being the volatility of trimethylphosphine. Similar displacement reactions are known for tetraalkylammonium ions[19] and 1,1,1-trialkylhydrazinium ions (*vide supra*). In order to test this hypothesis, samples of pure aminotrimethylphosphonium chloride were placed in a solvent and equilibrated with pure tributylphosphine. In solutions of the concentrations employed in the competition reactions, trimethylphosphine was identified in the vapor phase over the reaction mixture, and aminotributylphosphonium chloride was formed. In more dilute solutions, however, less trimethylphosphine was formed, indicating consequently that less tributylphosphine had reacted, reflecting the fact that at higher dilution trimethylphosphine is less volatile and tributylphosphine has therefore less tendency to displace it from the corresponding aminophosphonium salt. When the trimethylphosphine–tributylphosphine competition for chloramine was run in more dilute solution, it was found that some aminotrimethylphosphonium chloride could be isolated (see Table I).

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Vapor-Phase Studies of Hydrogen Bonding in the Trimethylamine–Methanol System[1a]

BY MANFRED FILD,[1b] MARY F. SWINIARSKI, AND ROBERT R. HOLMES

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Hydrogen bond formation in the vapor phase of the methanol–trimethylamine system has been investigated by infrared spectroscopy as well as vapor pressure measurements. From intensity measurements in the infrared region made as a function of temperature and pressure, a value for the heat of formation of $CH_3OH-N(CH_3)_3$ of -7.1 ± 0.2 kcal/mol is obtained. The corresponding value from the pressure study is -7.5 ± 0.3 kcal/mol. These results are compared with ΔH values on other hydrogen-bonded complexes studied in the vapor phase by these same techniques as well as by nmr.

Spectroscopic examination of simple hydrogen-bonded systems in the vapor phase has attracted increasing attention. Thus, the presence of hydrogen bonding in alcohol–amine,[2] hydrogen halide–ether,[3,4] and nitric acid–ether[2c,5,6] complexes has been detected in the vapor phase by infrared measurements.

Recently, Clague, Govil, and Bernstein studied gas-phase chemical shifts in the methanol–trimethylamine[7] and hydrogen chloride–dimethyl ether[8] systems. From the temperature and pressure variation of the proton nmr signals, the enthalpy for the dissociation of the complexes was obtained. In the case of the hydrogen chloride–dimethyl ether complex, a value of ΔH of 7.1 ± 0.8 kcal/mol was reported.[8] Interpretation of pressure measurements on this system by Gladishev and Syrkin[9] has yielded a value of 7.6 kcal/mol while infrared studies by Bilozerska and Shchepkin[10] gave a value of 5.6 kcal/mol.

The reason for the discrepancy in these results is not clear. The pressure measurements were performed some time ago. In the nmr study the necessity of estimating a chemical shift for the fully complexed hydrogen chloride molecule introduces appreciable error, while in the infrared study the quantitative assessment of intensity changes is difficult in such systems if overlapping bands are present.

The potential usefulness of vapor-phase studies of hydrogen-bonding phenomena in an environment relatively free of many of the difficulties accompanying solution work provides the impetus for the present investigation. In this paper, we report vapor-phase studies using both the infrared and the vapor-pressure methods. The results allow comparison with values on other hydrogen-bonded complexes studied in the vapor phase by these same techniques as well as by the nmr method.

Experimental Section

Methanol (Fisher) was passed through Linde molecular sieves and distilled before use. Trimethylamine (Matheson LB) was fractionated in the vacuum system by trap to trap distillation.

For the vapor-pressure measurements a Pyrex vacuum system was used. Individual samples of the components, trimethyl-

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[1] (a) This research was supported by a grant from the Office of Saline Water, U. S. Department of the Interior. (b) Postdoctoral Research Associate.

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[9] A. T. Gladishev and Ya. K. Syrkin, *Compt. Rend. Acad. Sci. URSS*, **20**, 145 (1938).

