[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Computation of Entropy Increments in Gaseous Bimolecular Associations. I. Donor–Acceptor Reactions

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In this paper, it is first demonstrated that good values for the over-all entropy increments in gaseous bimolecular addition reactions, of the type A + B = AB, can be computed from our knowledge of, or from judicious estimates of, the structural and spectroscopic parameters of each species involved. These values were combined with available ΔH^0's, to deduce equilibrium constants. This was done for several systems for which direct equilibrium studies do not appear feasible. It is also shown that the vibrational entropy increment in addition compound formation, which may be computed by subtracting $\Delta S^0_{\text{tr.+r.}}$ from the available $\Delta S^0_{\text{total}}$, has particular significance in that it gives a measure of the tightness of the new A–B bond. A plot of ΔS_{v} against the reduced mass at the A and B groups is proposed as a quantitative measure of this bond tightness.

In this paper we wish to report on the calculations we have made for the entropy changes which accompany homogeneous gas phase reactions between Lewis type acids and bases; in particular, reactions of acids in which the acceptor atom is boron. Calculations were first carried out for a system for which experimental data were available. The resulting agreement between experimental and calculated ΔS^0 values, served to check the structural and spectroscopic parameters assigned to the species involved, and to give an indication of the accuracy to be expected for calculations done on other reactions. The calculations of ΔS^0 values were then carried through for several reactions for which the enthalpy increments only were available, so that the equilibrium constants could be estimated. As yet, these constants cannot otherwise be determined.

Thermodynamic data are available for the decompositions of borine carbonyl ($OC:BH_3$) and deuterated borine carbonyl ($OC:BD_3$), as reported by Burg.[1] Our values of ΔS^0 were obtained by

		Experimental	Computed
(1)	$2OC:BH_3 = B_2H_6 + 2CO$	$\Delta H^0 = 9.142$ kcal./mole	32.11
		$\Delta S^0 = 32.51 \pm 0.5$ e.u.	± 0.5
(2)	$2OC:BD_3 = B_2D_6 + 2CO$	$\Delta H^0 = 8.465$ kcal./mole	31.64
		$\Delta S^0 = 32.47 \pm 0.5$ e.u.	± 0.7

computing the entropy of each species in the usual manner, from structural and spectroscopic parameters, as indicated below.

The translational plus rotational entropies of B_2H_6 and B_2D_6 were computed from the structural parameters given by Hedberg and Schomaker.[2] The vibrational assignment for diborane used was that given by Anderson and Barker.[3] For the frequencies of B_2D_6, the eight infrared bands reported by Webb, Neu and Pitzer[4] were considered along with those of diborane, and by using the Teller–Redlich product rule, all the fundamental frequencies were estimated. The resultant entropies for the ideal gases are

$$B_2H_6:\ S^0_{300}(1\text{ atm.}) = (53.26)_{\text{tr.+r.}} + (2.34)_{\text{v}} = 55.60\text{ e.u.}$$

$$B_2D_6:\ S^0_{300}(1\text{ atm.}) = (55.22)_{\text{tr.+r.}} + (4.39)_{\text{v}} = 59.61\text{ e.u.}$$

This value for diborane is in agreement with that reported by Webb, *et al.* (55.74 e.u.), based on their own frequency assignments, and earlier structural work.

The translational plus rotational entropies of $OC:BH_3$ and of $OC:BD_3$ were computed from the structural parameters given by Gordy, Ring and Burg.[5] The fundamental frequencies of $OC:BH_3$ were reported by Cowan,[6] while those for $OC:BD_3$ were computed from Cowan's secular equation for the $W_3X–Y–Z$ molecule. To correct for non-ideality, critical constants were estimated from the vapor pressure curve,[7] and were used in the Berthelot equation in the usual manner. The resulting entropies are

$$OC:BH_3:\ S^0_{300}(1\text{ atm.}) = (55.62)_{\text{tr.+r.}} + (3.52)_{\text{v}} - (0.043)_{\text{n.i.}} = 59.10\text{ e.u.}$$

$$OC:BD_3:\ S^0_{300}(1\text{ atm.}) = (56.94)_{\text{tr.+r.}} + (4.44)_{\text{v}} - (0.043)_{\text{n.i.}} = 61.34\text{ e.u.}$$

The entropy of CO as determined by Johnston and Davis[8] is 47.357 e.u. at 300°K. and one atmosphere.

Using the above entropies, our values given in equations 1 and 2 are readily deduced; the assigned limits of error result from an analysis of the uncertainties in the calculations. These check the experimental values rather well.

The key reaction to further calculations is the *equilibrium between diborane and borine* (BH_3), for which we have reported thermodynamic constants in a previous letter[9]

$$(3)\quad 2BH_3 = B_2H_6 \quad \begin{array}{l} \Delta H^0_{273} = -28\text{ kcal./mole} \\ \Delta S^0_{300} = -34.22\text{ e.u.} \end{array}$$

The entropy increment is 0.4 unit numerically larger than the published value, resulting from slight revisions in the calculation; the enthalpy increment is 4 kcal. smaller, based on a reanalysis of kinetic data. The absolute entropy of borine was estimated as follows. A planar structure, with H–B–H angles of 120° (sp^2 type bonding) was assumed. The B–H distance is very likely of order 1.16 to 1.18 Å., and it is known that the B–H stretching force constants in $B_3N_3H_6$ and in $OC:BH_3$ are 3.42×10^5 and 3.21×10^5 dynes/cm., respectively.[6,10] Consistent with these

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(1) A. B. Burg, THIS JOURNAL, **74**, 3482 (1952).

