat lower than those of methyl and ethyl formiate (−56.9 and −57.8 kJ/mol, respectively, Part I) and *N*,*N*-diethyl acetamide can also be placed near the range of the H^0_{rel}s of the acetic acid esters (−96 to −110 kJ/mol, Part I).

The energy of the unsubstituted amides, as a consequence of the two N–H bonds that reduces the energy, is of course lower than that of the esters. If the two unsubstituted amides, formamide and acetamide are compared, as expected, the H^0_{rel} of the latter is considerably lower than that of formamide.

The possibility of extra stabilization due to the acetamido group in acetanilide relative to the methyl group in

Table 8 Relative enthalpies of carboxylic acid amides

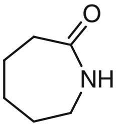
Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_f (kJ mol^{-1})	Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_f (kJ mol^{-1})
H–CO–NH_2	−107.3	−186.2	H–CO–$N(CH_3)_2$	−71.5	−191.6
Me–CO–NH_2	−138.8	−238 [10]	Me–CO–$N(C_2H_5)_2$	−96.3	−278.2 [11]
Bu–CO–NH_2	−128.9	−290.2	Me–CO–NH–Ph	−79.0	−128.9
Me–CO–NH–Bu	−122.7	−304.7		−107.5	−246.0

Table 9 Relative enthalpies of hydrazine derivatives

Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_f (kJ mol^{-1})	Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_f (kJ mol^{-1})
H_2N–NH_2	3.5	95.2	NH_3	−69.8	−45.7
Me–NH–NH_2	14.3	85.4	Me–NH–NH–Me	39.5	90.0
$(CH_3)_2N$–NH_2	34.4	84.9	Ph–NH–NH_2	62.1	203.8

toluene is revealed by considering the following comparisons. If one methyl group of pentane (0.0 kJ/mol) is replaced by the acetamido group to form *N*-butyl-acetamide the energy decreases by 122.7 kJ/mol. If the methyl group in toluene (64.0 kJ/mol) is replaced by the same acetamido group to form acetanilide the energy decreases by 143 kJ/mol. This indicates a −20 kJ/mol extra stabilization.

Hydrazine derivatives

Comparing the H^0_{rel} of hydrazine (Table 9) to the sum of H^0_{rel}s of two molecules of ammonia, one can conclude that the N–N bond in hydrazine is very unfavorable. Substitution of hydrogen atoms of hydrazine by methyl groups further increases the H^0_{rel}s.

Another comparison demonstrates that there is an energy reducing extra interaction in phenyl hydrazine. Replacing one methyl group of ethane (0.0 kJ/mol) by the –NH–NH_2 group to form methyl hydrazine the energy increases by 14.3 kJ/mol. Replacing the methyl group of toluene (64.0 kJ/mol) by the same group to form phenyl hydrazine the energy is reduced by 1.9 kJ/mol. This shows a −16 kJ/mol extra stabilization.

Nitriles

Nitriles are derivatives of hydrogen cyanide. Hydrogen cyanide contains a triple bond like acetylene. Comparison of the H^0_{rel}s of the two compounds listed in Table 10 reveals that the relative energy of hydrogen cyanide is much lower than that of acetylene. In other words the triple bond is much better accommodated by nitrogen than by carbon.

The data also show a considerable reduction of energy (around 22–39 kJ/mol) by replacing the hydrogen atom of hydrogen cyanide by alkyl groups.

It is a question whether or not there is a stabilizing interaction between the triple bonded carbon and the aromatic ring in benzonitrile. The difference of the H^0_{rel}s of propane (1.5 kJ/mol) and acetonitrile is 0.0 kJ/mol. The difference of the H^0_{rel}s of toluene (64.0 kJ/mol) benzonitrile is 14.4 kJ/mol. So instead of stabilization a destabilization of around 14 kJ/mol is observed.

