

Thermochemical Investigations on Organic Sulfur Compounds

V. On the Resonance Energy of Thiolacetic Acid, Thiourea, Thiosemicarbazide, Thiophene and Thianthrene

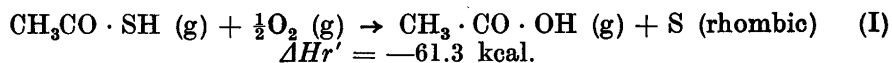
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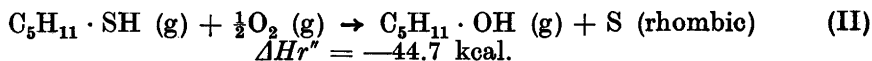
From determinations of heats of combustion and from values of thermochemical bond energies given in communication IV¹, the following resonance energy values have been computed: thiolacetic acid 4-5 kcal. mole⁻¹; thiourea 27 kcal. mole⁻¹; thiosemicarbazide 28 kcal. mole⁻¹; thiophene 20 kcal. mole⁻¹ and thianthrene (resonance energy in excess of that in the two benzene nuclei) 17 kcal. mole⁻¹.

The following heats of formation have been computed from combustion experiments: Thiophene ΔH_f° (liq) = 19.13 ± 0.15 kcal. mole⁻¹ at 25° C and Thiolacetic acid ΔH_f° (liq) = -51.5 ± 0.35 kcal. mole⁻¹ at 20° C.

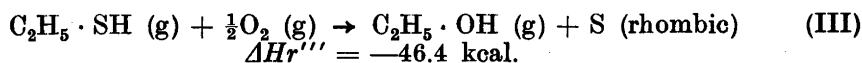
Thiolacetic acid. A comparison between the heats of formation of gaseous thiolacetic acid, ΔH_f (g) = -42.6 kcal. mole⁻¹, and gaseous monomeric acetic acid, ΔH_f (g) = -103.9^{2,3}, may be used to calculate the difference in resonance energy between the two acids, as follows:



Further, from the heats of formation of gaseous *n*-pentanol^{4,5}, -71.3 kcal. mole⁻¹, and 1-pentanethiol¹, -26.7 kcal. mole⁻¹:



By analogy, from ethanol² and ethanethiol²

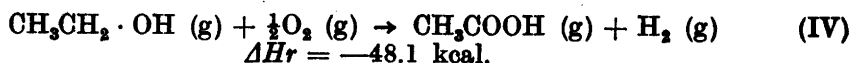


In a normal case, the substitution of an oxygen for a sulfur atom decreases the enthalpy of formation by an average of 45.5 kcal. In the case of the acids the decrease is 61.3 kcal. Thus, we can write

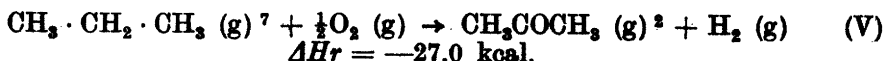
$$R_{\text{HSAC}} = R_{\text{HOAC}} - 16 \text{ kcal.} \quad (1)$$

where R_{HSAC} and R_{HOAC} are the resonance energies of thiolacetic and acetic acid, respectively.

To estimate the magnitude of the resonance energy for acetic and thiolacetic acid we proceed as follows: The resonance energy of acetic acid is found using the equation:



For the analogous reaction

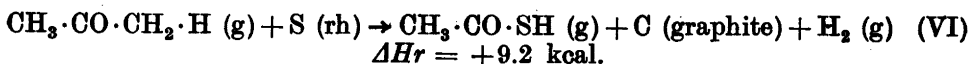


A comparison gives immediately

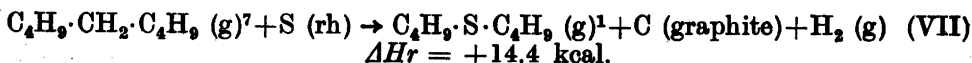
$$R_{\text{HOAC}} = 21 \text{ kcal.}$$

in agreement with the result of 22 kcal., obtained by the group equivalent method⁶. From equation 1 $R_{\text{HSAC}} = 5$ kcal. is deduced.

