© *1982 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***55***, *2808—2813 (1982)* [Vol. 55, No. 9

Thermochemical Studies on Thioacetamide and Tetramethylthiourea. Estimation of Stabilization Energies Due to Interaction between Thiocarbonyl Group and Neighbouring Nitrogen Atom**

Sadayasu Inagaki,† Shigeo Murata, and Minoru Sakiyama*
Chemical Thermodynamics Laboratory and Department of Chemistry,
Faculty of Science, Osaka University, Toyonaka 560

(Received March 10, 1982)

Standard energy of combustion at 298.15 K and standard enthalpy of sublimation as a function of temperature were determined for thioacetamide and tetramethylthiourea by oxygen bomb combustion calorimetry and sublimation calorimetry. Derived standard enthalpies of formation in crystalline and gaseous states at 298.15 K are $-(70.6\pm1.1)$ and (12.7 ± 1.2) kJ mol^{-1}, respectively, for thioacetamide, and $-(38.3\pm2.3)$ and (44.7 ± 2.4) kJ mol^{-1}, respectively, for tetramethylthiourea. Stabilization energies of these molecules were evaluated by estimating the standard enthalpies of formation in gaseous state for the hypothetical reference structures by use of the group contribution method.

While ketones are usually stable substances, thioketones are very unstable at ambient temperatures. This suggests the inherent instability of a thiocarbonyl group as compared with a carbonyl group. However, when a thiocarbonyl group neighbours a nitrogen atom in a molecule, the group is substantially stabilized: Thioamides and thioureas are fairly stable at room temperatures. The stabilization seems to be caused by the interaction of a thiocarbonyl π-electrons with nitrogen lone pair electrons. Analogous but more enhanced stabilization is observed in amides and ureas.

In this paper, standard enthalpies of combustion and of sublimation at 298.15 K are reported on thioacetamide and tetramethylthiourea. Derived standard enthalpies of formation in gaseous state are compared with those estimated for the hypothetical reference structures to evaluate the stabilization energies for these molecules.

Experimental

Materials. Thianthrene, which was used to test the reliability of our combustion calorimetric equipment and procedure for sulfur-containing organic compounds, was synthesized by the method of Fries and Vogt,[1] and was purified by recrystallization from benzene solution followed by vacuum fractional sublimation and zone-melting. Commercial thioacetamide (Nakarai, G. R.) and tetramethylthiourea (Tokyo Kasei, G. R.) were purified by recrystallization from benzene and ligroine solutions, respectively, followed by vacuum fractional sublimation. The purity of the samples was assessed from DSC heating curves in the melting region as follows: thianthrene, 99.93; thioacetamide, 99.99; and tetramethylthiourea, 99.97 mol%, respectively.

Combustion Calorimetry. An isoperibol rotating bomb calorimeter, described elsewhere,[2,3] was employed. The calorimeter was calibrated by burning thermochemical standard benzoic acid (U. S. National Bureau of Standards, SRM 39i) in the presence of 10 g of water at 3.040 MPa of oxygen pressure. The certified value for the specific energy of combustion of the benzoic acid is $-(26434\pm1)$ J g^{-1} under certificate conditions and it follows[4] that the specific energy of combustion is $-(26414\pm1)$ J g^{-1}, where uncertainties are our estimates of standard deviation of mean. The calibration experiments were carried out in the bomb rotation mode to be described below. Mean and standard deviation of the mean for the energy equivalent of the empty calorimetric system ε(calor),[7] derived from nine experiments, were (15162.31 ± 0.55) J K^{-1}.

Thianthrene, thioacetamide and tetramethylthiourea were pressed into pellets. The bomb was charged with a sample, water (10 g), and oxygen (3.040 MPa at 298.15 K). The bomb was not flushed before charging the oxygen in thianthrene and thioacetamide experiments. Every sample was ignited in an ordinary platinum crucible by discharging a 7.184 mF capacitor bank, previously charged to 36.5 V, through a platinum wire.

Both calibration and combustion experiments were designed to include successive four rating periods, denoted with $i(=1-4)$. Each period is composed of twelve 101.5 s intervals. At the end of each interval, a temperature reading displayed on a Hewlett-Packard quartz thermometer (2801A with option M40) with the resolution of 1×10^{-5} K was recorded. Although the temperature reading is the mean during a 100 s duration in the interval, it was taken to be the mean temperature for the whole interval. A sample was ignited at the end of the first rating period. Bomb rotation was started at the end of the first interval of the second rating period and continued to the end of the third rating period.