(2) K. Hedberg and V. Schomaker, *ibid.*, **73**, 1482 (1951).

(3) W. E. Anderson and E. F. Barker, *J. Chem. Phys.*, **18**, 698 (1950).

(4) A. N. Webb, J. T. Neu and K. S. Pitzer, *J. Phys. Chem.*, **17**, 1007 (1949).

(5) W. Gordy, H. Ring and A. B. Burg, *Phys. Rev.*, **78**, 1482 (1951).

(6) R. D. Cowan, *J. Chem. Phys.*, **18**, 1101 (1950).

(7) A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **59**, 780 (1937).

(8) H. L. Johnston and C. O. Davis, *ibid.*, **56**, 271 (1934).

(9) S. H. Bauer, A. Shepp and R. E. McCoy, *ibid.*, **75**, 1003 (1953).

(10) B. L. Crawford and J. T. Edsall, *J. Chem. Phys.*, **7**, 223 (1939).

values, one may apply Badgers rule,[11] which relates bond distance to stretching force constant to deduce 1.16 Å. and 3.38 × 10^5 dynes/cm. for the B–H distance and stretching force constant, respectively. To compute all vibrations of borine two more force constants are needed; k_d for in-plane bending, and k_D for out-of-plane bending. These force constants are available[12] for BF_3, BCl_3 and BBr_3, and by comparing ratios of k/k_d and k/k_D for the three halides we were able to estimate the values of k_d and k_D in BH_3 to be 0.13 × 10^5 and 0.30 × 10^5 dynes/cm., respectively. These lead to the fundamental frequencies: 2384 cm.$^{-1}$ (a), 802 cm.$^{-1}$ (a), 2976 cm.$^{-1}$ (e) and 1765 cm.$^{-1}$ (e). It is to be emphasized that these structural and spectroscopic parameters are estimates only. Nevertheless, the ideal gas entropy, depending only slightly on the magnitude of the frequencies, and on the logarithm of the products of the moments of inertia, should be accurate to half an entropy unit or better. Hence the entropy for the ideal gas is

$$BH_3\text{: } S^0_{300}(1 \text{ atm.}) = (44.69)_{\text{tr.+r.}} + (0.22)_{\text{v}} = 44.91 \text{ e.u.}$$

This value, combined with that for B_2H_6 leads to the ΔS^0 given in equation 3.

The Reaction of Borine with Carbon Monoxide.—One may combine equations 1 and 3, and their respective ΔH^0 values

$$(4) \quad BH_3 + CO = OC\text{:}BH_3 \quad \Delta H^0 = -18.6 \text{ kcal./mole}$$

The ΔS^0 for this reaction follows from the above listed absolute entropies. The equilibrium constant (which cannot be determined by experiment) may then be estimated.

$$\begin{aligned} \Delta S^0 &= -33.17 \text{ e.u., and} \\ \log (K_{\text{eq}})_{\text{atm}} &= -\ 7.25 + 4065/T \\ K_{300} &= \quad 2.0 \times 10^6 \text{ atm.}^{-1} \end{aligned}$$

The Hypothetical Reaction of Boron Trifluoride with Carbon Monoxide.—Efforts to prepare the addition compound $OC\text{:}BF_3$ according to the reaction

$$(5) \qquad BF_3(g) + CO(g) = OC\text{:}BF_3(g)$$

have not been successful. One may nevertheless estimate the anticipated entropy change. The entropy of BF_3 has been determined by Spencer[13] at 300°K. and one atmosphere; it is 60.77 e.u. In the structure of $OC\text{:}BF_3$, we assigned the B–F distance and F–B–C angles the values 1.38 Å. and 107°, respectively, corresponding to the ones observed in crystalline $H_3N\text{:}BF_3$.[14] The B–C and C–O distances were taken to be the same as in $OC\text{:}BH_3$. For the vibrational spectrum, the six BF_3 frequencies were taken to be the same as found in the compound $Me_2O\text{:}BF_3$, for which preliminary raman[15] and infrared[16] spectra have been recorded, *i.e.*, 804(a), 530(a), 1216(e), 496(e), in cm.$^{-1}$. The B–C, C–O, and B–C–O frequencies were taken to be 500, 1500 and 280 cm.$^{-1}$ by extrapolating Cowans[6] values for $OC\text{:}BH_3$ and our estimates for $OC\text{:}BD_3$. The $-BF_3$ rocking frequency was taken to be 365 cm.$^{-1}$, which is the assigned value for the rocking of the $-CF_3$ group in F_3CCH_3.[17] These estimates lead to 72 ± 1 e.u. for gaseous $OC\text{:}BF_3$, at 300°K. and one atmosphere (ideal state), and to the value $\Delta S^0_{300} = -36$ e.u., for 5.