The resonance energy of thiolacetic acid may be calculated using another approach. If we look at the acid as an acetone molecule, substituting a sulfur atom for a CH_2 group, we can write:



Comparing it with



we get directly

$$R_{\text{HSAC}} = 5.2 \text{ kcal.}$$

The difference between the resulting values R_{HOAC} and R_{HSAC} is 15.9 kcal., in excellent agreement with the 16 kcal. found above. According to the conventional procedure one calculates from bond energy term values and heats of atomization of the elements⁸

$$R_{\text{HOAC}} = 19.2 \text{ kcal. and } R_{\text{HSAC}} = 3.8 \text{ kcal.}$$

The difference, 15.4 kcal., is also in good agreement with the result from the direct comparison between acetic and thiolacetic acid.

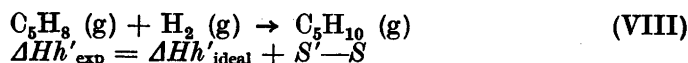
We conclude, that the resonance energy of thiolacetic acid is small compared with that of acetic acid, the value being only 4—5 kcal. mole⁻¹.

Thiophene. A cyclic, resonating molecule like thiophene may be thought of as possessing energy properties deviating from those of a normal molecule, mainly due to strain and resonance. Sketching the thiophene atom sequence

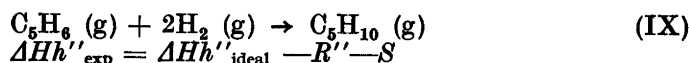
in the most stable configuration and with the ring opened up we get essentially a *trans*-1-mercapto-1,3-butadiene. This molecule is also stabilized by resonance, but it can be said — by definition — to be unstrained*.

By an adequate comparison between the structure — CH = CH — CH = CH — S — and selected structural elements the resonance energy in the mercaptobutadiene can be estimated. From experiments one should also be able to determine the energy difference between the butadienethiol and thiophene. The ring closure introduces an extra stabilization due to increased resonance and, at the same time, a strain labilization is created. It is not possible to separate these two effects by thermochemical experiments and we are therefore forced to incorporate the strain energy term into the resonance energy term. In doing this we must consider it desirable to put the strain energy solely into the cyclic, resonating moiety and select corresponding standard structural elements as free from strain as possible. The argument may be illustrated by the following example:

In estimating the resonance energy of *cyclopentadiene* from heats of hydrogenation by the Kistiakowsky method⁹, it has often been advocated that the best choice of a comparable molecule would be *cyclopentene*. Twice the heat of hydrogenation of *cyclopentene* should be identical to the ΔHh -value of *cyclopentadiene*, were it not for the presence of resonance in the lastmentioned molecule. Introducing $\Delta Hh'$ and $\Delta Hh''$ for the heats of hydrogenation of *cyclopentene* and *cyclopentadiene*, respectively; S and S' for the strain energy in *cyclopentane* and *cyclopentene*, R'' for the net stabilization energy (formally the difference resonance energy minus strain energy) of the *cyclopentadiene* moiety and the subscripts real and ideal to denote the character of the process, we can write



and

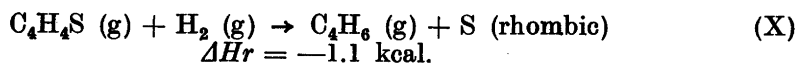


Remembering that $\Delta Hh''_{\text{ideal}} = 2 \Delta Hh'_{\text{ideal}}$, we get

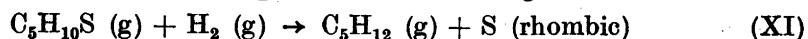
$$2\Delta Hh'_{\text{exp}} - \Delta Hh''_{\text{exp}} = R'' + 2S' - S$$

Only if $2S' = S$ can the Kistiakowsky method give information on the net stabilization (resonance) energy of *cyclopentadiene*.

The procedure may be used for the determination of the resonance energy of thiophene in the following reaction:



The heat of formation of butadiene $\Delta Hf(\text{g}) = +26.33 \text{ kcal. mole}^{-1}$ is obtained from Ref.². This reaction is compared to the following reaction:



* A discussion concerning the experimental approach to the problem of determining strain and resonance energies and the definition of these concepts will be published later.

ΔH_f (g) = -15.14 kcal. mole $^{-1}$ for thiacyclohexane¹ and -35.00 kcal. mole $^{-1}$ for pentane⁷.

$$\Delta H_r = -19.9 \text{ kcal.}$$

It has been shown¹ that thiacyclohexane is without strain, pentane is evidently also strainless. The resonance energy of 1,3-butadiene is 3.5 kcal. mole $^{-1}$ ⁹.

