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Reactions between Hydrazine, Thiocyanic Acid and Oxo-compounds

IV. Heats of Combustion and Derived Data for some Compounds Related to Thiosemicarbazide

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The heat of combustion was determined and the heat of formation at 20° was calculated for the following compounds: hydrazinium thiocyanate $\Delta Hf(\mathrm{s}) = 9.2 \pm 0.7$ kcal · mole^{-1} and $\Delta Hf(\mathrm{aq}) = 17.1 \pm 0.8$ kcal · mole^{-1}; thiosemicarbazide $\Delta Hf(\mathrm{s}) = 5.7 \pm 0.5$ kcal · mole^{-1} and $\Delta Hf(\mathrm{aq}) = 13.5 \pm 0.7$ kcal · mole^{-1}; acetaldehyde thiosemicarbazone $\Delta Hf(\mathrm{s}) = 15.0 \pm 0.8$ kcal · mole^{-1}; acetone thiosemicarbazone $\Delta Hf(\mathrm{s}) = 4.6 \pm 0.8$ kcal · mole^{-1} and compound A ($C_6H_{10}N_4S_2$) $\Delta Hf(\mathrm{s}) = 32.7 \pm 1.6$ kcal · mole^{-1}.

The thermochemical data have been used further to discuss the equilibrium between hydrazinium thiocyanate and thiosemicarbazide, to calculate the resonance energy of thiosemicarbazones and to compare the exothermicities of the reactions between hydrazinium thiocyanate and oxo-compounds.

THE EQUILIBRIUM BETWEEN HYDRAZINIUM THIOCYANATE AND THIOSEMICARBAZIDE

From a kinetic study at 100° of the isomerization of hydrazinium thiocyanate to thiosemicarbazide and of the reverse reaction in 0.4 M solution it was concluded that the equilibrium is composed of *ca.* 40 % thiosemicarbazide and 60 % hydrazinium thiocyanate *. Using an approximation of activity equal to molarity, one gets for the reaction

$$N_2H_5NCS \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NH_2 \cdot NH \cdot CS \cdot NH_2$$

$$\Delta F^\circ = -RT \ln K = 0.3 \text{ kcal} \cdot \text{mole}^{-1}$$

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* Ref.[1] From the data given in Table 2 the velocity constant, k_1 for the first order forward reaction, assuming $k_1/k_{-1} = 2/3$, was found to be 0.0016, 0.0016 and 0.0017 hour^{-1}. The data for the reverse reaction do not obey a simple first order rate equation.

From heat of combustion and solution data, the heat of formation of hydrazinium thiocyanate and thiosemicarbazide in aqueous solution at 20° was found to be 17.1 and 13.5 kcal · mole^{-1}, respectively. Thus, $\Delta Hr = -3.6 \pm 1.1$ kcal · mole^{-1}. Assuming ΔHr to be independent of temperature between 20 and 100°, the equilibrium constant at 20° is calculated to be 4.6, which gives $\Delta F^\circ = -0.56$ kcal · mole^{-1}. At 20° the equilibrium mixture therefore consists of about 80 % thiosemicarbazide and 20 % hydrazinium thiocyanate. Thus, the position of the equilibrium at room temperature is favourable for the synthesis of thiosemicarbazide from hydrazinium thiocyanate; however, the reaction was found to be too slow to be utilized for this purpose [1].

It is of interest to compare this reaction with the isomerization of hydrazinium cyanate to semicarbazide. Baker and Gilbert [2] investigated this reaction and found $k_1/k_{-1} = 200\,000$ at 15° and 30 000 at 25°. Thus 95 % of a 0.5 M hydrazinium cyanate solution should isomerize within 11 min.

