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Donor Abilities of Sulfoxides, Sulfinamides, and Thionylamides

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The enthalpies of adduct formation of a number of sulfoxides, sulfinamides, and thionylamides with trimethylalane, $Al(CH_3)_3$, have been determined using solution calorimetric techniques in hexane and 5% benzene in hexane solution. The enthalpies of adduct formation of the same compounds with phenol were estimated using an infrared technique.[1]

Previous work with trimethylalane has shown that enthalpies obtained in hexane are good approximations of gas-phase enthalpies.[2] In this work it was found that enthalpies in 5% benzene in hexane solutions, which are used in the dimethyl sulfoxide and tetramethylene sulfoxide systems for solubility reasons, are the same as those observed in hexane. The enthalpies obtained with trimethylalane result in a basicity sequence which is the same as that found with phenol.

Experimental Section

Dimethyl sulfoxide and tetramethylene sulfoxide were distilled from CaH_2 (bp 74.5° (11.5 mm) and 76.5° (1.0 mm), respectively). Methanesulfinyl chloride was prepared by the method of Douglass and Farah.[3] N,N-Dimethylmethanesulfinamide was prepared by slowly adding 1 mole of methanesulfinyl chloride to 2 moles of dimethylamine in ether at −10°. After work-up, the product was distilled (bp 37° (2.0 mm)). *Anal.* Calcd: C, 33.63; H, 8.47; N, 13.08. Found: C, 33.95; H, 8.21; N, 13.29. N-Methylmethanesulfinamide was prepared by adding an ether solution of 2 moles of methylamine to an ether solution of 1 mole of methanesulfinyl chloride at −20°. After removal of the salts and ether the product was distilled (bp 63° (0.15 mm)). *Anal.* Calcd: C, 25.80; H, 7.60; N, 15.05. Found: C, 26.36; H, 7.46; N, 14.83. Methanesulfinamide was prepared by addition of an ether solution of methanesulfinyl chloride to liquid NH_3 at −60°. After refluxing for 8 hr the salts were removed, the ether was pulled off, and the solid product was extracted with methyl ethyl ketone and recrystallized from chloroform (mp 70°). *Anal.* Calcd: C, 15.19; H, 6.38; N, 17.72. Found: C, 15.20; H, 6.14; N, 17.80. Tetramethylthionylamide was prepared by slowly adding 1 mole of thionyl chloride to 4 moles of dimethylamine in ether at 0°. The salts were removed in a dry atmosphere, the ether was removed, and the product was distilled (bp 59° (6.0 mm)). *Anal.* Calcd: C, 35.27; H, 8.88; N, 20.56. Found: C, 35.53; H, 8.89; N, 20.13. 1,3-Dimethyl-2-oxo-1,3-diaza-2-thiacyclopentane was prepared in a manner similar to the method of Abel and Bush[4] (bp 80° (2.6 mm)). *Anal.* Calcd: C, 35.80; H, 7.51. Found: C, 35.48; H, 7.83. Trimethylalane was provided by Ethyl Corp. and distilled immediately prior to use. Phenol was purified by distillation followed by sublimation just prior to use. Analytical Reagent grade CCl_4 was used as received.

All adducts were prepared by adding a stoichiometric quantity of base to the alane dissolved in benzene at 0° under nitrogen. The volatile materials were pumped off at 0° and then at 25°. Attempts to prepare trimethylalane adducts of N-methylmethanesulfinamide and methanesulfinamide were unsuccessful owing to a condensation reaction involving the amino proton. The active alkyl analysis entailed measuring the volume of methane evolved in the hydrolysis of the adduct. Aluminum was determined using an EDTA titration scheme.