Temperature readings of the first and fourth rating periods and of the third rating period were fitted to the following integrated forms of the Newton's cooling law equation:
For $i=1$ or 4,

$$\theta = \theta^{\mathrm{s}}_{\infty} - (\theta^{\mathrm{s}}_{\infty}-\theta^{0}_{i})\exp\left[-k(t-t^{0}_{i})\right], \tag{1}$$

and for $i=3$,

$$\theta = \theta^{\mathrm{r}}_{\infty} - (\theta^{\mathrm{r}}_{\infty}-\theta^{0}_{i})\exp\left[-k(t-t^{0}_{i})\right], \tag{2}$$

where $\theta^{\mathrm{r}}_{\infty}$ and $\theta^{\mathrm{s}}_{\infty}$ are the convergence temperatures for the calorimeter in which the bomb is rotating and not rotating, respectively, θ^{0}_{i} is the temperature at time t^{0}_{i}, which is the starting time of the i-th rating period, and k is the cooling constant throughout an experiment.

In the first step of analysis, an appropriate value was assumed for k and a least squares procedure for linear relation between θ and $\exp[-k(t-t^{0}_{i})]$ was conducted for the temperature readings of the first and fourth rating periods, respectively, to determine $\theta^{\mathrm{s}}_{\infty}$ and θ^{0}_{i}. By use of the derived equations, temperature and rate of temperature change were calculated for the midtimes of the first and fourth rat-

---

** Contribution No. 31 from Chemical Thermodynamics Laboratory, Faculty of Science, Osaka University.

† Present address: Chofu Factory, Kobe Steel, Ltd., Shimonoseki, Yamaguchi 752.

TABLE 1. AUXILIARY QUANTITIES

	Formula	ρ / g cm^{-3}	c_p / J K^{-1} g^{-1}	$-(\partial U/\partial p)_T$ / J MPa^{-1} g^{-1}	$-(\Delta U_c^\circ/M)$ / J g^{-1}
Thioacetamide	C_2H_5NS	1.273	(1.21)	(0.052)	—
Tetramethylthiourea	$C_5H_{12}N_2S$	1.17	(1.21)	(0.052)	—
Fuse	$CH_{1.86}O_{0.93}$	1.5	1.70	0.29	16507

ing period. Then, k was calculated with the following equation:

$$k = [(d\theta/dt)_1^m - (d\theta/dt)_4^m]/(\theta_4^m - \theta_1^m),$$

where θ_1^m and θ_4^m are the tempertures at the midtimes of the first and fourth rating periods, respectively, and $(d\theta/dt)_1^m$ and $(d\theta/dt)_4^m$ are the corresponding rates of temperature change. By using successively renewed k values, the procedure described above was repeated, until a consistent set of k and θ_∞^s was obtained. The temperature readings of the third period were fitted to Eq. 2 by the least squares procedure by use of the final k value to determine θ_∞^r and $\theta_3{}^0$.

Corrected temperature rise, $\Delta\theta_c$, was calculated with the following equation:

$$\Delta\theta_c = \theta_e - \theta_b - 101.5k[\theta_\infty^s + 11\theta_\infty^r - \sum_1^{12} \theta_2(j)],$$

where θ_b and θ_e are the temperatures at the start and end of the second rating period, respectively, and $\theta_2(j)$ is the j-th reading of the period. θ_b was calculated from Eq. 1 with $i=1$ by letting $(t-t^0{}_1)=1218$ s, and θ_e is equal to $\theta^0{}_3$. Nitric acid in the bomb solution was converted to ammonia with Devarda's alloy and the ammonia was absorbed in aqueous sulfuric acid of known concentration. The unreacted sulfuric acid was determined with aqueous sodium hydroxide. Nitrous acid was determined by use of Griess-Ilosvay reagent. The amount of nitrous acid was less than 0.1% of nitric acid. Carbon monoxide was scarcely detected from the bomb gas after combustion experiments.

Sublimation Calorimetry. Sublimation enthalpy was measured as a function of temperature with a sublimation calorimetric system described elsewhere,[5)] in which a Calvet microcalorimeter (DAM, ambient to 473 K type), home-made sublimation apparatus (Mark II) and sample containers (Mark C) were incorporated. Both the diameter and the depth of the effusion orifice were 1.0 mm.

Auxiliary Quantities. Relative atomic masses were taken from the recommendation of IUPAC Commission on Atomic Weights (1977). Densities, specific heat capacities, $(\partial U/\partial p)_T$ values, and other auxiliary quantities, which were used to reduce weights to masses in vacuum and to deduce standard energies of combustion from observed calorimetric data, are collected in Table 1. The internal volume of the bomb was 0.3469 dm^3.