Table 10 Relative enthalpies of nitriles

Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_f (kJ mol^{-1})	Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_f (kJ mol^{-1})
H–C≡C–H	224.5	226.7	Pr–CN	5.5	34.1
H–CN	40.1	130.5	iPr–CN	−3.1	25.4
Me–CN	18.1	87.9	Ph–CN	78.4	218.8
Et–CN	1.5	50.6	NC–C≡C–CN	259.4	529.3

Heteroaromatic compounds

Table 11 comprises the relative enthalpies of heterocyclic compounds and those of benzene and cyclopentadiene for comparisons. These data are expected to reveal the effect of substitutions by nitrogen of the CH groups in aromatic rings.

Table 11 shows that H^0_{rel} of pyridine is lower than that of benzene by 31 kJ/mol. This means that nitrogen is well accommodated in the aromatic ring with reduction of energy. Introduction of a second nitrogen into the ring into non-vicinal positions, as H^0_{rel}s of pyrimidine and pyrazine demonstrate, reduces the energy by a second 31 kJ/mol. The presence of three nitrogen atoms in the ring in 1,3,5 positions further reduces the energy. Replacement of two vicinal CH groups by nitrogen atoms, however, increases the energy relative to benzene. Bonding of the two nitrogen atoms in pyridazine is unfavorable like in hydrazine.

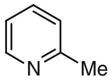
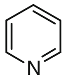
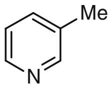
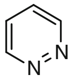
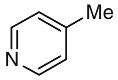
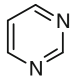
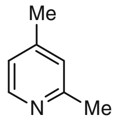
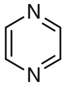
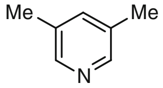
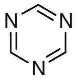
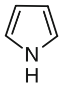
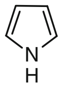
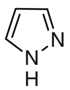
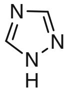
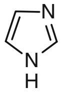
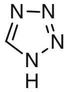
Methyl substitution in the ring of pyridine decreases the energy by 13–21 kJ/mol. The most favorable substitution is in the position vicinal to the nitrogen atom.

Stabilization energy of pyrrole

Pyrrole is considered to be an aromatic compound. In order to deduce its stabilization energy the H^0_{rel}s of pyrrole and cyclopentadiene (Table 11) are compared. It is a problem, however, that the available experimental heats of formation of pyrrole, [3] and [13] in the table, differ too much. Stabilization energies are deduced from both H^0_{rel}s calculated from the two heats of formation.

Using the higher H^0_{rel} value of pyrrole in comparison, calculated from the newer experimental heat of formation [13], shows that replacing the CH_2 group by NH group brings about a 78.7 kJ/mol decrease of energy. About 14 kJ/mol of this can be assigned to the N–H bond in

Table 11 Relative enthalpies of heteroaromatic compounds

Compound	H^o_{rel} (kJ mol^{-1})	ΔH^o_f (kJ mol^{-1})	Compound	H^o_{rel} (kJ mol^{-1})	ΔH^o_f (kJ mol^{-1})
	76.3	82.9		24.8	99.0
	45.4	140.2		32.0	106.1
	95.4	278.4		28.0	102.2
	13.6	196.6		10.3	63.8
	13.1	196.1		19.2	72.8
	−45.4	225.9 [12]		150.1	133.9
	36.3	106.1 [3]		71.4	143.2 [13]
	17.1	177.4 [13]		−55.7	192.7 [14]
	−30.7	129.5 [13]		−16.53	320.0 [15]

pyrrole. The rest, about 65 kJ/mol, can be attributed to aromatic stabilization energy. From the lower H_{rel}^{0} of pyrrole, the same way, around 100 kJ/mol can be deduced for stabilization energy. This value seems to be unbelievably large. For comparison, stabilization energy of benzene is 90.5 kJ/mol (see Part I).