The calorimeter used is similar to that described by Arnett.[5] The calorimetric procedure was the same as previously described.[2] This involved measuring the enthalpy associated with each of six to eight successive additions of 0.04–0.06 g of trimethylalane to excess base in *n*-hexane. In each experiment the initial base concentration was approximately 1.5 times the trimethylalane concentration accumulated over all of the successive additions. In this way, even though with each successive addition of trimethylalane the base concentration decreased and the adduct concentration increased, there was virtually no variation of the observed molar enthalpies over the entire concentration range. These results have been interpreted as an indication that the reaction goes to completion over the trimethylalane concentration range 0.010–0.06 *M*. The O–H stretching frequencies were measured using 0.1-mm NaCl cells and a Perkin-Elmer 421 spectrophotometer. The interactions with phenol were estimated using the shifts of the O–H stretching frequency of 0.15 *M* phenol solutions in carbon tetrachloride. The shifts of the O–H frequency used to calculate ΔH_f were obtained by extrapolating to infinite dilution data collected over a base concentration range of 0.2–1.3 *M*.

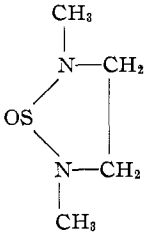
Results and Discussion

The results of the trimethylalane studies are found in Table I. The enthalpies reported include the enthalpy of dimerization of trimethylalane, −20.40 ± 0.34 kcal/mole of dimer,[2] and the enthalpy of solution of trimethylalane, +0.45 ± 0.02 kcal/mole of dimer,[3] and are corrected total solution enthalpies as defined in the table. The data were treated in this way since it is established that trimethylalane exists as an undissociated dimer in hydrocarbon solvents in the concentration range 0.05–0.25 *M*.[6,7] Partial dissociation of even 1% of the dimeric liquid trimethylalane upon dissolution in *n*-hexane would be expected to increase the enthalpy of solution by approximately +0.2 kcal/mole of dimer (1% of the enthalpy of dissociation of dimeric trimethylalane). The fact that the molar heats of solution of trimethylalane in hexane show a random deviation of ±0.02 kcal/mole of dimer over the concentration range 0.015–0.060 *M* suggests that trimethylalane exists as an undisassociated dimer at 0.015 *M* in *n*-hexane.[2] Adduct formation is through the oxygen of the sulfur–oxygen donor as shown by the ν_{S-O} shift to lower frequencies upon coordination.

(1) T. D. Epley and R. S. Drago, *J. Am. Chem. Soc.*, **89**, 5770 (1967).
(2) C. H. Henrickson and D. P. Eyman, *Inorg. Chem.*, **6**, 1461 (1967).
(3) J. Douglass and B. Farah, *Org. Syn.*, **40**, 62 (1960).
(4) E. W. Abel and R. P. Bush, *J. Organometal. Chem.* (Amsterdam), **3** 245 (1965).
(5) E. M. Arnett, W. E. Bentrude, J. J. Burke, and P. MacDuggleby, *J. Am. Chem. Soc.*, **87**, 1541 (1965).
(6) A. L. Otermat, Ph.D. Thesis, Purdue University, 1964.
(7) K. S. Pitzer and H. S. Gutowsky, *J. Am. Chem. Soc.*, **68**, 2204 (1946).

TABLE I

TRIMETHYLALANE ADDUCTS

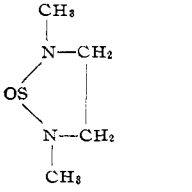
Base	State	% Al Calcd	% Al Found	% active alkyl Calcd	% active alkyl Found	ν_{S-O}, cm^{-1} Free	ν_{S-O}, cm^{-1} Adduct	$-\Delta H_f$,[a] kcal/mole
$OS(CH_3)_2$	Solid	19.24	19.32	30.03	29.73	1055	1000	28.64 ± 0.27[b]
$OS(CH_2)_4$	Solid	15.38	15.59	25.59	25.85	1025	968	28.25 ± 0.17[b]
$OS<^{CH_3}_{N(CH_3)_2}$	Liquid	15.05	15.26	25.16	25.64	1078	983	26.27 ± 0.11
$OS[N(CH_3)_2]_2$	Liquid	12.96	13.26	21.65	22.24	1116	1017	24.56 ± 0.10
	Liquid	13.08	13.34	21.87	22.54	1106	988	24.32 ± 0.10

[a] For 0.5(acid)$_2$(soln) + base(soln) = adduct(soln): $\Delta H_f = -0.5\Delta H_{soln}[(acid)_2] + \Delta H_{f(obsd)} + 0.5\Delta H_{dim}[(acid)_2]$. [b] In 5% benzene in hexane. $CH_3S(O)N(CH_3)_2$ produces identical enthalpies in hexane and in 5% benzene in hexane.