Results

Molar standard energies of combustion given in this paper refer to the following idealized combustion reaction at 298.15 K:

$$C_aH_bN_cS_d(c) + [(4a+b+6d)/4]O_2(g)$$
$$+ (116d-b/2)H_2O(l)$$
$$= aCO_2(g) + (c/2)N_2(g) + d[H_2SO_4 + 115H_2O](l),$$

where $a=12$, $b=8$, $c=0$, and $d=2$ for thianthrene, $a=2$, $b=5$, $c=1$, and $d=1$ for thioacetamide, and finally $a=5$, $b=12$, $c=2$, and $d=1$ for tetramethylthiourea.

TABLE 2. COMPARISON OF THE PRESENT RESULT ON THIANTHRENE WITH LITERATURE VALUES

Investigator	$-\Delta H_c^\circ$(c)/kJ mol^{-1}
Hubbard *et al.*[10)]	7251.5±2.2
Keith and Mackle[11)]	7250.3±2.9
Sunner and Lundin[12)]	7252.1±1.2
Hu *et al.*[13)]	7252.6±2.2
Johnson[14)]	7253.6±1.4
Recommened value[15)]	7252.0
Present result	7255.7±1.8

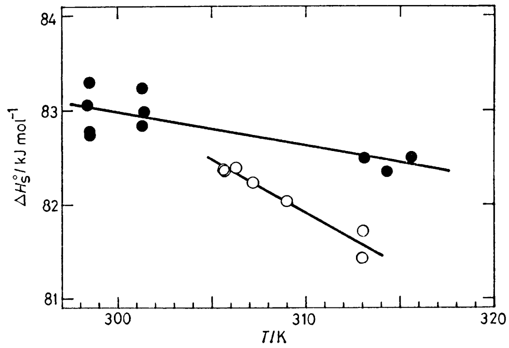

Fig. 1. Standard enthalpy of sublimation versus temperature plot of thioacetamide(○) and tetramethylthiourea(●).

Standard energies of combustion of thianthrene obtained from four experiments were −7241.71, −7245.19, −7242.42, and −7244.05 kJ mol^{-1} with the mean and standard deviation of the mean of −(7243.34±0.79) kJ mol^{-1}. Derived standard enthalpy of combustion is compared with literature values in Table 2. The uncertainty assigned to the present value given in Table 2 is twice the overall standard deviation of mean, to be described below.

Six combustion experiments were carried out for thioacetamide and tetramethylthiourea, respectively. Clean combustion was achieved in every combustion experiment. Combustion calorimetric results on thioacetamide and tetramethylthiourea are presented in Tables 3 and 4, respectively. Most of the symbols in these tables are essentially similar to those used by Hubbard *et al.*[7)] ΔU_Σ denotes the contribution from items 81—85, 87—91, and 93—94 defined by Hubbard *et al.*[7)] The mean and standard deviation of the mean for molar standard energies of combustion were −(2027.79±0.17) and −(4238.05±0.40) kJ mol^{-1} for thioacetamide and tetramethylthiourea, respectively.

Sublimation calorimetric results are summarized in

TABLE 3. SUMMARY OF COMBUSTION CALORIMETRIC RESULTS ON THIOACETAMIDE

	Experiment					
	1	2	3	4	5	6
m'(compd)/g	1.19724	1.01014	1.01226	1.01446	1.00841	1.01502
m'''(fuse)/g	0.00190	0.00190	0.00219	0.00229	0.00184	0.00224
$m^i(H_2O)$/g	9.822	9.800	10.027	9.834	9.924	9.996
θ_i/°C	23.12846	23.13300	23.13625	23.13091	23.12903	23.13003
θ_f/°C	25.27055	24.95798	24.96516	24.96313	24.95129	24.96262
$\Delta\theta_{corr}$/°C	0.01239	0.02654	0.02654	0.02614	0.02731	0.02599
$n^f(HNO_3)$/mmol	1.262	1.241	1.173	1.260	1.225	1.260
$n^f(HNO_2)$/μmol	0.1	0.0	0·1	0.1	0.1	0.0
ΔU_{ign}/J	4.0	4.9	4.4	4.3	4.8	4.8
ε^i(cont)/J K^{-1}	54.1	53.8	54.7	53.9	54.3	54.6
ε^f(cont)/J K^{-1}	54.9	54.4	55.3	54.5	54.9	55.2
$\Delta U_{dec}(HNO_3+HNO_2)$/J	74.3	73.1	69.1	74.2	72.1	74.2
$-\Delta U_{dil}(H_2SO_4)$/J	19.1	13.2	12.9	13.3	13.0	13.1
$-\Delta U_\Sigma$/J	16.8	11.3	10.8	11.3	10.9	11.0
$-\Delta U_{IBP}$/J	32402.2	27360.4	27421.7	27477.6	27307.7	27486.0
$-\{\Delta U_c^\circ/M\}$/kJ g^{-1}	26.9898	26.9936	26.9963	26.9867	26.9892	26.9806
$-\Delta U_c^\circ$/kJ mol^{-1}	2027.82	2028.10	2028.31	2027.59	2027.77	2027.13