The fact that $OC\text{:}BF_3$ has not been prepared in the laboratory indicates either that equilibrium had not been attained in these experiments, or that the equilibrium constant for reaction 5 must be such that undetectably small amounts of the addition compound exist at equilibrium. If we assume the maximum value for the equilibrium constant to be of order 10^{-2} atm.$^{-1}$, the maximum value (in the negative sense) of ΔH^0 is of order -8 to -10 kcal./mole. When this enthalpy increment is compared to that of 4 and of 1, it appears that BF_3 is a weaker acid than BH_3 by about 10 to 12 kcal./mole, while it is stronger than B_2H_6 by about 3.5 to 5.5 kcal./mole, with respect to CO as the reference base. [With trimethylamine as a reference base, BF_3 appears to be weaker than BH_3 by 1 to 2 kcal.[18] Hence we believe that it was lack of activation of the CO rather than the weakness of BF_3 which led to no addition compound.]

Reactions of Boron Acids with Trimethylamine.—The entropy of gaseous trimethylamine (Me_3N) may be computed at any temperature from the data given by Aston, *et al.*,[19] and the tables by Pitzer[20] for the entropy contribution due to restricted rotation. At 300°K. and one atmosphere, it is 69.31 e.u. To compute the entropy of the addition compound $Me_3N\text{:}BH_3$ first note that it is isoelectronic with neopentane (Me_3CCH_3) and, therefore, to a good approximation, the vibrational plus restricted rotational entropies of the two molecules are the same. According to Pitzer,[21] the value of $S^0_{\text{v+rr}}$ for neopentane, and hence for $Me_3N\text{:}BH_3$, is 14.15 e.u., at 300°K. To compute the translational plus rotational entropy, we used the interatomic distances determined for $Me_3N\text{:}BH_3$ by electron diffraction,[22] but for the angles, we used the more accurate values determined in the solid for the molecule $Me_3N\text{:}BF_3$,[23,24] which has been shown to be isomorphous with $Me_3N\text{:}BH_3$. The resultant translational plus rotational entropy at 300°K. and one atmosphere is 62.27 e.u., and the total entropy (ideal gas) is estimated to be 76.42 e.u. Thus we arrive at the estimates

$$(7) \quad Me_3N + BH_3 = Me_3N\text{:}BH_3(g) \qquad \Delta S^0_{300} = -37.80 \text{ e.u.}$$

$$(8) \quad Me_3N + {}^1/{}_2B_2H_6 = Me_3N\text{:}BH_3(g) \qquad \Delta S^0_{300} = -20.69 \text{ e.u.}$$

For the addition compound $Me_3N\text{:}BF_3$, we felt that we could deduce an approximate value for the

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[11] R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934).

[12] G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 178.

[13] H. M. Spencer, *J. Chem. Phys.*, **14**, 729 (1946).

[14] J. L. Hoard, S. Geller and W. M. Cashin, *Acta Cryst.*, **4**, 396 (1951).

[15] F. V. Bunderman and S. H. Bauer, *J. Phys. Chem.*, **50**, 32 (1946).

[16] S. H. Bauer, unpublished work.

[17] J. R. Nielsen, H. H. Claasen and D. C. Smith, *J. Chem. Phys.*, **18**, 1471 (1950).

[18] R. E. McCoy, Doctor's Thesis, Department of Chemistry, Cornell University, 1952.

[19] J. G. Aston, M. Sagenkahn, G. Szasz, G. Moessen and H. Zuhr, THIS JOURNAL, **66**, 1171 (1944).

[20] K. S. Pitzer, *J. Chem. Phys.*, **5**, 469 (1937).

[21] K. S. Pitzer, *ibid.*, **5**, 473 (1937).

[22] S. H. Bauer, THIS JOURNAL, **54**, 1804 (1937).

[23] S. Geller and J. L. Hoard, *Acta Cryst.*, **4**, 399 (1951).

[24] S. Geller, R. E. Hughes and J. L. Hoard, *ibid.*, **4**, 380 (1951).

vibrational plus restricted rotational entropy by correcting $Me_3N:BH_3$ for the replacement of a BH_3 group by a BF_3 group. To do this, we noted that in the cases of $OC:BH_3$ and $OC:BF_3$, a detailed comparison of the spectra showed that such a replacement caused a change of 4.5 e.u. We assumed that the same increment may be assigned in comparing $Me_3N:BF_3$ with $Me_3N:BH_3$. Also, we assumed that the change from BH_3 to BF_3 would reduce the restricted rotational entropy by one unit. Using the structural parameters available for $Me_3N:BF_3$,[23] we determined the translational plus rotational entropy at 300° and one atmosphere to be 66.37 e.u. As a result, we estimate the total entropy of the ideal gas to be 84.0 e.u., and

(9) $Me_3N(g) + BF_3(g) = Me_3N:BF_3(g)$

$\Delta S^0_{300} = -46.1$ e.u.

The ΔH^0 values for reactions 8 and 9, and by using 3, that for 7 also, have been measured in this Laboratory by R. E. McCoy.[18] The actual measurements were made between the gaseous reactants to produce the solid addition compounds, but reported heats of sublimation were used to convert the data to the homogeneous gas phase reactions. These ΔH^0 values, the computed ΔS^0 values, and resulting equilibrium constants are summarized with our other results in Table I.