[10] L. P. Bilozerska and N. D. Shchepkin, *Opt. Spektrosk.* (Akad. Nauk SSSR, Otd. Fiz. Mat. Nauk), **3**, 290 (1968); *Opt. Spectrosc. Suppl.*, **3**, 146 (1968).

TABLE I

THE EQUILIBRIUM CONSTANTS FOR THE FORMATION OF $CH_3OH\cdots N(CH_3)_3$

Mixtures at 25°		Temp, °K	Total pressure, mm	Equil pressure of $CH_3OH–N(CH_3)_3$, p_C, mm	Equil pressure of CH_3OH, $p_M - p_C$, mm	Equil pressure $(CH_3)_3N$, $p_A - p_C$, mm	Equil constant, $K_p \times 10^4$, mm^{-1}
	CH_3OH	319.27	171.05	1.79	30.21	139.04	4.27
	p_M = 29.89	317.40	169.71	2.11	29.70	137.89	5.16
I		311.35	166.05	2.50	28.71	134.84	6.46
	$(CH_3)_3N$	306.96	163.50	2.68	28.09	132.73	7.18
	p_A = 131.52	304.20	161.72	2.96	27.54	131.23	8.19
		299.28	158.57	3.45	26.55	128.56	10.12
		296.33	156.81	3.61	26.09	127.10	10.90
		289.78	152.68	4.19	24.86	123.64	13.65
		285.11	148.88	5.47	23.11	120.30	19.68
	CH_3OH	315.47	131.94	1.34	30.60	100.00	4.37
	p_M = 30.19 mm	310.58	129.47	1.75	29.70	98.03	6.00
II		306.44	127.48	1.98	29.04	96.46	7.07
	$(CH_3)_3N$	302.84	125.67	2.28	28.38	95.00	8.45
	p_A = 95.78 mm	302.41	125.42	2.34	28.27	94.80	8.74
		298.19	123.34	2.63	27.55	93.15	10.26
		294.16	121.43	2.85	26.93	91.65	11.54
		290.12	119.29	3.28	26.10	89.92	13.96
	CH_3OH	321.22	104.45	1.00	30.80	72.64	4.47
	p_M = 29.52 mm	313.30	101.67	1.18	29.84	70.65	5.59
III		307.77	99.59	1.44	29.03	69.12	7.18
	$(CH_3)_3N$	304.38	98.37	1.55	28.59	68.23	7.95
	p_A = 68.36 mm	295.65	95.00	2.05	27.22	65.73	11.46
		292.47	93.63	2.38	26.58	64.68	13.81
		289.83	92.64	2.51	26.19	63.94	14.96
		282.65	89.84	2.95	25.04	61.86	19.02

amine and methanol, were expanded into a bulb of approximately 375 cm^3. The pressure was recorded with a Texas Instruments quartz Bourdon gauge. The bulb was thermostated in a large dewar containing methylcyclohexane and temperature control to ±0.01° was readily maintained. The temperature was measured by a Pt-resistance thermometer and associated Leeds and Northrup K3 potentiometer. After pressure measurements, the component samples were condensed together in the thermostated bulb. Each mixture was held at 50° for 10 hr to ensure proper mixing and attainment of equilibrium. Pressure measurements on the mixtures were recorded to ±0.001 mm in the temperature range from 10 to 48°.

Infrared spectra were recorded on a Beckman IR 11-12 spectrophotometer in the range from 3200 to 3500 cm^{-1}. A 10-cm Pyrex cell equipped with NaCl windows was used for the study. The instrument was operated in the double-beam mode and purged with nitrogen to provide reproducibility in the background spectra. The mixture was prepared as in the pressure measurements. The individual component pressures were recorded and the samples condensed together in a small finger attached to the infrared cell. After warming, the mixture was held overnight to allow equilibrium to be reached. The cell was then placed in a housing made of 0.25-in. Plexiglas. Inlet and exit ports allowed entry and escape of precooled nitrogen gas. By varying the flow rate the desired temperature was maintained to ±0.05°. The temperature sensor consisted of a calibrated thermocouple. Spectra were recorded in absorbance units and integrated intensities were obtained with the use of a planimeter.