TABLE 4. SUMMARY OF COMBUSTION CALORIMETRIC RESULTS ON TETRAMETHYLTHIOUREA

	Experiment					
	1	2	3	4	5	6
m'(compd)/g	1.04506	0.86498	0.85530	0.85992	0.86037	0.86476
m'''(fuse)/g	0.00251	0.00243	0.00233	0.00256	0.00196	0.00211
$m^i(H_2O)$/g	10.019	9.947	9.984	9.948	9.964	9.945
θ_i/°C	23.12913	23.13125	23.13736	23.13179	23.12721	23.13513
θ_f/°C	25.34762	24.98626	24.97193	24.97671	24.97241	24.98906
$\Delta\theta_{corr}$/°C	0.00892	0.02504	0.02629	0.02627	0.02583	0.02491
$n^f(HNO_3)$/mmol	1.378	1.047	1.022	1.007	1.061	1.054
$n^f(HNO_2)$/μmol	0.2	0.4	0.2	0.6	0.6	0.9
ΔU_{ign}/J	5.0	4.8	4.8	4.8	4.9	4.9
ε^i(cont)/J K^{-1}	54.7	54.2	54.4	54.2	54.3	54.2
ε^f(cont)/J K^{-1}	56.5	55.6	55.8	55.6	55.7	55.6
$\Delta U_{dec}(HNO_3+HNO_2)$/J	81.1	61.6	60.2	59.3	62.5	62.0
$-\Delta U_{dil}(H_2SO_4)$/J	3.6	1.9	1.8	1.8	1.8	1.9
ΔU_Σ/J	7.6	7.6	7.6	7.6	7.5	7.6
$-\Delta U_{IBP}$/J	33618.7	27840.4	27511.0	27668.6	27680.0	27826.4
$-\{\Delta U_c^\circ/M\}$/kJ g^{-1}	32.0446	32.0599	32.0411	32.0489	32.0534	32.0575
$-\Delta U_c^\circ$/kJ mol^{-1}	4237.21	4239.24	4236.75	4237.79	4238.36	4238.92

Tables 5 and 6 for thioacetamide and tetramethylthiourea, respectively. The sublimation enthalpies are plotted against temperature in Fig. 1 in the temperature range below 320 K. Molar standard enthalpy of sublimation $\Delta H_s^\circ(T)$, was calculated with the following equation:

$$\Delta H_s^\circ(T) = E_{calib}(S_T/S_B)(M/m),$$

where E_{calib} is the electrical energy used in the calibration, (S_T/S_B) is the ratio of sublimation enthalpy to the electrical energy, as determined by calorimetry, and m and M are the mass and the molar mass, respectively, of the material effused from the sample container.

Observed enthalpies of sublimation for each substance were subjected to a regression analysis for linear relations between two variables.[8] Derived results are as follows: $\Delta H_s^\circ/\text{kJ mol}^{-1} = -(0.11314\pm0.03179)(T/\text{K}) + (116.99\pm9.81)$ with estimated standard deviation from the fit s_f of 0.10 kJ mol^{-1} for thioacetamide, and $\Delta H_s^\circ/\text{kJ mol}^{-1} = -(0.03534\pm0.00965)(T/\text{K}) + (93.57\pm2.93)$ with s_f of 0.21 kJ mol^{-1} for tetramethylthiourea, where uncertainties are those at the 95% confidence level. Three values at 320.8 K of thioacetamide were not employed in the analysis, since they showed significant deviations from the fit.

Standard enthalpies of sublimation at 298.15 K were obtained by extrapolation of the smoothed functions to the reference temperature. Derived values were (83.26±0.34) and (83.04±0.20) kJ mol^{-1} for thioacet-

TABLE 5. SUMMARY OF SUBLIMATION CALORIMETRIC RESULTS ON THIOACETAMIDE

$\frac{T}{\mathrm{K}}$	$\frac{t}{\mathrm{ks}}$	$\frac{m}{\mathrm{mg}}$	$\frac{E_{\mathrm{calib}}}{\mathrm{J}}$	$\frac{S_{\mathrm{T}}}{S_{\mathrm{B}}}$	$\frac{\Delta H_{\mathrm{s}}^{\circ}(T)}{\mathrm{kJ\ mol^{-1}}}$
305.6	17.04	7.91	1.1225	7.728	82.38
305.7	15.00	6.61	0.9283	7.803	82.37
306.3	54.80	22.65	14.760	1.683	82.39
307.2	127.20	64.57	1.6570	42.656	82.24
309.0	142.60	77.65	26.753	3.169	82.04
313.0	52.00	41.25	8.4759	5.275	81.43
313.0	104.60	86.96	4.4871	21.082	81.72
320.8	45.80	84.64	20.124	4.649	83.05
320.8	95.70	174.92	8.6817	22.407	83.56
320.8	72.45	131.63	24.474	5.984	83.60