TABLE I

THERMODYNAMIC DATA FOR HOMOGENEOUS GAS PHASE REACTIONS

$\Delta S°$ in e.u. at 300° and one atmosphere (ideal gas state): $\Delta H°$ in kcal./mole; K_{eq} in units of $[\text{atmospheres}]^{-1}$ at 300°K.

						$\Delta S^0_{\text{computed}}$	ΔH^0	K_{eq}
(3)	BH_3	+	BH_3	=	B_2H_6	−34.22	−28.0	8.2×10^{12}
(4)	CO	+	BH_3	=	$OC:BH_3$	−33.17	−18.6	2.0×10^{6}
(5)	BF_3	+	CO	=	$OC:BF_3$	−36.0	17(?)	10^{4}(?)
(6)	CO	+	$^1/_2B_2H_6$	=	$OC:BH_3$	−16.05	− 4.57	0.66
(7)	Me_3N	+	BH_3	=	$Me_3N:BH_3$	−37.80	−31.3	3.5×10^{14}
(8)	Me_3N	+	$^1/_2B_2H_6$	=	$Me_3N:BH_3$	−20.69	−17.5	1.7×10^{8}
(9)	Me_3N	+	BF_3	=	$Me_3N:BF_3$	−46.1	−26.6	2.0×10^{9}

Reactions of Boron Acids with Ethers.—The entropy of gaseous dimethyl ether (Me_2O) has been determined[25] at 298.16°K. (we may take the value to be that at 300°K.) and one atmosphere to be 63.72 e.u. The structure of the addition compound $Me_2O:BF_3$ has been determined in the gas phase by electron diffraction.[26] The values so found may be used to deduce its translational plus rotational entropy to be 67.65 e.u. at 300°K. and one atmosphere. From the available spectra of the molecule,[15,16] all the frequencies except the torsions about the C–O and O–B bonds have been tentatively assigned. It is difficult to make an acceptable guess for the degree of restriction of free rotation about these bonds, but we may compute a *maximum* value for the entropy of the molecule by assuming completely free rotation. Under this assumption, the vibrational entropy is 10.0 e.u., and the free-rotational entropy is 11.1 e.u. The *maximum* value of the entropy is therefore 88.75 e.u. at 300°K. and one atmosphere (ideal gas). From this, we may estimate the *minimum* value for ΔS^0 of the reaction

(10) $Me_2O(g) + BF_3(g) = Me_2O:BF_3(g)$

$(\Delta S^0_{300})_{\min} = -35.7$ e.u.

where the subscript implies a *minimum absolute* quantity. This is in contrast to the experimental value which has been reported[27] to be −32.2 e.u. Two other entropy changes were quoted in the same paper, and are likewise too small

(11) $Et_2O(g) + BF_3(g) = Et_2O:BF_3(g)$

$\Delta S^0 = -27.5$ e.u.

(12) $C_4H_8O(g) + BF_3(g) = THF:BF_3(g)$

$\Delta S^0 = -27.1$ e.u.

(THF = tetrahydrofurane)

Qualitatively, one may compare these ΔS^0 values with those for other reactions of two to one stoichiometry appearing in Table I. When this is done, it becomes apparent that the values for these three reactions are appreciably smaller than what one expects for molecules of their size and molecular weight. Below, we shall demonstrate in a more quantitative manner (with the aid of Fig. 1) that the value of ΔS^0 for 10 is 8 or 9 e.u. too small (in magnitude), and that the values for reactions 11 and 12 are presumably also too small by about the same amount.

The Significance of $\Delta S^0_{\text{vibration}}$.—It is of interest to consider the factors which determine the magnitude of the entropy increment accompanying the reaction A + B = AB, where the A···B linkage need not be restricted to a single bond. All that is required is that the complex be a specific molecular species. The total change in entropy may be considered as being the sum of two terms

$$\Delta S^0 = \Delta S^0_{\text{tr.+r.}} + \Delta S^0_{\text{v}}$$

where $\Delta S^0_{\text{tr.+r.}}$ is the entropy increment which would have been observed were all the molecules rigid bodies, and ΔS^0_{v} includes the difference in the entropy contributions from the non-rigid degrees of freedom (vibration and restricted rotation). Since the system loses three translational and three rotational degrees of freedom due to the association, $\Delta S^0_{\text{tr.+r.}}$ must be negative. For ideal gases this is given (cal./deg./mole of product) by

$$\Delta S^0_{\text{tr.+r.}} = 2.2868\,[8 \log_{10} T + 3 \log_{10}(M_{AB}/M_AM_B) + \log_{10}(I_{AB}/I_AI_B) - 2 \log_{10}(\sigma_{AB}/\sigma_A\sigma_B)] - 7.6973$$

where M_{AB}, I_{AB}, σ_{AB} are the molecular weight, the product of the principal moments of inertia (at. wgt. $A^2)^3$, and the symmetry number, respectively, of the species AB, etc. The term in (log T) is the largest, but over the usual experimental range of temperature it varies little. Of the remaining terms, that in (log M_{AB}) changes most from one reaction to another; it is always larger than the quantities involving I and σ. Since the nature of the bond which produces the complex affects I and σ only (as it determines the structure of the molecule), and since these introduce small contributions, a plot of $\Delta S^0_{\text{tr.+r.}}$ *versus* log (M_{AB}/M_AM_B) is fairly linear, covering many different bimolecular association reactions.