THE RESONANCE ENERGY OF THIOSEMICARBAZONES

The resonance energy of thiosemicarbazide was recently estimated [3] to be 28 kcal · mole^{-1}. It is of interest to compare this value with estimated values of the resonance energy of the thiosemicarbazones. For the purpose of calculating these quantities we computed the change in enthalpy of the reactions:

$$NH_2NHCSNH_2(g) + CH_3CHO(g) \rightarrow CH_3CH{=}N \cdot NHCSNH_2(g) + H_2O(g) \quad (1)$$

$$NH_2NHCSNH_2(g) + (CH_3)_2CO(g) \rightarrow (CH_3)_2C{=}N \cdot NHCSNH_2(g) + H_2O(g) \quad (2)$$

The following data were used for the computation: thiosemicarbazide [3] $\Delta Hf(g) = +24.7$ kcal · mole^{-1}; acetaldehyde [4] $\Delta Hf(g) = -39.76$ kcal · mole^{-1}; acetone [5] $\Delta Hf(g) = -52.6$ kcal · mole^{-1}; water [4] $\Delta Hf(g) = -57.80$ kcal · mole^{-1}.

The heats of sublimation of the thiosemicarbazones were related to that of thiosemicarbazide. A comparison between different amines and their corresponding aldehyde and ketone derivatives (aniline — anils; phenyl hydrazine — phenyl hydrazones; methoxamine — methyl oximes; ethoxamine — ethyl oximes; hydrazine — hydrazones — azines) showed that the boiling points of the aldehyde compounds are in average 5° lower, and of the acetone compounds in average 20° higher than those of the corresponding amines. Using Klages equation [6], the differences between the heats of sublimation of the aldehyde and acetone compounds and the parent amine was calculated to be -0.2 kcal · mole^{-1} and $+0.7$ kcal · mole^{-1}, respectively. The heat of sublimation of thiosemicarbazide [3] was estimated to be 19 kcal · mole^{-1} and thus for acetaldehyde thiosemicarbazone $\Delta Hf(g) = 33.8$ kcal · mole^{-1} and for the acetone compound $\Delta Hf(g) = 24.3$ kcal · mole^{-1}. This gives

$$\Delta Hr_1 = -9 \text{ kcal} \cdot \text{mole}^{-1} \text{ and } \Delta Hr_2 = -6 \text{ kcal} \cdot \text{mole}^{-1}\ *$$

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* The thermochemical bond energy term value of the C = O double bond is 3 kcal larger for ketones than it is for aldehydes [8].

These values may be compared with the heat of reaction for

$$Me_2CH \cdot CHO(g)+H_2N \cdot n\text{-}Bu(g) \rightarrow Me_2CH \cdot CH = N \cdot Bu(g)+H_2O(g) \quad (3)$$

The heat of combustion of the aldimine was determined by Coates and Sutton [7]; for n-BuNH$_2$ a value is found in Kharasch's compilation [5].

The heat of combustion of *iso*butyraldehyde can be computed from known data [5] for heptaldehyde, (ΔHc(liq) $= -1\,062.4$ kcal · mole^{-1}), methyl n-propyl ketone, (-735.6 kcal · mole^{-1}) and methyl i-propyl ketone, (-733.9 kcal · mole^{-1}), by adjustment to the gaseous phase [6] and utilizing the known CH$_2$-increment from values of heats of combustion of a homologue series [9], -154.6 kcal · mole^{-1}. Thus, for *iso*butyraldehyde $\Delta Hc(g) = -607.3$ kcal · mole^{-1}. The formation of the aldimine is therefore accompanied by a change in enthalpy of $\Delta Hr_3 = -9.5$ kcal.

Thus, within the limits of error, the resonance energy for the thiosemicarbazones is the same as it is for the thiosemicarbazide.

REACTIONS BETWEEN HYDRAZINIUM THIOCYANATE AND OXO-COMPOUNDS

When a solution of hydrazinium thiocyanate reacts with acetone, acetone thiosemicarbazone is formed in good yield; the reaction with acetaldehyde is much more complex and a compound with a bicyclic structure is formed [10]. From the thermochemical data [5,4] the following values of the heats of reaction are calculated:

$$N_2H_5NCS(aq)+Me_2CO(aq) \rightarrow Me_2C = N \cdot NHCSNH_2(s)+H_2O(liq) \quad (4)$$
$$\Delta Hr_4 = -18.5 \text{ kcal} \cdot \text{mole}^{-1}$$
$$2N_2H_5NCS(aq)+2MeCHO(aq) \rightarrow C_6H_{10}N_4S_2(s)+2H_2O(liq)+N_2H_4(aq) \quad (5)$$
$$\Delta Hr_5 = -31 \text{ kcal} \cdot \text{mole}^{-1}$$

