Heats of Formation of Adducts between Antimony Pentachloride and N,N-Dimethylacetamide and Tetramethylurea

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The donor strengths of dimethylacetamide and tetramethylurea have previously been discussed [1] on the basis of qualitative thermochemical experiments. Quantitative measurements have now been performed on heats of formation of adducts between antimony pentachloride and dimethylacetamide and tetramethylurea with both reactants and reaction products in ethylene chloride solution in accordance with earlier works.[2,3] The values obtained have already been reported and discussed by Lindqvist.[4]

*Experimental**. Materials.* Ethylene chloride and antimony pentachloride were treated as given in Ref.[2]

N,N-Dimethylacetamide (Fluka) and tetramethylurea (Schukardt) were dried with Drierite and then distilled under reduced pressure. Melting intervals [2] of the samples were both 1°. A second distillation at a slightly different pressure and careful drying using Micro Sieves A4 left melting curves unchanged.

Dimethylacetamide, b.p. 55.5° at 12 mm Hg n_D^{25} 1.4363, d_4^{25} 0.9363. (Found: C 55.1; H 10.6; N 16.1. Calc. for C_5H_9NO: C 55.1; H 10.4; N 16.1).

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** *Apparatus, Calibration, Calorimetric procedure* and *Correction to standard states;* see Ref. [2]

Table 1. Heat of reaction measurements performed in ethylene chloride solution containing an excess of $SbCl_5$ as acceptor.

Donor	mmole	g $SbCl_5$	$10^4 \log R_i/R_f$	$-\Delta H_1$ kcal/mole
Dimethylacetamide (I)	0.738	1.07	52.69	28.57
q = 0.00 cal	1.109	1.10	80.05	28.89
	1.124	1.03	80.79	28.76
	2.609	1.15	187.86	28.85
	3.158	1.32	224.46	28.49
				28.71 ± 0.08
Tetramethylurea (I)	0.515	1.24	39.58	30.77
q = 0.00 cal	1.057	1.10	80.97	30.67
	1.661	1.22	127.16	30.66
(II)	0.559	1.01	51.92	30.72
	0.800	1.26	74.34	30.75
	1.197	0.98	110.83	30.63
	1.213	1.31	112.14	30.62
				30.69 ± 0.03

Table 2. Heat of solution measurements of donors in ethylene chloride.

Donor	mmole	$10^4 \log R_i/R_f$	$-\Delta H_2$ kcal/mole
Dimethylacetamide (II)	3.044	8.34	0.91
q = 0.02 cal	3.103	8.39	0.90
	3.345	9.18	0.91
			0.91 ± 0.00
Tetramethylurea (II)	1.104	3.41	1.04
q = 0.02 cal	2.672	8.55	1.06
	2.790	8.91	1.06
			1.05 ± 0.01

Table 3. Enthalpy changes accompanying the formation of adducts between $SbCl_5$ and given donors in ethylene chloride solution. ΔH-values are expressed in kcal per mole.

Donor	$-\Delta H_1$	$-\Delta H_2$	$-\Delta H$
$Me_2N(Me)CO$	28.71	0.91	27.80 ± 0.08
$(Me_2N)_2CO$	30.69	1.05	29.64 ± 0.03

Tetramethylurea, b.p. 64.5° at 13 mm Hg, n_D^{25} 1.4493, d_4^{25} 0.9619. (Found: C 51.7; H 10.4. Calc. for $C_5H_{12}N_2O$: C 51.7; H: 10.4).

Units of measurements. The results of the calorimetric experiments are expressed in terms of the defined calorie equal to 4.1840 abs. joules, and refer to the isothermal process at 25° and to the true mass. The molecular weights were computed from the 1961 table of atomic weights.[5]

Results. The experimental results are summarized in Tables 1—3. Two different systems were used, I and II, with heat equivalents 3996 ± 4 and 3302 ± 2 cal per unit of log R_i/R_f, respectively. In the heat of reaction measurements (Table 1) the first column gives the name of the donor together with a sum correction, q, compensating for a number of small heat effects.[2] Columns 2 and 3 give the amounts of donor and acceptor. The $SbCl_5$ was added in excess prior to the experiment to take care of traces of water inside the calorimeter and in the solvent. Column 4 gives the corrected temperature rise expressed in units of 10^4 log R_i/R_f, where R_i and R_f are the extrapolated initial and final thermistor resistances. The last column gives the molar enthalpy change. The heat of solution experiments (Table 2) were performed in pure ethylene chloride. The data obtained are given in Table 3 together with the calculated values of the enthalpy change for the formation of the adducts in solution.

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Spectroscopic Studies on Metal Carbonyls

II. Generalized Mean-Square Amplitudes of Chromium and Molybdenum Hexacarbonyls

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In this work the mean-square parallel and perpendicular amplitudes, and mean cross products[1] of $Cr(CO)_6$ and $Mo(CO)_6$ have been calculated. Because of the high symmetry of the appropriate model (O_h), all mean cross products vanish except for one type of distances. Numerical results are given in Table 1, where the atom pairs, which define the types of distances, refer to the numbering previously adopted.[2] As to the orientation of the perpendicular amplitudes, all Δy have been referred to the XZ plane, except for the 1—8 and 7—8 type distances, where the appropriate plane is 1—4—6. These quantities as referred to somewhat arbitrary orientations, are not of much interest. But so are the quantities obtained as the sum $\langle \Delta x \rangle^2 + \langle \Delta y \rangle^2$, which is invariant with respect to the individual orientations. This sum enters