The vibrational increment, on the other hand, is

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[25] R. M. Kennedy, M. Sagenkahn and J. G. Aston, THIS JOURNAL, **63**, 2267 (1941).

[26] S. H. Bauer, G. R. Findlay and A. W. Laubengayer, *ibid.*, **67**, 339 (1945).

[27] H. C. Brown and R. M. Adams, *ibid.*, **64**, 2557 (1942).

TABLE II

ΔS^0 in units of cal./mole/deg.

Molecule AB for the reaction A + B = AB	$-\Delta S^0$	$-(\Delta S^0_{tr.+r.})_{300}$	ΔS^0v	Ref.
B_2H_6	34.22	36.12	1.90	
C_2H_6	37.24	39.39	2.15	28, 29
	40.12	42.27		
N_2O_4	42.21	49.55	7.34	30
$OC:BH_3$	33.17	36.47	3.30	
$OC:BF_3$	36.0	42.30	6.30	
$Me_3N:BH_3$	37.80	42.63	4.83	
$Me_3N:BF_3$	46.06	52.70	6.64	
$(Me_2NBH_2)_2$	50.90	58.64	7.74	31, 32, 40
$Me_2O:BF_3$	32.2(?)	49.40	17.2(?)	26, 27
$(AlMe_3)_2$	42.44	54.91	12.47	33, 34
$(AlCl_3)_2$	34.65	59.02	24.37	35, 36
$(AlBr_3)_2$	36.18	63.95	27.77	35, 36
$(AlI_3)_2$	33.53	67.73	34.20	35, 36
$(HCOOH)_2$	35.98	52.09	16.11	37, 38
$(H_3CCOOH)_2$	36.84	56.57	19.73	37, 38
$(C_2H_5COOH)_2$	36.39	58.64	22.25	37, 38
$(F_3CCOOH)_2$	36.30	61.47	25.17	39

positive, since six new vibrational degrees of freedom result from the association process. Considering the form of these six vibrations, there is first the A · · · B bond stretching, resulting from the loss of translational freedom in the x-direction (taking the x-axis along the A · · · B bond). The loss of rotational freedom about the x-axes gives rise to another vibration; the bond torsion. Rotation about the y-axes gives rise to two bending vibrations, one symmetric, and one asymmetric. Likewise, rotations about the z-axes give rise to two bendings, one symmetric and one asymmetric. If the product molecule has sufficient symmetry (for example, ethane) the latter two symmetric and two asymmetric vibrations reduce to two doubly degenerate frequencies. Now if the new bond is weak (as measured by properties of the bond at the equilibrium inter-nuclear separations) these frequencies *will* be low, since the motions *will* involve the relative displacements of massive units held together by a small force constant, and the entropy associated with them will be large. On the other hand, if the new bond is strong, the new vibrational frequencies will be tight, comparable to those present in the parent molecules, and the entropy gain will be small. As will be seen in Table II, ΔS^0_v varies from a few per cent. of ΔS^0 in the case of tight bonds, to as much as 70 or 80% of ΔS^0, for loose bonds. In addition, by virtue of the formation of a new bond (or bonds) with the same number of valence electrons, the bonds initially present in the reactant molecules may become slightly weaker, with a resultant entropy increment. This effect is quite small, however. Hence the magnitude of ΔS^0_v is very sensitive to the nature of the bonding which produces the AB complex. For this reason, ΔS^0_v is a useful criterion for judging bond type, and relative bonding tightness, giving in some ways more information about the A · · · B bond itself, than does ΔH^0, [which is usually taken as the definition of "bond strength" of the A · · · B link]. For, consider that ΔH^0 is a sum of three terms

$$\Delta H^0 = \Delta E^0_0 + \Delta H^0_{tr.+r.} + \Delta H^0_v$$

By far the largest term is ΔE^0_0, the difference between the energies of product and reactants in their lowest states, since $\Delta H^0_{tr.+r.}$ and ΔH^0_v together are never more than 4 or 5 kcal./mole. Thus a small value for ΔH^0 can be interpreted as indicating either the formation of a weak A · · · B bond, or the formation of a strong bond with compensating en-

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(28) The entropy of CH_3 was computed by us on the basis of a planar model with the C–H distance 1.09 Å., and $\sigma = 6$; and of a pyramidal model, with the C–H distance 1.09 Å. $\sigma = 3$. The vibrational entropy is very small (0.05 e.u.) as estimated from known frequencies attributed to bonded CH_3. The term $R \ln 2$ is included.

(29) The entropy of C_2H_6 was computed from the known structure, and from the spectral assignment of G. E. Hansen and D. M. Dennison, *J. Chem. Phys.*, **20**, 313 (1952).

(30) The total entropy increment for the NO_2 dimerization has been reported by W. F. Giauque and J. D. Kemp [*ibid.*, **6**, 40 (1938)]. To compute $S^0_{tr.+r.}$ for NO_2, we used the value of I_{NO_2} reported in that paper. To compute that of N_2O_4, we assumed the distances 1.18 Å. for the N–O bond, 1.62 for the N–N bond, and an O–N–O angle of 140°. We assumed that the two NO_2 groups are in perpendicular planes.