This reaction, however, is much better carried out in an acid, where an additional decrease in enthalpy of 10 kcal · mole^{-1} occurs due to the neutralization reaction:

$$N_2H_4(aq)+HCl(aq) \rightarrow N_2H_5Cl(aq) \quad (6)$$

The competing process (which does not occur):

$$N_2H_4NCS(aq)+CH_3CHO(aq) \rightarrow CH_3CH = N \cdot NHCSNH_2(s)+H_2O(liq) \quad (7)$$

is accompanied by a $\Delta Hr_7 = 21$ kcal · mole^{-1} which is almost the same value as in reactions 5 to 6 counted on a molar basis. The explanation for the easiness of formation of the more complex reaction product cannot therefore be sought in an extra stabilization of compound A ($C_6H_{10}N_4S_2$) but must be caused by different rates of reaction for the competing mechanisms.

HEATS OF COMBUSTION * AND SOLUTION

Materials. The samples of the substances were purified by repeated recrystallizations from at least two different solvents, pulverized and carefully dried. The purity was check-

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* Dr. Lars Bjellerup made the combustions. I am very grateful for his kind co-operation.

ed by elementary analyses and titrimetric determinations[1]. From the analyses the lower limits of the purity of the substances were estimated and are given below.

Hydrazinium thiocyanate: m.p. 77.5°. Purity better than 99.8 % .
Acetaldehyde thiosemicarbazone: m.p. 146°. Purity better than 99 %.
Acetone thiosemicarbazone: m.p. 179°. Purity better than 99 %.

Compound A (tetrahydro-3,7-dimethyl-s-triazolo(a)-s-triazol-1,5-dithione)[10]: m.p. (decomp.) 170°. The purity could not be estimated from the analyses. The method of synthesis and the low solubility make a good reason for the belief, that the purity is fairly high.

Apparatus and method. The calorimeter and experimental procedure was described in a previous communication[11].

Units of measurement and auxiliary quantities. The results of the combustions are expressed in terms of the 15° calorie in which unit the certified heat of combustion of the benzoic acid (Kahlbaum, 6 324 cal/g "auf den luftleeren Raum bezogen") was given. Unfortunately, the conditions are not precisely known under which this value was obtained. Therefore, the reduction to standard conditions can be slightly uncertain, a value of 6 319 cal/g mass was used. The observed values for the heat of the bomb process were corrected to obtain values for the idealized combustion reaction in which all the reactants and products are in their standard states at 20° and no external work is performed[12].

The accuracy of the obtained results. The combustion experiments referred to in this paper were performed several years ago. At that time the method for the determination of heats of combustion of organo-sulfur compounds was not very well established. The results are therefore not as accurate as they may be obtained to-day, but are believed to be accurate to within 3 to 5 parts in a thousand. The internal consistency, however, is higher and probably about one part in a thousand. For this reason, the usual practice of giving primary data for the combustion experiments was considered of no real use and only the final results will be given.

Energy equivalent of the calorimeter: 4 707.7, 4 709.1, 4 708.7 and 4 712.2, average 4 709.5±1.4 (average deviation) cal/degree.

Heat of combustion of paraffin oil: 10 986, 10 976, 10 969, 10 971, and 10 988, average 10 978±7 cal/g mass.

Heat of combustion of rhombic sulfur: 4 559, 4 570, 4 540, 4 587, average 4 562±15 cal/g mass.

For the reaction

$$\text{S(rhombic)} + 1.5\ \text{O}_2\text{(g)} + 10\,001\ \text{H}_2\text{O(liq)} = \text{H}_2\text{SO}_4,\ 10\,000\ \text{H}_2\text{O}$$
$$\Delta Ec\ (293°) = 146.3 \pm 0.4\ \text{kcal} \cdot \text{mole}^{-1}$$

Recalculated to the formation of H_2SO_4, 115 H_2O the value becomes

$$\Delta Ec\ (293°) = 143.3 \pm 0.4\ \text{kcal} \cdot \text{mole}^{-1}$$

which is almost identical to that obtained when the method became better established[12].

