Vapor Phase Association in Acetic and Trifluoroacetic Acids. Thermal Conductivity Measurements and Molecular Orbital Calculations

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Abstract: Thermal conductivity measurements are reported for the vapors of acetic acid and trifluoroacetic acid in the temperature range 350–415 K over the pressure range 100–2000 Torr. Very large enhancements of the thermal conductivity were found and analysis of the data is consistent with a monomer-dimer equilibrium for both vapors. The standard thermodynamic parameters for the dimerization reactions are $-\Delta H_2 = 14.64$ kcal mol^{-1} and $-\Delta S_2 = 35.50$ cal mol^{-1} K^{-1} for acetic acid, and $-\Delta H_2 = 13.66$ kcal mol^{-1} and $-\Delta S_2 = 36.15$ cal mol^{-1} K^{-1} for trifluoroacetic acid. No evidence was found for the presence of significant amounts of associated species larger than the dimer. Ab initio molecular orbital calculations were performed on the monomers and dimers of both acids to determine the lowest energy structures. Both dimers are found to contain two nearly parallel C═O···H—O hydrogen bonds.

I. Introduction

It is well established that vapors of the carboxylic acids undergo a dimerization reaction to form cyclic structures containing two equivalent C═O···H—O hydrogen bonds. The extent of this dimerization is very large so that, for example, acetic acid vapor is ca. 50% dimer at its normal boiling point (391 K). Owing to the unusually large amount of associated species present in the vapor, the carboxylic acids afford the investigator an excellent system with which to study the details of gas-phase hydrogen bonding.

We have recently undertaken a systematic study of a number of associating vapors using a thermal conductivity technique to determine the thermodynamic quantities of the associated species and ab initio molecular orbital theory to help understand the hydrogen bonding that is present.[1-5] All of these studies have been performed on vapors which are weakly associating, such as methanol, acetone, and water, with quite encouraging results. Because of the large amount of association in the carboxylic acid vapors, as well as the wealth of information on the subject,[6,7] these systems provide a good test of the ability of the thermal conductivity technique to abstract reliable thermodynamic quantities for associated species. In addition, the thermal conductivity data on the carboxylic acid vapors by themselves are of interest because of the large enhancement as a function of pressure (approximately four times its zero-pressure value at the maximum). This large enhancement is the result of the large degree of association in the vapor and has been found in substances such as NO_2[8] and HF.[9]

In this paper we will present and discuss thermal conductivity measurements on acetic and trifluoroacetic acid vapors at pressures up to 2000 Torr and temperatures up to 416 K. The data are analyzed in terms of the thermodynamic quantities of the dimerization reactions. The possibility of higher polymers being present in the vapor is also investigated. Finally, ab initio molecular orbital calculations using a minimal basis set are carried out to determine the conformations of the acetic acid and trifluoroacetic acid monomers and the structures and binding energies of their corresponding dimers.

II. Experimental Section

Measurements of the thermal conductivity, λ, of acetic acid and trifluoroacetic acid vapors were carried out as a function of the pressure in the range 100–2000 Torr. Data were obtained at four temperatures for acetic acid, 355–416 K, and six temperatures for trifluoroacetic acid, 351–413 K. The apparatus employed in these experiments was of a slightly modified design from that used previously.[2] These modifications allow thermal conductivities to be measured at higher temperatures (ca. 473 K) and pressures (ca. 5 atm). The major change is in the design of the thick hot wire cell. A platinum wire, 0.020 in. in diameter, was mounted along the axis of a tube which was 4 in. long and had an internal diameter of 0.25 in. The new cell consisted of Kovar metal ends with a center section of Pyrex glass to prevent electrical conduction through the tube. The wire was secured under tension to each end of the tube by silver soldering it to stainless-steel end plugs that had been previously silver soldered to the Kovar ends. The samples were admitted to the cell by a 1/8 in. Pyrex-Kovar tube attached to the center of the cell.

Our technique is a relative one, whereby the cell is calibrated with high-purity gases of known thermal conductivity: He, Ne, N_2, and Ar. The reference gas thermal conductivities were obtained from both experimental thermal conductivity data and calculations from experimental viscosities.[10] The data were then least squares fitted to a quadratic in the temperature. The resulting equations for N_2 and Ar have been reported previously.[1] The equations for He and Ne are given by

$$10^5\lambda_{He} = 9.855 + 9.680 \times 10^{-2}T - 2.095 \times 10^{-5}T^2 \quad (1)$$

$$10^5\lambda_{Ne} = 2.076 + 3.843 \times 10^{-2}T - 2.035 \times 10^{-5}T^2 \quad (2)$$

where the thermal conductivity, λ, is in units of cal cm^{-1} s^{-1} K^{-1} and T is the temperature in degrees Kelvin.