TABLE 6. SUMMARY OF SUBLIMATION CALORIMETRIC RESULTS ON TETRAMETHYLTHIOUREA

$\frac{T}{\mathrm{K}}$	$\frac{t}{\mathrm{ks}}$	$\frac{m}{\mathrm{mg}}$	$\frac{E_{\mathrm{calib}}}{\mathrm{J}}$	$\frac{S_{\mathrm{T}}}{S_{\mathrm{B}}}$	$\frac{\Delta H_{\mathrm{s}}^{\circ}(T)}{\mathrm{kJ\ mol^{-1}}}$
298.5	24.45	28.89	2.2374	8.084	82.78
298.4	23.70	27.74	2.4405	7.140	83.06
298.5	20.40	23.87	2.2371	6.721	83.30
298.5	24.60	29.09	2.8476	6.393	82.74
301.3	31.90	52.20	2.8236	11.638	83.24
301.3	21.60	35.36	2.8235	7.847	82.84
301.4	21.70	35.37	4.8003	4.625	82.98
313.1	16.40	107.49	13.185	5.086	82.49
314.3	14.80	113.39	15.180	4.653	82.35
315.6	11.40	101.74	14.604	4.346	82.50

TABLE 7. STANDARD THERMODYNAMIC QUANTITIES AT 298.15 K OF THIOACETAMIDE AND TETRAMETHYLTHIOUREA

Compound	Thioacetamide	Tetramethyl-thiourea
$-\Delta U_{\mathrm{c}}^{\circ}(\mathrm{c})/\mathrm{kJ\ mol^{-1}}$	2027.8 ±1.1	4238.1 ±2.2
$-\Delta H_{\mathrm{c}}^{\circ}(\mathrm{c})/\mathrm{kJ\ mol^{-1}}$	2033.4 ±1.1	4246.7 ±2.2
$-\Delta \mathrm{H}_{\mathrm{f}}^{\circ}(\mathrm{c})/\mathrm{kJ\ mol^{-1}}$	70.6 ±1.1	38.3 ±2.3
$\Delta H_{\mathrm{s}}^{\circ}/\mathrm{kJ\ mol^{-1}}$	83.26±0.34	83.03±0.20
$\Delta H_{\mathrm{f}}^{\circ}(\mathrm{g})/\mathrm{kJ\ mol^{-1}}$	12.7 ±1.2	44.7 ±2.3

amide and tetramethylthiourea, respectively, where uncertainties are those at the 95% confidence level.

Derived standard thermodynamic quantities are presented in Table 7. Uncertainties given in this table are the overall values. The following contributions were taken into consideration in assigning uncertainties to $\Delta U_{\mathrm{c}}^{\circ}(\mathrm{c})$: (1) Calculated standard deviation of mean (sdm) for the experimental values of $\Delta U_{\mathrm{c}}^{\circ}(\mathrm{c})$, $s(\overline{U})$; (2) calculated sdm for those of ε(calor), $s(\varepsilon)$; (3) estimated sdm for the certified specific energy of combustion of the thermochemical standard benzoic acid $\Delta u_{\mathrm{c}}(\mathrm{ba})$, $s(\mathrm{ba})$; and (4) likely systematic error of 0.05%. The former three were used to calculate the overall standard deviation of mean for $\Delta U_{\mathrm{c}}^{\circ}(\mathrm{c})$, $s(\overline{U})_{\Sigma}$:

$$s(\overline{U})_{\Sigma} = [s(\overline{U})^2+\{\Delta U_{\mathrm{c}}^{\circ}(\mathrm{c})s(\varepsilon)/\varepsilon(\mathrm{calor})\}^2 + \{\Delta U_{\mathrm{c}}^{\circ}(\mathrm{c})s(\mathrm{ba})/\Delta u_{\mathrm{c}}(\mathrm{ba})\}^2]^{1/2}.$$