Results

Table I shows data obtained in the vapor pressure study of methanol–trimethylamine mixtures. Data for three mixtures made up of varying ratios of amine to methanol are listed. The initial pressures of the components at 25° are recorded in column 1. The total pressure at equilibrium (column 3) is given as a function of temperature (column 2) in the range 10–48° (see Experimental Section). Assuming ideal gas behavior for the components in the absence of complexing, equilibrium pressures for the reaction

$$\underset{p_M - p_C}{CH_3OH} + \underset{p_A - p_C}{(CH_3)_3N} \rightleftharpoons \underset{p_C}{CH_3OH \cdots N(CH_3)_3}$$

are readily calculable. These values are shown in columns 4–6. The resulting equilibrium constant for the above reaction as a function of temperature is given in the last column for each mixture.

That there is little deviation from ideality (*i.e.*, no self-association) in the pressure and temperature ranges of interest is verified by intensity measurements in the infrared spectrum of the free CH_3OH band at 3682 cm^{-1} and the amine band at 3405 cm^{-1}. Integrated areas from absorbance measurements as a function of concentration show no deviation from Beer's law.[11]

A plot of $-\ln K$ *vs.* $1/T$ is shown in Figure 1 for the equilibrium constants in Table I. A least-squares treatment resulted in the straight line in Figure 1 with remarkably little scatter for any of the individual mixtures. The reasonable assumption of a 1:1 complex for this system thus is supported. The enthalpy for the formation of the methanol–amine complex is calculated to be −7.5 ± 0.3 kcal/mol. The enthalpies for the different mixtures are listed in Table II.

In the infrared study in addition to establishing the Beer's law relationship for trimethylamine and methanol, it is necessary to do so for the band assigned to the hydrogen-bonded complex.

Infrared spectra corresponding to mixture III of Table III scanned at 10.0, 21.0, and 39.6° are displayed

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(11) At higher methanol pressures association predominantly to dimers is known to become increasingly more important: C. B. Kretschmer and R. Wiebe, *J. Am. Chem. Soc.*, **76**, 2579 (1954).