(31) The experimental entropy increment for the dimerization of Me_2NBH_2 has been reported by A. B. Burg and C. L. Randolph, Jr., THIS JOURNAL, **73**, 953 (1951), [$\Delta H^0 = -20.74$ kcal./mole dimer].

(32) The value of $S^0_{tr.+r.}$ for $(Me_2NBH_2)_2$ was computed on the basis of a preliminary structural study of the solid by J. L. Hoard and P. J. Schapiro. The dimer consists of a square four membered B–N ring with distances of 1.60 Å. for B–N, 1.45 Å. for N–C, and 1.33 for B–H. The CH_3 groups, and H atoms extend symmetrically from the ring. For the monomer, we assumed the distances, 1.42 Å. for C–N, 1.50 Å. for N–B and 1.33 Å. for B–H, and that the C–N–C angle is 110°, and the H–B–H angle is 120°. Also, we assumed that the Me_2N group and the BH_2 group are in perpendicular planes.

(33) The experimental entropy increment for the dimerization of $AlMe_3$ has been reported by A. W. Laubengayer and W. F. Gilliam, THIS JOURNAL, **63**, 477 (1941).

(34) The structure of $(AlMe_3)_2$ was investigated by L. O. Brockway and N. R. Davidson, *ibid.*, **63**, 3287 (1941). Their model for the ethane like structure offered the best fit to their experimental results. It is now believed however that the structure is a four-membered bridge type, similar to that present in the other $(AlX_3)_2$ dimers. This point of view has just been confirmed by an X-ray analysis of $Al_2(CH_3)_6$ crystals (P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953)). Of the bridge structures which Brockway and Davidson tried, Model 6 fits the data best. On the basis of model 6, we computed $S^0_{tr.+r.}$ for the dimer. For the monomer, we assumed a planar structure with C–Al–C angles of 120°, and a C–Al distance of 2.0 Å.

(35) Experimental data on the association of the aluminum trihalide series have been published by W. Fischer and O. Rahlfs, *Z. anorg. allgem. Chem.*, **205**, **1** (1932). Equilibrium constants as a function of temperature are given. By plotting their data, we arrived at the ΔS^0 values appearing in Table II. Since these data have not been plotted carefully by the original authors, the ΔH^0 values which they quote are not the best obtainable from the data. We deduced the values 29.6, 28.8 and 23.9 kcal./mole for ΔH^0 of dissociation of the chloride, bromide, and iodide dimers, respectively, in contrast to the reported values of 29.0, 26.5 and 22.5.

(36) The structures of the three aluminum trihalide dimers have been determined in the gas phase by K. J. Palmer and N. Elliot, THIS JOURNAL, **60**, 1852 (1938). For the monomers, planar structures with X–Al–X angles of 120° were assumed. The values 2.10, 2.25 and 2.55 Å. were assumed for the Al–Cl, Al–Br, and Al–I distances, respectively.

(37) The experimental values for ΔS^0 for the dimerization of formic, acetic, and propionic acids in the vapor phase were reported by M. D. Taylor and J. Burton, *ibid.*, **74**, 4151 (1952).

(38) The values for $\Delta S^0_{tr.+r.}$ were computed by L. Slutsky and S. H. Bauer, *ibid.*, **76**, 270 (1954).

(39) R. E. Lundin, F. E. Harris and L. K. Nash, *ibid.*, **74**, 4654 (1952).

(40) Data on the equilibrium $(Me_2NBCl_2)(s) = 2Me_2NBCl_2(g)$ have been presented by C. A. Brown and R. C. Osthoff, *ibid.*, **74**, 2340 (1952). The magnitudes of the enthalpy and entropy increments are about twice those expected, from analogy with $(Me_2NBH_2)_2$ and other N:B systems. We can offer no explanation for these data. On the other hand, the magnitudes for ΔH^0 and ΔS^0 for the association of Me_2NBCl_2 with HCl also reported by these authors are completely consistent with the analysis given in this paper.

thalpy changes due to a general weakening, by small amounts, of many of the original bonds in the unassociated molecules. This latter interpretation is possible because all the energy changes are additive in their contribution to ΔE^0_o, and hence to ΔH^0. In ΔH^0_v, or ΔS^0_v, however, these energy changes appear weighted by an exponential (in the partition function) so that only the large changes in tight bonds, or the formation of new loose bonds make appreciable contributions. However, ΔH^0_v cannot be computed without a knowledge either of all the frequencies of the AB complex, or its specific heat as a function of temperature, whereas ΔS^0_v can be estimated from ΔS^0 and $\Delta S^0_{tr.+r.}$. Hence values of ΔS^0_v which are large for one type of bond, as compared to values for another type of bond, indicate unambiguously that the A · · · B bond *itself* is weaker in the former than that in the latter.