The results of the phenol studies are in Table II. The coordination to phenol is through the oxygen of the sulfur–oxygen donor as indicated by the shift of ν_{S-O} to lower frequency in each case. The similarity of ν_{S-O} for N-methylmethanesulfinamide in the pure liquid and when coordinated to phenol in CCl_4 suggests that in the pure liquid itself hydrogen-bonding interactions result in a perturbation of ν_{S-O} almost equal to that induced by hydrogen bonding with phenol.

TABLE II

PHENOL ADDUCTS

Base	$\Delta\nu_{OH}$, cm^{-1}	ν_{S-O}, cm^{-1} Free	ν_{S-O}, cm^{-1} Adduct	$-\Delta H_{f(calcd)}$,[a] kcal/mole
$OS(CH_3)_2$	405 ± 10 (359)[b]	1055	1011	7.2
$OS(CH_2)_4$	415 ± 10 (400)[c]	1055	1014	7.3
$H_2CS(O)NH_2$	<355[d]	1018 1067[e]	1055	>6.7
$H_2CS(O)NHCH_3$	420 ± 10	1054 1084[f]	1053	7.4
$H_2CS(O)N(CH_3)_2$	355 ± 10	1073 1078[f]	1051	6.7
$OS[N(CH_3)_2]_2$	325 ± 10	1116	1084	6.4
	310 ± 10	1106	1075	6.2

[a] Estimated enthalpies calculated using the following relationship found in ref 1: $-\Delta H_{f(calcd)} = 0.011\Delta\nu_{OH} + 2.79$ kcal/mole. [b] M. D. Joesten, Ph.D. Thesis, University of Illinois, 1962. [c] R. S. Drago, B. Wayland, and R. L. Carbon, *J. Am. Chem. Soc.*, **85**, 3125 (1963). [d] Insolubility prevented measurements at high base concentrations. [e] Maximum observable shift upon dilution in $CHBr_3$ before solvent cutoff. [f] Infinite dilution in CCl_4.

In both methanesulfinamide and N-methylmethanesulfinamide the alternate possibility of coordination of phenol at the sulfur or nitrogen sites is not expected because of the established oxygen coordination site in N,N-dimethylmethanesulfinamide.

The magnitudes of the enthalpies of adduct formation with trimethylalane are large and compare with that measured for trimethylamine (−29.96 ± 0.19 kcal/mole).[8] The relative basicities of these sulfur–oxygen bases indicate that successive replacement of methyl groups by amino groups decreases the electron-donating ability of the oxygen. The basicity sequence toward trimethylalane is qualitatively the same as that indicated by estimated phenol enthalpies. This correlation suggests that trimethylalane detects the variation in basicity in the same way as a proton. Steric effects in the trimethylalane adducts are either constant or not important since the relative order of interaction is similar to that found in the phenol adducts where steric effects are minimal.

The general basicity order of these sulfur–oxygen donors toward both trimethylalane and phenol is sulfoxide > sulfinamide > thionylamide. In carboxylic acid amides, where the nitrogen–carbon–oxygen bonding system very efficiently propagates the inductive influence of substituents on the nitrogen, the basicity at the oxygen atom is greater than in other carbonyl compounds such as ketones and esters. In the corresponding sulfur–oxygen systems as observed in this study substitution of an amino group for a methyl group decreases the donor ability at the oxygen site indicating that the lone pair of electrons on nitrogen is not effectively delocalized to the oxygen atom. However, the lack of interaction of phenol with the amino nitrogen in the sulfinamides and the thionylamides suggests that the lone pair of electrons on the nitrogen may be involved in $p\pi$–$d\pi$ bonding with an acceptor d orbital on sulfur, reducing the availability of the electron pair for coordination. It is also plausible that the inductive effects of the methanesulfinyl group or the aminosulfinyl group are sufficient to decrease the nitrogen lone pair availability below that of the lone pairs on oxygen.

(8) C. H. Henrickson, D. Duffy, and D. P. Eyman, in preparation.