Replacing a CH group in the pyrrole ring by a second nitrogen atom in position 3, a very large reduction of energy is observed (67 and 102 kJ/mol depending on the lower or higher H_{rel}^{0} of pyrrole used in comparisons, respectively). A smaller but also considerable energy reduction can be deduced if the second nitrogen is in position 2 (19 and 54 kJ/mol). The presence of three nitrogen atoms in positions 1,2,4 is a source of a further energy reduction. As reflected by the negative value of the H_{rel}^{0} of tetrazole, the presence of even four nitrogen atoms in the ring is favorable.

Nitrocompounds

Introduction of nitro groups into organic compounds considerably raises their energy. This is clearly reflected by the H_{rel}^{0}s listed in Table 12. Among the mononitro alkanes the H_{rel}^{0} of nitromethane is the highest. The nitro group increases the energy relative to methane (−10.8 kJ/mol) by about 140 kJ/mol. Substitution at the end of longer chains increases the energy only around 120 kJ/mol. The increment is even smaller in the case of the secondary and tertiary nitroalkanes.

The H_{rel}^{0}s of tetranitro methane is exceptionally high. The increment per nitro group is near 180 kJ/mol.

The energy of benzene derivatives is also increased by the presence of nitro groups. The increment is about 120–140 kJ/mol per nitro group. The H_{rel}^{0} of 2,4,6-trinitrotoluene, that is an explosive, is also very high.

Organic nitrites and nitrates

If the H_{rel}^{0}s of alkyl-nitrites listed in Table 13 are compared to those of the corresponding nitro-alkanes of Table 12 it can be observed that their relative energies are about the same.

One of the parent compounds of the alkyl-nitrates is nitric acid. According to H_{rel}^{0}s listed in Table 13 both the nitric acid itself and its alkyl derivatives are high energy compounds. The H_{rel}^{0}s of the alkyl-nitrates are even higher than those of the corresponding nitro derivatives. H_{rel}^{0} of the explosive glycerine trinitrate is particularly high. The energy increment per nitrate group is 211 kJ/mol even larger than that per nitro group of tetranitro-methane.

Inorganic compounds

Table 14 demonstrates the H_{rel}^{0}s of some nitrogen containing inorganic compounds that are calculated using the

Table 12 Relative enthalpies of nitro-compounds

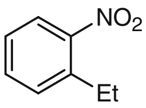
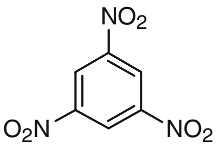
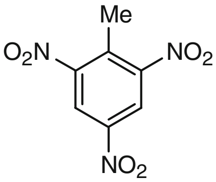
Compound	H_{rel}^{0} (kJ mol^{-1})	$\Delta H_{\mathrm{f}}^{0}$ (kJ mol^{-1})	Compound	H_{rel}^{0} (kJ mol^{-1})	$\Delta H_{\mathrm{f}}^{0}$ (kJ mol^{-1})
Me–NO_2	130.0	−74.7	$C(NO_2)_4$	706.9	80.3
Et–NO_2	124.1	−101.3		186.6	11.3
Pr–NO_2	120.3	−124.7		471.4	56.1
iPr–NO_2	105.8	−140.2		487.4	51.5
tBu–NO_2	89.4	−177.1 [16]			

Table 13 Relative enthalpies of organic nitrites and nitrates

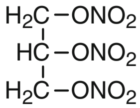
Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_{f} (kJ mol^{-1})	Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_{f} (kJ mol^{-1})
Me–ONO	140.7	−64.0	Me–ONO_2	210.0	−120.5
Et–ONO	121.5	−103.8	Et–ONO_2	197.2	−154.0
iBu–ONO	103.0	−163.6	Pr–ONO_2	197.7	−174.1
HNO_3	175.9	−134.0	iPr–ONO_2	180.7	−191.0
			 $H_2C{-}ONO_2$ $HC{-}ONO_2$ $H_2C{-}ONO_2$	634.0	−270.7

Table 14 Relative enthalpies of inorganic nitrogen compounds

Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_{f} (kJ mol^{-1})	Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_{f} (kJ mol^{-1})
N_2O	28.7	81.5	$ClNO_2$	196.4	−13.1
NO	126.9	90.4	Me–CN	18.1	87.9
NO_2	196.2	33.8	ClCN	67.2	132.2
FNO	168.9	−65.7	BrCN	27.9	136.0
FNO_2	280.9	−78.5	ICN	59.2	225.1

same H^0_{rel}s of the elements that are used in calculation of the organic compounds.