The difference between the ΔH_r -values equals the resonance energy of thiophene less that of butadiene, thus $R = 22.3$ kcal. mole $^{-1}$.

A different approach gives a comparison with the indirectly obtained value for the heat of hydrogenation of thiophene to thiacyclopentane:



ΔH_f (g) = $+27.5$ kcal. mole $^{-1}$ for thiophene and -8.1 kcal. mole $^{-1}$ for thiacyclopentane^{*}

$$\Delta H_h = -35.6 \text{ kcal.}$$

However, the hydrogenation product, the thiacyclopentane molecule, is strained. It has been found that thiacyclohexane is unstrained¹ and from the heat of formation values of the five- and six-membered rings, -8.1 and -15.14 kcal., respectively, and the CH_2 -increment in the heat of formation of *n*-alkanes, -4.926 kcal.¹², the strain energy of the ring is found to be 2.1 kcal. Thus, the heat of hydrogenation of thiophene to a hypothetical strainless thiacyclopentane should have been $-35.6 - 2.1 = -37.7$ kcal. mole $^{-1}$. This result should be compared with the heat of hydrogenation of a *trans*-alkene (since the *cis*-alkene is 'strained' in comparison with the *trans*-alkene and we want to get strain energy only in the thiophene moiety). From the heat of formation of *trans*-3-hexene⁷ and hexane⁷ $\Delta H_h = -27.4$ kcal. mole $^{-1}$ is obtained. Combining this value and the ΔH_h -value for thiophene to a strainless thiacyclopentane one gets $R = 17.1$ kcal. mole $^{-1}$.

In the literature the resonance energy of thiophene is usually given as about 30 kcal. However, using Cottrell's thermochemical bond energy terms and the sulfur-carbon bond energy term from Ref.¹ one gets $R = 22$ kcal. According to the group equivalent method, using data given by Franklin¹³ R becomes also 22 kcal. From Pauling's data in the same way $R = 20$ kcal. is obtained. The best estimate of the resonance energy of thiophene is probably therefore 20 kcal. mole $^{-1}$.

Thianthrene. The heat of formation of thianthrene has been determined to be: ΔH_f° (s) = $+43.15$ kcal. mole $^{-1}$ **.

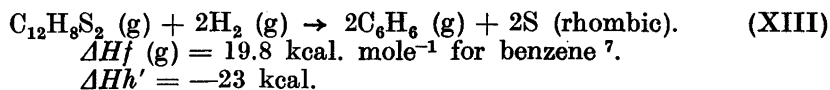
The heat of sublimation of thianthrene was estimated to be 20 kcal. mole $^{-1}$ from a comparison between vapor pressure data of naphthalene, anthracene and phenanthrene⁵, combined with melting and boiling temperatures of these

* Ref.¹⁰. The author obtained -6.6 kcal.¹¹. The difference is partly due to an erroneous value of the heat of vaporization. The USBM-value is believed to be more reliable and it has therefore been used here.

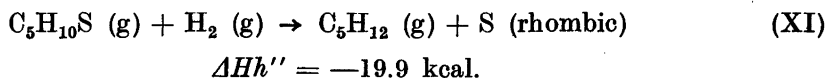
** Average of the values obtained at this laboratory¹⁴ and at US Bureau of Mines, Bartlesville¹⁰.

compounds and thianthrene. Klages' equation gives 18.5 kcal.¹⁵ Thus, $\Delta H_f(g) = +63$ kcal. mole⁻¹.

The resonance energy of thianthrene in excess of that of the two benzene nuclei is obtained from the following formal reaction.



For comparison we chose reaction (XI) above.



Thus, $\Delta Hh' - 2 \Delta Hh''$ becomes 17 kcal. which equals the resonance energy of thianthrene in excess of that of the two benzene nuclei. Thus, the total resonance energy of thianthrene is 89 kcal. (The resonance energy of benzene, 36 kcal., is the value obtained by use of the group equivalent method ⁶). Using the thermochemical bond energy terms on reaction (XIII) one also gets $R = 17$ kcal. and 89 kcal., respectively.