To illustrate this, we have assembled in Table II, ΔS^0 values for several series of reactions, along with computed values for $\Delta S^0_{tr.+r.}$. We have set $\Delta S^0_v = (\Delta S^0 - \Delta S^0_{tr.+r.})$, except for those cases above where this quantity was actually computed. Since most of the experimental values for the total entropy increments were deduced from equilibrium data, generally taken far above room temperature, a question arose as to a proper temperature convention. Fortunately, it appears that to the precision of the available data, the ΔS^0's vary little over large temperature ranges. Hence by computing all $\Delta S^0_{tr.+r.}$'s at 300°K., the resultant ΔS^0_v are also for that temperature.

In Fig. 1, ΔS^0_v is plotted as a function of $\mu[=M_A \cdot M_B/(M_A + M_B)]$, the reduced mass of the AB molecule. The points clearly fall into two groups, corresponding to two distinctive bonding cases. We propose that the position of these groups relative to each other indicates the relative tightness of the A · · · B bonds in the molecules considered. The association reactions which fall into group 1 show small $[\Delta S^0_v/\log \mu]$ values, and are typical of a large number of donor–acceptor reactions which generally have been considered as resulting from the formation (essentially) of an electron-pair bond. The force constants for these charge-transfer bonds are comparable to those for the corresponding single bonds, because the *isovalent* dissociation of the complexes would require dissociation energies comparable to those for normal single bonds. In contrast, the *adiabatic* dissociation energies may be comparatively small. In other words, group 1 is characterized by an adiabatic dissociation path which, due to appreciable hybridization changes, may lie considerably below that for the rather steep isovalent path. This is the case for $(BH_3)_2$, $(Me_2NBH_2)_2$ and $(AlMe_3)_2$ even though these dissociations require the rupture of bridges rather than of single bonds.

The second group consists of the dimers of the aliphatic acids and aluminum trihalides. These associations show larger $[\Delta S^0_v/\log \mu]$ values, indicating appreciably lower force constants, in agreement with the very low frequencies which have been reported for the Al_2X_6 family.[41,42] A complete analysis of the ΔS^0_v's for the carboxylic acids, including a normal coördinate treatment of the vibrations of the dimers is presented in the following paper.[38] It is obvious that the large values for the vibrational entropy increments parallel in magnitude the increasing weights of the groups attached to the carboxylic carbon, and must be interpreted as arising from the very low frequency vibrations of massive units, weakly bonded to one another. For this group the *isovalent* and *adiabatic* dissociation paths are close to one another, neither being steep, and neither involving significant hybridization changes.

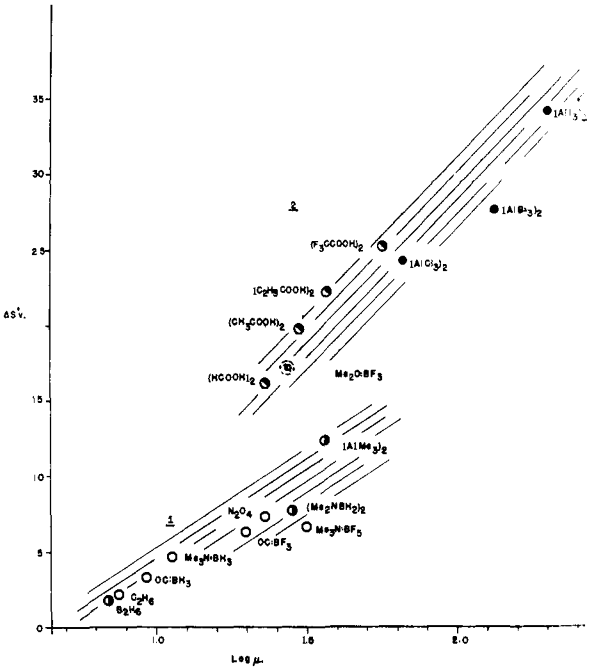

Fig. 1.

The reported value for $Me_2O:BF_3$ has been included in Fig. 1. The structural study[26] as well as the spectroscopic data[15,16] give no indication of excessive loosening of the B–F or C–O bonds, but are consistent with the model in which the B–O distance is approximately equal to the sum of the single bond radii. Hence, this point should lie in group 1, and we venture to suggest that the reported value is in error by 8 or 9 e.u.

The following qualitative argument demonstrates that the proper variable against which to plot ΔS^0_v should be logarithmically related to the reduced mass. We have already stated that the vibrational entropy increment is due almost entirely to the entropy contributions by the six new vibrations about the A · · · B bond. For heavy AB complexes all of these frequencies are low, and even for the lightest molecules, the torsional and symmetric wagging frequencies are quite low. Now, for a sufficiently low value of the frequency (ω), the entropy associated with that vibration is given by

$$(S^0_v)_i/R = 1 - \ln (h\omega_i/ckT) + (h\omega_i/ckT)^2/24 - \ldots$$

For the stretching frequency, $\omega_s \propto (k_s/\mu)^{1/2}$ where k_s is the stretching force constant, and μ the reduced mass. The wagging frequencies are each proportional to a term of the form $(k_b r_e^2/I_x)^{1/2}$ where k_b

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(41) E. J. Rosenbaum, *J. Chem. Phys.*, **8**, 643 (1940).