Of the compound listed, H^0_{rel}s of NO, NO_2, FNO, FNO_2, and $ClNO_2$ are exceptionally high. It can also be seen that replacing the methyl group of acetonitrile by halogen atom considerably raises the energy.

Sulfur compounds

In contrast to oxygen, sulfur is a low energy element. Its H^0_{rel} has a considerable negative value (Table 15). This is in part a consequence of the fact that its H^0_{rel} refers to solid state.

Organic sulfides

The reference substances of the sulfur containing organic compounds are the unbranched dialkyl sulfides. H^0_{rel}s of some representatives are listed in Table 15. Like in other reference compound series the first member is again an exception. The H^0_{rel} of dimethyl sulfide is slightly over zero. If the sulfide bond is formed by *sec*-propyl or *tert*-butyl groups the H^0_{rel}s are considerably lower than zero.

In the series of cyclic sulfides the representatives of the strained ring compounds have large positive H^0_{rel}s as expected. It seems worthwhile to note, however, that the H^0_{rel}s of the oxygen containing counterparts are even larger (ethylenoxide: 114.4, oxetane: 107.2 kJ/mol). This indicates that sulfur is better accommodated in strained rings than oxygen.

In aryl-alkyl-sulfides the sulfur atom is attached to the aromatic ring. It is a question whether the sulfur atom or an alkyl group has a larger energy reducing effect. In order to answer the question the H^0_{rel} of phenyl-ethyl-sulfide is compared to that of toluene (64.0 kJ/mol). Although the H^0_{rel} of the sulfide is somewhat lower than that of benzene (73.6) it is higher (by 6 kJ/mol) than the H^0_{rel} of toluene. It can be concluded that although the sulfur atom has a slight energy reducing effect this effect is lower than that of a methyl group. The result is about the same if the H^0_{rel} of diphenyl sulfide is compared to the sum of the H^0_{rel}s of two toluene molecules or to that of diphenyl methane (128.5 kJ/mol).

The relative energies of acetals are lower than their corresponding oxo-compounds (see Part I). The H^0_{rel} of di(ethylthio)methane (Table 15) is also lower than that of formaldehyde (30.5 kJ/mol) by 32 kJ/mol.

Stabilization energy of thiophene

Thiophene is considered to be an aromatic compound. Its stabilization energy can be deduced by comparing its H^0_{rel} to that of cyclopentadiene. The problem is, like in the case of pyrrole, that the available experimental heats of formation [4] and [13] in the table, differ too much. If the lower value of H^0_{rel} is used in the comparison 80.4 kJ/mol comes out for stabilization energy. From the newer and

Table 15 Relative enthalpies of sulfides and thioacetals

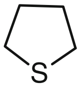
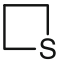
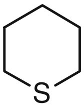
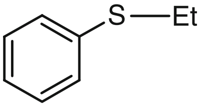
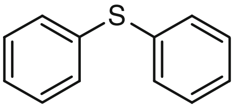
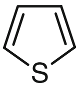
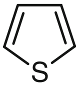
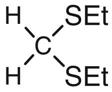
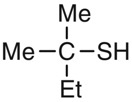
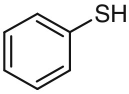
Compound	H^{o}_{rel} (kJ mol^{-1})	ΔH^{o}_{f} (kJ mol^{-1})	Compound	H^{o}_{rel} (kJ mol^{-1})	ΔH^{o}_{f} (kJ mol^{-1})
S(solid)	−41.62	0	O_2	251.66	0
Me–S–Me	5.5	−37.5	Pr–S–Bu	0.2	−145.9
Et–S–Et	0.8	−83.5	Bu–S–Bu	−0.6	−167.3
Et–S–Pr	0.3	−104.6	iPr–S–iPr	−15.7	−141.3
Pr–S–Pr	0.2	18.5	tBu–S–tBu	−40.4	−207.1
	81.8	82.2		7.0	−33.8
	81.3	61.1		−1.6	−63.3
	70.0	77.0		145.6	243.9
	69.7	115.7 [4]		150.1	133.9
	172.3	218.4 [13]		−1.9	−65.2 [17]