$s(\overline{U})_{\Sigma}$ was 0.20 and 0.46 kJ mol^{-1} for thioacetamide and tetramethylthiourea, respectively. The overall uncertainty for $\Delta U_{\mathrm{c}}^{\circ}(\mathrm{c})$, $\delta(\Delta U_{\mathrm{c}}^{\circ}, \mathrm{c})$, was calculated by combining $\{2s(\overline{U})\}$ with the likely systematic error, mentioned above, by use of the following equation:

$$\delta(\Delta U_{\mathrm{c}}^{\circ}, \mathrm{c}) = [\{2s(\overline{U})_{\Sigma}\}^2+\{0.0005\Delta U_{\mathrm{c}}^{\circ}(\mathrm{c})\}^2]^{1/2}.$$

The overall uncertainty for $\Delta H_{\mathrm{c}}^{\circ}(\mathrm{c})$ is equal to that for $\Delta U_{\mathrm{c}}^{\circ}(\mathrm{c})$ and that for $\Delta H_{\mathrm{s}}^{\circ}$ is the uncertainty at the 95% confidence level.

The following CODATA recommended key values for thermodynamics[9] and the value[6] compatible with them were used to calculate standard enthalpies of formation in the crystalline state: $\Delta H_{\mathrm{f}}^{\circ}(\mathrm{CO_2}, \mathrm{g}) = -(393.51 \pm 0.13)$,[9] $\Delta H_{\mathrm{f}}^{\circ}(\mathrm{H_2O}, \mathrm{l}) = -(285.830 \pm 0.042)$,[9] and $\Delta H_{\mathrm{f}}^{\circ}(\mathrm{H_2SO_4}\ \mathrm{in}\ 115\mathrm{H_2O}) = -(888.263 \pm 0.042)$[6] kJ mol^{-1}, respectively, where uncertainties are those at the 95% confidence level for the former two, and that for the latter one is an estimated value.

The overall uncertainties for $\Delta H_{\mathrm{f}}^{\circ}(\mathrm{c})$ and for $\Delta H_{\mathrm{f}}^{\circ}(\mathrm{g})$, $\delta(\Delta H_{\mathrm{f}}^{\circ}, \mathrm{c})$ and $\delta(\Delta H_{\mathrm{f}}^{\circ}, \mathrm{g})$, respectively, were calculated according to:

$$\delta(\Delta H_{\mathrm{f}}^{\circ}, \mathrm{c}) = [\delta(\Delta U_{\mathrm{c}}^{\circ}, \mathrm{c})^2+\{\mathrm{a}\delta(\mathrm{CO_2})\}^2 + \{(\mathrm{b}/2-\mathrm{d})\delta(\mathrm{H_2O})\}^2+\{\mathrm{d}\delta(\mathrm{H_2SO_4})\}^2]^{1/2},$$

and

$$\delta(\Delta H_{\mathrm{f}}^{\circ}, \mathrm{g}) = [\delta(\Delta H_{\mathrm{f}}^{\circ}, \mathrm{c})^2+\delta(\Delta H_{\mathrm{s}}^{\circ})^2]^{1/2},$$

where $\delta(\mathrm{CO_2})$, $\delta(\mathrm{H_2O})$, $\delta(\mathrm{H_2SO_4})$ and $\delta(\Delta H_{\mathrm{s}}^{\circ})$ are the uncertainties assigned to $\Delta H_{\mathrm{f}}^{\circ}(\mathrm{CO_2}, \mathrm{g})$, $\Delta H_{\mathrm{f}}^{\circ}(\mathrm{H_2O}, \mathrm{l})$, $\Delta H_{\mathrm{f}}^{\circ}(\mathrm{H_2SO_4}\ \mathrm{in}\ 115\mathrm{H_2O})$, and $\Delta H_{\mathrm{s}}^{\circ}$, respectively.

Discussion

Thianthrene is a test substance for combustion calorimetry of organic sulfur compounds, recommended by IUPAC.[15] The standard enthalpy of combustion of thianthrene, obtained in this study, agrees with the value of Hu *et al.*[13] and that of Johnson[14] within the sum of each uncertainty, among the literature values given in Table 2. The difference between the recommended value[15] and the present value amounts to 3.7 kJ mol^{-1}, which is 0.05% of total. The relative deviation of 0.05% was assumed to be the relative systematic error for $\Delta H_{\mathrm{c}}^{\circ}(\mathrm{c})$ and the contribution from this source has been included in the overall uncertainties for $\Delta U_{\mathrm{c}}^{\circ}(\mathrm{c})$ and $\Delta H_{\mathrm{c}}^{\circ}(\mathrm{c})$, $\delta(\Delta U_{\mathrm{c}}^{\circ}, \mathrm{c})$, as described in the preceding section. Standard enthalpy of combustion has not been reported so far for thioacetamide and tetramethylthiourea.