(42) K. W. F. Kohlrausch, "Ramanspektren, Becker and Erler," Leipzig, 1943, p. 196.

is a bending force constant, I_x is a reduced moment of inertia about whichever of the three axes is appropriate, and r_e is a radius of extension of the vibrating groups from their pivot, and is numerically not very different from the magnitude of the length which is included in I_x. Dimensionally, these $(\text{lengths})^2$ cancel, so that the wagging frequencies as well are proportional to $(k_b/<\mu>)^{1/2}$, where $<\mu>$ is a properly averaged mass. Hence

$$\Delta S^0{}_v/R \cong \text{constant} - \frac{1}{2}\ln \overset{6}{\underset{i=1}{\pi}} k_i + 3\ln <\mu> + \frac{1}{24}\left(\frac{h}{2\pi kT}\right)\sum_{i=1}^{6}\frac{k_i}{<\mu>} + \ldots$$

It follows that when ΔS^0_v is plotted against log μ, a straight line with slope 13.7 would result, provided (a) k_i did not vary from one molecule to the next; (b) the simple reduced masses were equal to the properly averaged masses; and (c) the magnitudes of the remaining terms in the expansion are negligible. In Fig. 1, group 2 has roughly a slope of 14, while group 1 has roughly a slope 5.5.

Analyses of other bimolecular association reactions in this manner will be of interest, particularly where the vibrational spectra are unknown, or have not been worked out. We are currently investigating the tri-aryl methyl radical dimers.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Computations of Entropy Increments in Gaseous Bimolecular Associations. II. The Dimerization of Carboxylic Acids, and the Addition of Fluorine to Halogen Fluorides

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The procedures described in the preceding paper (I)[6] have been extended to two groups of reactions, the dimerization of carboxylic acids and the addition of fluorine to three halogen fluorides. For the first group, the magnitude of $\Delta S^0{}_{vib}$ has been cited as an argument for describing the dimers as consisting of weakly coupled monomers, according to the principle discussed in paper I. A highly simplified model for the structure of the dimers permitted a normal coördinate treatment which led to the six new fundamental frequencies ascribed to each dimeric species (formic, acetic, trifluoroacetic acids), as a consequence of the association process. The fact that the computed entropy increments check the reported values to better than one entropy unit lends strong quantitative support to the model proposed. Since the addition of fluorine to the three halogen fluorides involves the rupture of one bond, the formation of two new bonds, and extensive rearrangements of the original structures, the magnitudes of the entropy increments do not have a simple interpretation. They are useful in the making of estimates of average bond energies. Interesting differences between the several central halogen atoms appear when their fluorine ligancies go up by two. Arguments are presented for selecting the "higher" of the two possible values for the heats of dissociation of ClF, BrF and IF.

The Carboxylic Acids.—That the equilibrium constants for the dimerization of carboxylic acids differ appreciably, depending on the group substituted into the carboxyl carbon atom has been known for some time. Recently[1] speculations have appeared as to whether such differences are due primarily to enthalpy or entropy factors. The literature is replete with reports of experimental results regarding these systems, from which one may select values to prove either conclusion. Where available we prefer the data by Taylor and Bruton[2,3] since these investigators worked in the low pressure region where corrections for higher degrees of polymerization and deviation from ideal behavior are unnecessary. In the case of trifluoroacetic acid, Nash[1] computed equilibrium constants after he had extrapolated isothermal density curves to zero pressure. Reference to Table I shows that small differences appear both in the enthalpy and entropy terms, and that due to the rather close balance between them, appreciable variations in the magnitudes of the equilibrium constants result. Indeed, closer inspection of the reported entropy increments raises the question why these should be so nearly alike, since the masses and moments of inertia of the molecular species vary over a considerable range. The computations described below permitted the unscrambling of the effects due to mass, moments of inertia, internal rotations and molecular vibrations.

TABLE I

	$\Delta H^0{}_{433}$, kcal./mole	$\Delta S^0{}_{433}$, e.u.	$K_p(433)$, atm.$^{-1}$	Ref.
HCOOH	−14.1	−35.98	0.299	2
H_3CCOOH	−15.3	−36.84	.474	3
F_3CCOOH	−14.0	−36.30	.135	1
CH_3H_2CCOOH	−15.2	−36.39	.503	2

The structures for which the moments of inertia were computed are those given by Karle and Brockway,[4] *cf.* Table II. From these and the known molecular weights, one may readily compute $\Delta S^0{}_{tr.+r.}$ (rigid molecules). These are summarized in Table III.

The deduced values for $\Delta S^0{}_{(rigid)}$ first must be corrected for contributions due to restricted internal rotation. For simplicity we have assumed that the heights of the barriers hindering free rotation about C–C bonds remain unaltered due to the association process, and that both in acetic and trifluoroacetic acids the magnitude is 2500 cal./mole, with three equal minima in the angular potential function. Although these are not valid assumptions, the errors introduced thereby are of the order of one entropy unit, which is within other limitations to be introduced later. For acetic acid

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(1) R. E. Lundin, F. E. Harris and L. K. Nash, THIS JOURNAL, **74**, 4654 (1952).

(2) M. D. Taylor and J. Bruton, *ibid.*, **74**, 4151 (1952).

(3) M. D. Taylor, *ibid.*, **73**, 315 (1951).

(4) J. Karle and L. O. Brockway, *ibid.*, **66**, 574 (1944).