Table 16 Relative enthalpies of thiols and thioacetals

Compound	H^{0}_{rel} (kJ mol^{-1})	$\Delta H^{0}_{\mathrm{f}}$ (kJ mol^{-1})	Compound	H^{0}_{rel} (kJ mol^{-1})	$\Delta H^{0}_{\mathrm{f}}$ (kJ mol^{-1})
H–S–H	−18.4	−20.2	Et–OH	−24.3	−234.8
Me–SH	−0.6	−23.0	iPr–SH	−12.6	−76.2
Et–SH	−3.1	−46.1	 $\mathrm{Me{-}\overset{\displaystyle Me}{\underset{\displaystyle Et}{C}}{-}SH}$	−22.1	−127.0
Pr–SH	−4.2	−67.9			
Bu–SH	−3.8	−88.1		63.3	111.5

higher H^0_{rel} no stabilization energy can be deduced. The comparison shows an unbelievable 22 kJ/mol destabilization.

Thiols

Thiols can be deduced from hydrogen sulfide. H^0_{rel} (Table 16) shows hydrogen sulfide to be a relatively low energy compound although its H^0_{rel} is nearly not as low as that of water (−72.6 kJ/mol). Thiols are also slightly low energy compounds, H^0_{rel}s of the primary representatives are 0 to −4 kJ/mol, not as low as those of alcohols (−11 to −26 kJ/mol, see Part I). The H^0_{rel}s of the secondary and tertiary thiols are lower than those of the primary ones like in the case of alcohols.

Considering thiophenol, it is a question whether or not there is an energy reducing interaction between the –SH group and the aromatic ring. The energy reducing effect of the mercapto group is compared to that of the methyl group of toluene (64.0 kJ/mol) taking into account that the free SH group in itself reduces the energy by 3–4 kJ/mol as reflected by the H^0_{rel}s of primary thiols. So the expected H^0_{rel} of thiophenol, if there is no special energy reducing effect, would be 60–61 kJ/mol. Since the H^0_{rel} of thiophenol is not lower but rather somewhat higher, it can be concluded that there is no special energy reducing interaction between the sulfur atom and the aromatic ring.

Disulfides

Data of Table 17 show that in contrast to the high energy peroxides (H^0_{rel} of EtOOEt is 184.7 kJ/mol, Part I) disulfides are relatively low energy compounds. Except dimethyl disulfide, the H^0_{rel}s of the unbranched dialkyl disulfides are −33 kJ/mol. These H^0_{rel}s characterize the S–S bond as an energetically favorable one. If the SS group is bonded to higher order carbon atoms the H^0_{rel}s are further reduced.

Sulfoxides and sulfones

Except dimethyl sulfoxide, H^0_{rel}s of unbranched dialkyl sulfoxides are about −3 to 4 kJ/mol (Table 18). The H^0_{rel} of dimethyl sulfoxide is considerably higher. If the SO group is bonded to a higher order carbon atom H^0_{rel} is reduced.

By replacing of one of the ethyl groups of diethyl sulfoxide by an allyl group the H^0_{rel} is increased as expected by about the H^0_{rel} of propene (82.3 kJ/mol). By replacing both the ethyl groups of diethyl sulfoxide by phenyl groups the H^0_{rel} increment is, also as expected, near to that of diphenyl methane (128.5 kJ/mol).