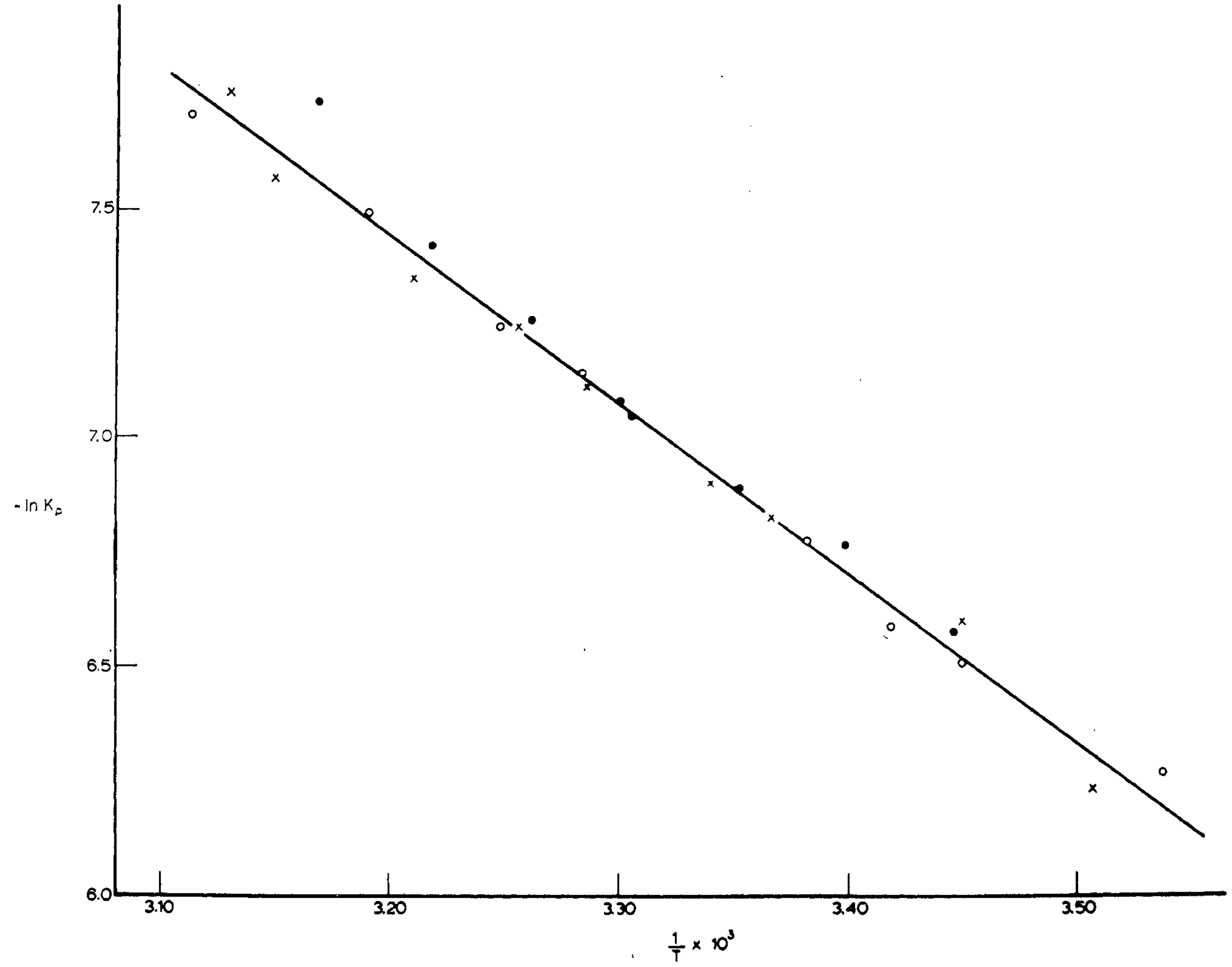

Figure 1.—Plot of $-\ln K_p$ *vs.* $1/T$ for the formation of the methanol–trimethylamine complex. The points are ×, mixture I, ●, mixture II, and ○, mixture III of Table I. The line is that computed from a least-squares treatment.

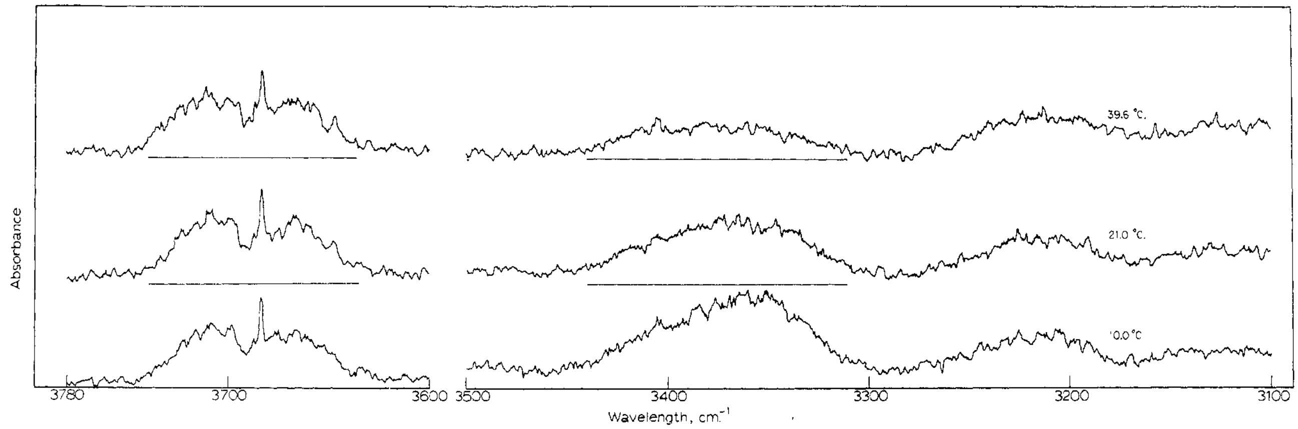

Figure 2.—Temperature-dependent spectra of a gaseous mixture of 30.43 mm of methanol and 122.30 mm of trimethylamine at 25° in a 10-cm cell.