Thiourea and thiosemicarbazide. In an early paper from this laboratory the heats of combustion for thiourea and urea ¹⁶ were given. Although the results were not very accurate they have been recalculated according to later requirements ¹¹. The value of the heat of combustion of crystalline thiourea to water, carbon dioxide and rhombic sulfur thus becomes $\Delta Ec^\circ = -209.4$ kcal. mole⁻¹ and the heat of formation is calculated to $\Delta H_f(c) = -21.4$ kcal. mole⁻¹. (*Selected Values* ² gives -22.1 kcal.). The heat of sublimation has been roughly estimated to be 15 kcal. mole⁻¹. Pauling used $\Delta H_{\text{vap}} = 18$ kcal. mole⁻¹ for urea ¹⁷ and Wheland's estimate ⁹ was 16 kcal. mole⁻¹. Considering the differing hydrogen bonding in the two substances estimated to 6 kcal. mole⁻¹ for urea and 1 kcal. mole⁻¹ for thiourea and the ca. 2 kcal. higher ΔH_{vap} value for a C=S compound compared with the corresponding oxygen analogue, the difference between the heats of sublimation of urea and thiourea was estimated to be 3 kcal. mole⁻¹. The heat of formation of gaseous thiourea thus becomes $\Delta H_f(g) = -6$ kcal. Using thermochemical bond energy and heat of atomization values from Cottrell ⁸, we get

$$E_{\text{C}=\text{S}} + R_{\text{thiourea}} = 142 \text{ kcal.}$$

where R_{thiourea} is the resonance energy. Comparing the analogous equations for CS₂, COS and MeCNS ¹ we find:

$$E_{\text{C}=\text{S}} + R_{\text{MeCNS}} = 118 \quad (1)$$

$$E_{\text{C}=\text{S}} + 0.5 R_{\text{CS}_2} = 121 \quad (2)$$

$$E_{\text{C}=\text{S}} + R_{\text{COS}} = 134 \quad (3)$$

$$E_{\text{C}=\text{S}} + R_{\text{thiourea}} = 142 \quad (4)$$

The equations clearly show that the interaction energy increases in the series from MeCNS to thiourea. This is an obvious reason for treating the bond energy

term and the resonance energy term separately (*cf.* previous paper). Equations (1)—(3) were used to deduce the C=S bond energy value 115 kcal. mole⁻¹. Substituting this value for E_{C-S} in equation (4) we get

$$R_{\text{thiourea}} = 27 \text{ kcal.}$$

The heat of formation of thiosemicarbazid has been deduced from its heat of combustion, determined in this laboratory*.

$$\Delta H_f (c) = +5.8 \text{ kcal. mole}^{-1}.$$

The heat of vaporization is very roughly estimated to 19 kcal. mole⁻¹ (from boiling point differences between amines and hydrazines, Klages' equation for ΔH_{vap} at 25° C, and the value 16 kcal. for the heat of sublimation of thiourea). Thus $\Delta H_f (g) = 25 \text{ kcal. mole}^{-1}$ for gaseous thiosemicarbazide. By a calculation similar to that used for thiourea we obtain ($E_{N-N} = 21 \text{ kcal.}^8$, R_{td} is the resonance energy of thiosemicarbazid):

$$E_{C-S} + R_{\text{td}} = 143$$

The value is almost identical with that obtained for thiourea. This is also to be expected, as the electrons on the 1-nitrogen atom do not participate in the resonance of the NH—CS—NH₂-system. The resonance energy of thiosemicarbazid thus becomes 28 kcal. mole⁻¹.

HEATS OF COMBUSTION

Materials. The thiophene was obtained in a vacuum sealed glass ampoule from US Bureau of Mines, Thermodynamics Laboratory, Bartlesville, USA, as "Samples of API — BM certified sulfur compounds purified at the Laramie Station of the Bureau of Mines and made available by American Petroleum Institute Research Project 48 A on the Production, Isolation and Purification of Sulfur Compounds and the Measurement of their Properties"**. The purity of the thiophene was given as 99.96 ± 0.02 mole-%.

The ampoule was sealed to a Pyrex-glass system, the break-off seal broken in vacuum and the thiophene distilled into the tube where the small glass ampoules for the combustions were placed.

The thiolacetic acid was synthesized according to a method recently described by Sjöberg¹⁸ and distilled five times *in vacuo* in an atmosphere of nitrogen. The main fraction had a b.p. range of 0.01° C; the determination of condensation point differences had to be abandoned due to the catalytic decomposition of the substance in the presence of platinum¹⁹.

Immediately after the last distillation, the ampoules were filled *in vacuo* and the combustions performed without delay***.

Apparatus and method; Units of measurement and auxiliary quantities; Energy equivalent of the calorimeter; Heat of combustion of paraffin oil and Correction for the heat of formation of sulfuric acid. See Ref.¹.