H^0_{rel}s of dialkyl sulfones are large negative values. Dimethyl sulfone the first member of the series is again an exception. Its H^0_{rel} is about 16 kJ/mol higher than that of the other members of the series. The H^0_{rel} of diphenyl sulfone is higher than that of diethyl sulfone by about the sum of H^0_{rel}s of two toluene molecules (128 kJ/mol) indicating no larger energy reducing effect than that of two methyl groups.

Organic sulfites and sulfates

As reflected by the H^0_{rel}s of Table 19 dialkyl sulfites are low energy compounds. H^0_{rel}s of the corresponding sulfates are considerably lower. The energies of the dimethyl derivatives in both groups are about 20–28 kJ/mol higher than those of the diethyl, dipropyl, or dibutyl counterparts.

Table 17 Relative enthalpies of disulfides

Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_f (kJ mol^{-1})	Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_f (kJ mol^{-1})
Me–SS–Me	−22.8	−24.1	C_5H_{11}–SS–C_5H_{11}	−33.3	−199.6
Pr–SS–Pr	−33.3	−117.2	iBu–SS–iBu	−45.2	−170.3
Bu–SS–Bu	−33.3	−158.4	tBu–SS–iBu	−70.0	−197.1

Table 18 Relative enthalpies of sulfoxides and sulfones

Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_f (kJ mol^{-1})	Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_f (kJ mol^{-1})
Me–SO–Me	24.1	−144.8	Me–SO_2–Me	−78.1	−372.8
Et–SO–Et	4.6	−205.4	Et–SO_2–Me	−94.3	−409.6
Pr–SO–Pr	−3.5	−254.8	Et–SO_2–Et	−94.6	−430.5
tBu–SO–Et	−22.7	−274.1	Pr–SO_2–Pr	−96.9	−474.0
Et–SO–CH_2–CH=CH_2	83.9	103.3	iPr–SO_2–Me	−96.3	−432.2
Ph–SO–Ph	134.2	106.7	Ph–SO_2–Ph	36.6	−116.7

Table 19 Relative enthalpies of alkyl sulfites and sulfates

Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_{f} (kJ mol^{-1})	Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_{f} (kJ mol^{-1})
Me_2SO_3	−62.8	−483.3	Me_2SO_4	−140.2	−686.6
$EtMeSO_3$	−82.7	−523.8	Et_2SO_4	−168.5	756.0
Et_2SO_3	−90.1	−551.9	Pr_2SO_4	−162.8	−791.6
Pr_2SO_3	−84.9	−587.9	Bu_2SO_4	−158.4	−828.4

Table 20 Relative enthalpies of inorganic sulfur compounds

Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_{f} (kJ mol^{-1})	Compound	H^0_{rel} (kJ mol^{-1})	ΔH^0_{f} (kJ mol^{-1})
CS	165.6	230.1	CO	−7.5	−110.5
CS_2	10.9	117.1	CO_2	−164.7	−393.5
COS	−77.1	−138.4	SO_2Cl_2	−53.1	−357.3
SO_2	−86.9	−296.9	SF_4	22.1	−728.4
SO_3	−59.5	−395.3	S_2Cl_2	−6.6	−19.5
$SOCl_2$	−33.3	−211.7			

Inorganic sulfur compounds

In Table 20 relative enthalpies of some inorganic sulfur compounds are listed that may occur in organic reactions as reactants or byproducts. The relative energies of carbon monoxide and carbon dioxide are included for comparisons.

It can be seen that while H^0_{rel} of carbon monoxide is slightly lower than zero carbon monosulfide is a high energy compound. Furthermore, in contrast to carbon dioxide that has a large negative H^0_{rel} that of carbon disulfide is slightly above zero. These data reflect the substantial differences between the properties of oxygen and sulfur.

Oxides of sulfur are low energy compounds as well as their chlorine derivatives. Even thionyl chloride which is a reactive reagent shows up as a relatively low energy compound.

Conclusions

The examples discussed in this article demonstrate that the relative enthalpies are very useful tools for expressing and comparing the energies of organic compounds. They help to better understand and interpret the large amount of information hidden in the experimental heats of formation.

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