As was pointed out briefly, amides are stabilized considerably due to interaction between a carbonyl group and a neighbouring nitrogen atom, as compared with the hypothetical reference structures, where no such interaction exerts. Stabilization energy may be evaluated by comparing observed and calculated standard enthalpies of formation in gaseous state, for example, as shown in Table 8 for normal alkanamides, $\mathrm{CH_3(CH_2)_{\mathit{n}-1}CONH_2}$. The calculated values were obtained by means of the group contribution method[16] as follows:

TABLE 8. ESTIMATED STABILIZATION ENERGIES, U_s, OF NORMAL ALKANAMIDES, $CH_3(CH_2)_{n-1}CONH_2$

n	$-\Delta H^\circ_\mathrm{f}(\mathrm{g})$/kJ mol^{-1}		U_s [c]
	Obsd [a]	Calcd [b]	kJ mol^{-1}
1	238.3	155.5	82.8
2	258.9	176.1	82.8
3	278.1	196.7	81.4
4	290.2	217.3	73.0
5	328.1	237.8	90.3
6	—	258.4	—
7	362.7	279.0	83.7

a) Ref. 20. b) See the text. c) $U_\mathrm{s}=\Delta H^\circ_\mathrm{f}(\mathrm{g, calcd})-\Delta H^\circ_\mathrm{f}(\mathrm{g, obsd})$.

$$\Delta H^\circ_\mathrm{f}(\mathrm{g, calcd}) = [\mathbf{C}\text{-}(\mathrm{C})(\mathrm{H})_3] + (n-1)[\mathbf{C}\text{-}(\mathrm{C})_2(\mathrm{H})_2] + [\mathbf{CO}\text{-}(\mathrm{C})_2] + [\mathbf{N}\text{-}(\mathrm{C})(\mathrm{H})_2],$$

where $[\mathbf{C}\text{-}(\mathrm{C})(\mathrm{H})_3]$, $[\mathbf{C}\text{-}(\mathrm{C})_2(\mathrm{H})_2]$, $[\mathbf{CO}\text{-}(\mathrm{C})_2]$, and $[\mathbf{N}\text{-}(\mathrm{C})(\mathrm{H})_2]$ are the contributions from methyl, methylene, ketonic carbonyl, and amino groups, respectively. These contributions are such that standard enthalpies of formation in gaseous state at 298.15 K for normal alkanes, normal alkanones, and normal alkylamines are reproduced satisfactorily as an appropriate sum of these contributions. Values selected by Cox and Pilcher[21] were used for these contribution terms. Table 8 shows that the normal alkanamides are stabilized as much as 83 kJ mol^{-1} in average, as compared with the corresponding reference structures.

In order to achieve a similar analysis for thioacetamide and tetramethylthiourea, it is necessary to know the value of an additional contribution, $[\mathbf{CS}\text{-}(\mathrm{C})_2]$, which is the contribution from a thioketonic thiocarbonyl group. Since thioketones are very unstable compounds, this value has not been presented. Only thermochemical data that is available for unstabilized thiocarbonyl compounds is the standard enthalpy of formation in gaseous state of thioformaldehyde, $\Delta H^\circ_\mathrm{f}(\mathrm{H_2C{=}S, g})$, of (100 ± 11) kJ mol^{-1}, which was determined by electron impact method.[17] Consequently, the value of $[\mathbf{CS}\text{-}(\mathrm{C})_2]$ was estimated by adding the difference $\{\Delta H^\circ_\mathrm{f}(\mathrm{H_2C{=}S, g})-\Delta H^\circ_\mathrm{f}(\mathrm{H_2C{=}O, g})\}$ to $[\mathbf{CO}\text{-}(\mathrm{C})_2]$ $(=-132.47$ kJ mol$^{-1})$.[21] By adopting $-(108.7\pm0.7)$ kJ mol^{-1} [20] for $\Delta H^\circ_\mathrm{f}(\mathrm{H_2C{=}O, g})$, $[\mathbf{CS}\text{-}(\mathrm{C})_2]$ was estimated to be 77 kJ mol^{-1}.

Standard enthalpies of formation in gaseous state were calculated for hypothetical reference structures:[21] For thioacetamide,

$$\begin{aligned}\Delta H^\circ_\mathrm{f}(\mathrm{g, calcd}) &= [\mathbf{C}\text{-}(\mathrm{C})(\mathrm{H})_3] + [\mathbf{CS}\text{-}(\mathrm{C})_2] + [\mathbf{N}\text{-}(\mathrm{C})(\mathrm{H})_2]\\ &= (-42.34) + (77) + (19.33)\\ &= 54\ \mathrm{kJ\ mol^{-1}},\end{aligned}$$

and for tetramethylthiourea,

$$\begin{aligned}\Delta H^\circ_\mathrm{f}(\mathrm{g, calcd}) &= 4[\mathbf{C}\text{-}(\mathrm{N})(\mathrm{H})_3]^\mathrm{ass}+2[\mathbf{N}\text{-}(\mathrm{C})_3] + [\mathbf{CS}\text{-}(\mathrm{C})_2]\\ &= 4\times(-42.34) + 2\times(103.30) + (77)\\ &= 114\ \mathrm{kJ\ mol^{-1}},\end{aligned}$$

where $[\mathbf{C}\text{-}(\mathrm{N})(\mathrm{H})_3]^\mathrm{ass}$ and $[\mathbf{N}\text{-}(\mathrm{C})_3]$ are the contributions from a methyl group attached to a nitrogen atom and from a tertiary nitrogen atom, respectively.