TABLE II

ENERGY OF FORMATION ($-\Delta H$, KCAL/MOL) OF THE GASEOUS METHANOL–TRIMETHYLAMINE COMPLEX

	$-\Delta H$	
Mixture	Pressure study	Ir study
I	7.4	7.4
II	8.0	7.1
III	7.1	6.9

in Figure 2. The bands are, in order of decreasing frequency: the methanol band at 3682 cm^{-1}, an amine band at 3405 cm^{-1} overlapping the shifted O–H band at 3380 cm^{-1} (which is assigned to the hydrogen-bonded complex), and further amine bands at lower frequencies.

No shift in frequency of any of the bands was de-

TABLE III

RELATIVE ABSORBANCE OF THE HYDROGEN-BOND BAND FOR $CH_3OH-N(CH_3)_3$ AS A FUNCTION OF TEMPERATURE

	Mixture at 25°	Temp, °C	Rel abs
I	CH_3OH	283.0	4.15
	$p_M = 30.32$ mm	289.7	2.92
		295.1	2.34
	$(CH_3)_3N$	301.2	1.84
	$p_A = 66.26$ mm	304.0	1.52
		308.7	1.57
		311.4	1.12
II	CH_3OH	282.8	5.56
	$p_M = 30.02$ mm	286.8	4.96
		291.3	3.96
	$(CH_3)_3N$	296.1	2.89
	$p_A = 96.00$ mm	301.2	2.76
		312.1	1.73
III	CH_3OH	285.2	8.23
	$p_M = 30.43$ mm	289.1	6.88
		294.2	5.25
	$(CH_3)_3N$	301.3	3.61
	$p_A = 122.30$ mm	306.7	3.53
		312.8	2.53

TABLE IV

RELATIVE ABSORBANCE OF THE HYDROGEN-BOND BAND FOR $CH_3OH-N(CH_3)_3$ AS A FUNCTION OF CONCENTRATION AT 27.2°

Initial CH_3OH pressure, p_M, mm	Initial $(CH_3)_3N$ pressure, p_A, mm	Rel abs of 3380-cm^{-1} band	p_C, mm	
			Pressure study	Least-squares treatment
30.54	66.74	2.05	1.75	1.77
30.24	96.70	2.70	2.45	2.37
30.40	168.30	2.85	2.51	2.51
30.65	123.19	3.55	3.10	3.16
30.31	146.7	4.11	3.58	3.69
30.40	168.3	4.38	4.05	3.94

tected with pressure and temperature changes in the regions studied. The intensity changes with temperature follow that expected for complex formation. Figure 2 shows a small decrease in methanol intensity with decreasing temperature accompanied by a pronounced increase of intensity of the band for the complex. Since the trimethylamine is present in relatively large excess, its bands show substantially no detectable change in intensity, especially since the equilibrium for the formation of the complex lies far to the left.

That the intensity change for the band associated with the complex follows Beer's law behavior was verified in the following way. Since there is no convenient way to establish experimentally the concentration of the complex in any one particular sample, reference concentrations of the complex for several mixtures were calculated from the equilibrium constant obtained from the pressure measurements at 27.17° ($K_p = 9.36 \times 10^{-4}$ mm^{-1}). At this same temperature the integrated absorbance of the 3380-cm^{-1} band was measured and corrected for the contribution to its intensity of the overlapping amine band at 3405 cm^{-1}.