* To be published in *Svensk Kem. Tidskr.* 1955.

** I am much indebted to Dr. Guy Waddington and Mr. Ward Hubbard of the Thermodynamics Laboratory, US Bureau of Mines, Bartlesville, USA for furnishing this sample.

*** Data for the main fraction before the last distillation: B. p. 61.42 at 310 mm Hg, n_D^{20} 1.4648; d_4^{20} 1.0689.

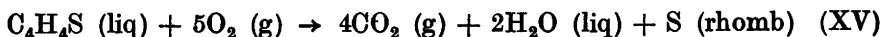
RESULTS OF COMBUSTION EXPERIMENTS **

$$S_B = 5251.3 \text{ cal. per I.U.}, 5255.1 \text{ cal. (x)}.$$

Sample mg mass	Oil mg mass	ΔT_{corr} I.U.	q_{fuse} cal.	q_N cal.	q_{CO_2} cal.	$\Delta E_c/M$ cal. g mass ⁻¹
Thiophene.						
$M = 84.138$; $D_4^{20} 1.065$ $S_F = 0.5 \text{ cal.}$, $q_{\text{wc}} = 0.7 \text{ cal.}$						
362.97 x	214.26	1.00888	14.7	10.7	6.0	6315.4
320.19	242.21	1.00341	16.2	10.5	5.9	6315.9
345.83	220.22	0.99602	14.4	10.7	6.0	6315.0
452.72 x	144.58	0.99975	14.6	10.5	6.3	6315.9
403.21 x	173.13	0.98376	13.4	9.9	6.1	6315.8
					Average	6315.6

Thiolacetic acid.						
$M = 76.118$; $D_4^{20} 1.0689$ $S_F = 0.7 \text{ cal.}$, $q_{\text{wc}} = -0.3 \text{ cal.}$						
244.38	345.85	0.98612	15.1	10.0	5.0	3584.0
203.33	364.42	0.98181	16.0	10.4	5.0	3580.3
219.48	361.33	0.99203	14.3	10.0	5.1	3587.6
					Average	3584.0

For the reaction



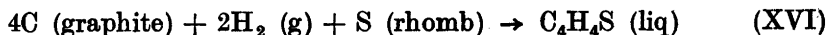
$$\Delta E_c^\circ = -531.38 \pm 0.02 \text{ kcal. mole}^{-1} \text{ and}$$

$$\Delta H_c^\circ = -531.96 \pm 0.02 \text{ kcal. mole}^{-1}.$$

At 25° C the heat of combustion of thiophene at unit fugacity is (heat capacities from Refs.^{2,20}):

$$\Delta H_c^\circ = -531.97 \text{ kcal. mole}^{-1}$$

The heat of formation of liquid thiophene at 25° C is thus

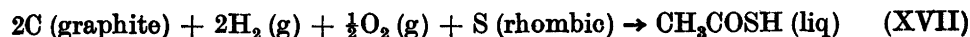


$$\Delta H_f^\circ (\text{liq}) = 19.13 \pm 0.15 * \text{ kcal. mole}^{-1}.$$

The heat of vaporization of thiophene at 25° C is 8.29 kcal. mole⁻¹ according to Waddington *et al.*²⁰.

Thus the heat of formation of gaseous thiophene at 25° C and unit fugacity from the elements in their thermodynamic standard states is $\Delta H_f^\circ (\text{g}) = 27.4 \text{ kcal. mole}^{-1}$.

For the reaction



$$\Delta H_f^\circ (\text{liq}) = -51.5 \pm 0.35 ** \text{ kcal. mole}^{-1} \text{ at } 20^\circ \text{C}.$$

From the boiling points measured at different pressures, the heat of vaporization is estimated to be $8.9 \pm 0.3 \text{ kcal. mole}^{-1}$. It had to be assumed that gaseous thiolacetic acid is monomolecular. Spectroscopic investigations^{21,22}

* Legend, see previous paper, Ref.¹.

** Twice the "overall" standard deviation.

have established, that the hydrogen bonding effect of the thiolcarboxyl group is very weak. One may conclude that the association in the gas phase is at least much less pronounced for thiolacetic acid than for acetic acid and so the error introduced cannot be of real significance for the calculation of the resonance energy.

The heat of formation of gaseous thiolacetic acid was thus computed to be

$$\Delta H_f = -42.6 \text{ kcal. mole}^{-1}.$$

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