Comparison of the observed values of $\Delta H^\circ_\mathrm{f}(\mathrm{g})$, given in Table 7, with these calculated values leads to stabilization energies of 41 and 69 kJ mol^{-1} for thioacetamide and tetramethylthiourea, respectively. The stabilization energy of thioacetamide amounts to about 50% of the corresponding value of acetamide and the value for tetramethylthiourea is 1.7 times as large as that of thioacetamide. Although uncertainties approaching 15 kJ mol^{-1} should be assigned to the estimated stabilization energies, in view of the large uncertainty of $\Delta H^\circ_\mathrm{f}(\mathrm{H_2C{=}S, g})$ and the assumption made in the course of estimation of $[\mathbf{CS}\text{-}(\mathrm{C})_2]$, it may be stated conclusively that thioacetamide and tetramethylthiourea are stabilized considerably, as compared with the corresponding reference structures. This fact may be the reason why these compounds are fairly stable at ambient temperatures, while thioketones are not. This stabilization is possibly due to the interaction between thiocarbonyl π-electrons and nitrogen lone pair electrons.

According to an X-ray diffraction study, a thioacetamide molecule is almost planar except for methyl hydrogen atoms.[18] Although the molecular structure is not known for tetramethylthiourea, sulfur, carbon and nitrogen atoms in a thiourea molecule are coplanar.[19] These findings seem to be an indication of possible intramolecular interaction between thiocarbonyl π-electrons and nitrogen lone pair electrons.

References

1) K. Fries and W. Vogt, *Ann.*, **381**, 320 (1911).

2) M. Sakiyama, T. Nakano, and S. Seki, *Bull. Chem. Soc. Jpn.*, **48**, 1705 (1975).

3) K. Nishiyama, M. Sakiyama, S. Seki, H. Horita, T. Otsubo, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **53**, 869 (1980).

4) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, London (1970), p. 70.

5) S. Murata, M. Sakiyama, and S. Seki, *J. Chem. Thermodyn.*, **14**, 707 (1982).

6) V. B. Parker, D. D. Wagman, and D. Garvin, "Selected Thermochemical Data Compatible with the CODATA Recommendations," *NBSIR* 75-968, NTIS (1975).

7) W. N. Hubbard, D. W. Scott, and G. Waddington, "Experimental Thermochemistry," ed by F. D. Rossini, Interscience, New York (1956), Vol. 1, Chap. 5.

8) "Statistical Method in Research and Production with Special Reference to Chemical Industry," 4th ed, ed by O. L. Davies and P. L. Goldsmith, Longman, London (1977).

9) CODATA Task Group on Key Values for Thermodynamics, 1977, *CODATA Bull.*, **1978**, 28; *J. Chem. Thermodyn.*, **10**, 903 (1978).

10) W. N. Hubbard, C. Katz, and G. Waddington, *J. Phys. Chem.*, **58**, 142 (1954).

11) W. A. Keith and H. Mackle, *Trans. Faraday Soc.*, **54**, 353 (1958).

12) (a) S. Sunner and B. Lundin, *Acta Chem. Scand.*, **7**, 1112 (1953); (b) S. Sunner, *ibid.*, **17**, 728 (1963).

13) J-H. Hu, H-K. Yen, and Y-L. Geng, *Acta Chim. Sin.*, **32**, 242 (1966).

14) W. H. Johnson, *J. Res. Natl. Bur. Stds.*, **79A**, 561

(1975).
15) J. D. Cox, *Pure Appl. Chem.*, **40**, 399 (1974).
16) S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **29**, 546 (1958).
17) A. Jones and F. P. Lossing, *J. Phys. Chem.*, **71**, 4111 (1967).
18) M. R. Truter, *J. Chem. Soc.*, **1960**, 997.
19) N. R. Kunchur and M. R. Truter, *J. Chem. Soc.*, **1958**, 2558.
20) J. B. Pedley and J. Rylance, "Sussex-N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds," University of Sussex, Brighton (1977).
21) Ref. 4, p. 590.