The latter correction was performed by obtaining calibration spectra of the amine band at 3405 cm^{-1} at known pressures. A Beer's law relation was found. Subtraction of the intensity corresponding to the amine pressure used in the mixture, corrected for the small amount of amine existing in the form of the complex, gave the intensity associated with the band due to the complex. A linear relation resulted between the absorbance and p_C indicating the validity of Beer's law for the complex band, at least in the pressure range studied. The deviation from linearity is seen in Table IV by comparing p_C calculated from the straight line (column 5) with p_C calculated from the pressure study (column 4).

Attempts to obtain p_C from the change in intensity of the methanol band in the various mixtures is not worthwhile. The change over the range investigated is too small to give any meaningful results. Consequently, only a rough approximation of p_C results from this consideration. As in solution work the hydrogen-bonded band has a pronounced enhancement in intensity with small changes in concentration.

As a result the equilibrium constant in this instance may be closely approximated merely by measuring the absorbance of the band for the complex and correcting it, as pointed out, for the neighboring amine band.

Table III lists the intensity of the band for the complex so obtained, as a function of temperature for three mixtures. From a plot of relative absorbance *vs.* $1/T$ for each of the mixtures, a heat of formation of the methanol–amine complex is calculated. The enthalpies for the different mixtures are listed in Table II. The average value is -7.1 ± 0.2 kcal/mol.

Discussion

The heat of formation of the methanol–trimethylamine complex in the gaseous state obtained by the pressure method (-7.5 ± 0.3 kcal/mol) and that from the infrared investigation (-7.1 ± 0.2 kcal/mol) are in reasonably good agreement considering the inherent difficulties in the procedures.

The value reported by Clague, Govil, and Bernstein[7] from an nmr study of this system (-5.8 ± 0.7 kcal/mol), however, is substantially lower. The larger uncertainty associated with their result stems primarily from a range of values considered for the proton chemical shift of the hydrogen-bonded complex. On the other hand, comparison of enthalpy data on the hydrogen chloride–dimethyl ether system obtained by the same three techniques that were used in the methanol–trimethylamine system shows good agreement between the nmr study by Govil, Clague, and Bernstein[8] (-7.1 ± 0.8 kcal/mol) and the pressure measurements[9] (-7.6 kcal/mol). The infrared result[10] is -5.6 kcal/mol. These results are summarized in Table V with other such systems where enthalpy data are available from vapor-phase studies of hydrogen bonding in relatively simple systems.

Using the known correlation of hydrogen-bond strength and shift $\Delta\nu$ in the hydrogen-bonded stretching frequency from that of the free band previously observed in solution phase work,[12] additional insight is

[12] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, pp 83–85.

TABLE V

HEATS OF FORMATION OF HYDROGEN-BONDED COMPLEXES FROM VAPOR-PHASE STUDIES

System	Method of investigation	$-\Delta H$, kcal/mol	$\Delta\nu$,[h] cm^{-1}
$CH_3OH-N(CH_3)_3$	Ir[a]	7.1 ± 0.2	302[a]
$CH_3OH-N(CH_3)_3$	Pressure meas[a]	7.5 ± 0.3	
$CH_3OH-N(CH_3)_3$	Nmr[b]	5.8 ± 0.7	
$CH_3OH-N(C_2H_5)_3$	Ir[c]	7.6 ± 0.5	362[c]
$CH_3OH-O(C_2H_5)_2$	Ir[d]	4.7 ± 0.7	124[d]
$HCl-O(CH_3)_2$	Nmr[e]	7.1 ± 0.8	
$HCl-O(CH_3)_2$	Pressure meas[f]	7.6	
$HCl-O(CH_3)_2$	Ir[g]	5.6	316[i]
$HCl-O(C_2H_5)_2$	Ir[g]	7.5 ± 0.3	336[i]