Heats of combustion: Hydrazinium thiocyanate: 4 605, 4 615, 4 628, 4 608, average 4 614 cal · g mass^{-1}

Thiosemicarbazide: 4 578, 4 562, 4 582, 4 576 ,average 4 574 cal · g mass^{-1}
Acetaldehyde thiosemicarbazone: 5 821, 5 827, 5 825, average 5 824 cal · g mass^{-1}
Acetone thiosemicarbazone: 6 365, 6 358, 6 345, 6 362, average 6 358 cal · g mass^{-1}
Compound A: 6 100, 6 083, 6 084, 6 069, average 6 084 cal · g mass^{-1}

These values are valid for the formation of gaseous carbon dioxide, liquid water and H_2SO_4, 10 000 H_2O at 20° and constant volume.

Heats of formation. By use of the obtained value for the heat of combustion of rhombic sulfur to H_2SO_2, 10 000 H_2O, $\Delta Ec(293°) = 146.3$ kcal · mole^{-1}, and the known heats of formation of carbon dioxide and water $\Delta Hf(293°) = 94\,050$ and 68 355 cal · mole^{-1}, respectively, the following values for the heats of formation from graphite, gaseous hydrogen, oxygen and nitrogen and rhombic sulfur were derived:

$\mathrm{C(graphite)} + 2\tfrac{1}{2}\ \mathrm{H_2(g)} + 1\tfrac{1}{2}\ \mathrm{N_2(g)} + \mathrm{S(rhombic)} = \mathrm{N_2H_5SCN(s)}$
$\Delta Hf\ (293°) = +9.2 \pm 0.7^{*}\ \mathrm{kcal \cdot mole^{-1}}$
$\mathrm{C(graphite)} + 2\tfrac{1}{2}\ \mathrm{H_2(g)} + 1\tfrac{1}{2}\ \mathrm{N_2(g)} + \mathrm{S(rhombic)} = \mathrm{NH_2NHCSNH_2(s)}$
$\Delta Hf\ (293°) = +5.7 \pm 0.5\ \mathrm{kcal \cdot mole^{-1}}$
$3\ \mathrm{C(graphite)} + 3\tfrac{1}{2}\ \mathrm{H_2(g)} + 1\tfrac{1}{2}\ \mathrm{N_2(g)} + \mathrm{S(rhombic)} = \mathrm{CH_3CH} = \mathrm{NNHCSNH_2(s)}$
$\Delta Hf\ (293°) = +15.0 \pm 0.2\ \mathrm{kcal \cdot mole^{-1}}$
$4\ \mathrm{C(graphite)} + 4\tfrac{1}{2}\ \mathrm{H_2(g)} + 1\tfrac{1}{2}\ \mathrm{N_2(g)} + \mathrm{S(rhombic)} = \mathrm{(CH_3)_2C} = \mathrm{NNHCSNH_2(s)}$
$\Delta Hf\ (293°) = +4.6 \pm 0.8\ \mathrm{kcal \cdot mole^{-1}}$
$6\ \mathrm{C(graphite)} + 5\ \mathrm{H_2(g)} + 2\ \mathrm{N_2(g)} + 2\mathrm{S(rhombic)} = \mathrm{C_6H_{10}N_4S_2(s)}$
$\Delta Hf\ (293°) = +32.7 \pm 1.7\ \mathrm{kcal \cdot mole^{-1}}$

Heats of solution. The heats of solution of hydrazinium thiocyanate and thiosemicarbazide were determined in an "isothermal" reaction calorimeter of the Dewar-type. The pulverized sample of the crystalline material was dissolved in distilled water and the temperature decrease was read on a Beckmann thermometer. The accuracy of the determinations was better than 1 %. The strengths of the final solutions were 1 % (hydrazinium thiocyanate) and 0.4 % (thiosemicarbazide).

$\mathrm{N_2H_5NCS(c)} = \mathrm{N_2H_5NCS(aq)};\ \Delta H = +7.9\ \mathrm{kcal \cdot mole^{-1}}$
$\mathrm{NH_2NHCSNH_2(c)} = \mathrm{NH_2NHCSNH_2(aq)};\ \Delta H = +7.7\ \mathrm{kcal \cdot mole^{-1}}$

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* Average error from the determinations of heat of combustion of the substances, all errors in common are not included. When comparing these values with those obtained in other laboratories the total error should be calculated and used.