[a] This work. [b] Reference 7. [c] Reference 2b. [d] R. G. Inskeep, F. E. Dickson, and J. M. Kelliher, *J. Mol. Spectry.*, **4**, 477 (1960). [e] Reference 8. [f] Reference 9. [g] Reference 10. [h] The shifts are calculated relative to the free OH band in methanol at 3682 cm^{-1} and the free band centered at 2886 cm^{-1} in HCl. The references to the numbers in this column refer to the frequencies for the shifted bands. [i] Reference 3.

gained. Figure 3 shows a continuous relation between the ΔH values obtained in the infrared studies and $\Delta\nu$ (Table V, column 4) in spite of the uncertainty assigned to the individual heats of formation of the complexes, if the infrared value of -5.6 kcal/mol for the hydrogen chloride–dimethyl ether complex is disregarded. The correlation indicates curvature similar to that displayed in condensed-state work, although an extrapolation to a zero value is purely arbitrary.[12] From the shift $\Delta\nu$, the implication is that the nmr value of -7.1 kcal/mol is correct for this system. On this basis the two systems requiring further attention are an nmr study of the methanol–trimethylamine system and an infrared study of the hydrogen chloride–dimethyl ether system. However, it is probably too much to expect that the hydrogen chloride and methanol systems will be represented by the same curve in Figure 3 since they represent two different acid systems. Such a correlation must await vapor-phase studies on additional hydrogen chloride–donor molecule systems.

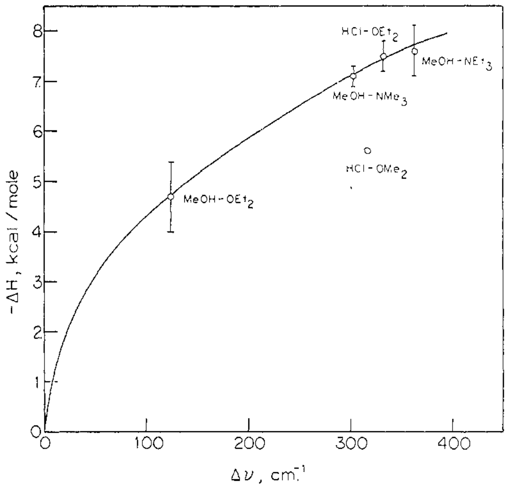

Figure 3.—Plot of the heat of formation ($-\Delta H$) *vs.* $\Delta\nu$ for hydrogen-bonded complexes in the vapor state.

Examination of the heats of formation for the methanol complexes determined from the infrared studies shows a lower value for the complex with diethyl ether, -4.7 kcal/mol, than that with trimethylamine, -7.1 kcal/mol. This behavior is expected on the basis of the donor properties of these molecules, diethyl ether being the weaker base and probably giving rise to a weaker complex. In this regard little can be said about the relative influence of the amines, trimethylamine and triethylamine, on complex stability, since the heats of formation reported in the infrared studies are not sufficiently different compared to the uncertainties assigned to the respective values. It seems clear, however, that the difference in donor properties of the amines and ether represent an important factor governing the hydrogen-bond energy in the methanol complexes.

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High-Pressure Synthesis of Rare Earth Polyselenides[1]

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New rare earth polyselenides were prepared from Tm, Yb, and Lu and have the tetragonal $ErSe_2$ ($LaTe_2$ type) structure. Synthesis was accomplished at pressures of 14–70 kbars and temperatures of 400–2000°. The X-ray powder diffraction patterns are given.

Introduction

The polyselenides of the elements from lanthanum through gadolinium with the exception of europium were synthesized by Benacerraf, *et al.*[3] The polyselenides were formed principally by a sealed-tube technique. Wang[4] synthesized the compounds of La, Ce,

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(1) This research was supported by the National Science Foundation and the Army Research Office (Durham) and is part of a dissertation by A. W. W.

(2) Now an NAS-NRC Fellow at the Naval Research Laboratory, Washington, D. C.

(3) A. Benacerraf, L. Domange, and J. Flahaut, *Compt. Rend*, **248**, 1672 (1959).

(4) R. Wang, Doctoral Dissertation, University of Texas, Austin, Texas, 1967.