For the cell just described, the reference gas thermal conductivities, to a very good approximation, were empirically found to be related to the measured cell voltage, V, at constant input current by the relation

$$\lambda^{-1} = a + bV + cV^2 \quad (3)$$

where a, b, and c are constants dependent on the temperature and are determined by a least-squares fit of eq 3 to the reference gas λ–V calibration points. We estimate that this procedure gives thermal conductivities with absolute errors of less than 1% and relative errors of less than 0.5%.

The acetic acid sample was obtained from the Scientific Products Co. and was found to contain 0.60 mol % water by a Karl Fischer analysis. The trifluoroacetic acid sample was obtained from the Aldrich Chemical Co. and stored over Linde molecular sieve (15 Å) prior to use. The dried trifluoroacetic acid sample was found to contain 0.25 mol % H_2O.

The experimental thermal conductivity data for acetic acid are listed in Table I and plotted in Figure 1. The corresponding data for trifluoroacetic acid are listed in Table II and plotted in Figure 2. The uncertainty in the measured pressure is estimated to be ±4 Torr over the entire range. Owing to the so-called "temperature-jump effect",[11] only the data above 100 Torr for acetic acid and above 200 Torr for trifluoroacetic acid were considered reliable.

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Table I. Experimental Thermal Conductivity (cal cm^{-1} s^{-1} K^{-1}) of Acetic Acid Vapor as a Function of Pressure at Four Temperatures

T = 354.6 K		T = 385.9 K		T = 397.8 K		T = 416.3 K	
p, Torr	$10^5 \lambda$	p, Torr	$10^5\lambda$	p, Torr	$10^5\lambda$	p, Torr	$10^5\lambda$
100	16.88	110	19.09	101	16.67	136	14.34
105	16.64	121	19.44	128	17.55	140	14.37
116	16.52	133	19.44	132	17.52	172	15.33
121	16.07	145	19.37	156	18.09	197	15.99
126	15.85	146	19.51	159	18.09	233	16.61
136	15.69	159	19.30	182	18.41	273	17.38
152	15.18	160	19.44	191	18.29	304	17.62
158	14.94	175	19.30	200	18.53	325	17.84
165	14.89	176	19.44	210	18.45	366	18.10
175	14.61	192	19.23	220	18.70	376	18.22
185	14.35	193	19.30	231	18.57	401	18.37
198	14.13	211	19.16	241	18.74	417	18.49
206	13.88	212	19.23	253	18.65	440	18.49
		233	19.09	265	18.82	456	18.57
		244	19.03	278	18.70	483	18.61
		294	18.50	290	18.70	529	18.69
		323	18.19	305	18.70	555	18.73
		354	18.06	318	18.74	566	18.81
		388	17.64	335	18.65	580	18.69
		425	17.53	349	18.70	609	18.81
		463	17.24	367	18.45	636	18.73
		465	17.08	383	18.61	700	18.73
				402	18.45	752	18.69
				415	18.49	810	18.73
				441	18.29	863	18.61
				455	18.33	894	18.65
				483	18.21	945	18.53
				499	18.13	972	18.49
				529	17.93	1034	18.37
				546	17.93	1072	18.37
				579	17.78	1116	18.29
				597	17.82	1150	18.29
				633	17.59	1192	18.18
				654	17.52	1274	18.07
				691	17.30	1297	18.03
				714	17.33	1387	17.88
				752	17.12	1398	17.77
				774	17.16		
				812	16.95		
				835	16.91		

III. Data Analysis

A. Theory of the Thermal Conductivity of an Associating Gas. The thermal conductivity of an associating gas is given by

$$\lambda = \lambda_f + \lambda_c + \lambda_R \tag{4}$$

where λ_f is the thermal conductivity of a hypothetically frozen (i.e., nonreacting) composition of all the vapor species, λ_c is the enhancement of the thermal conductivity due to "collisional transfer", and λ_R is the enhancement of the thermal conductivity from the transport of reaction enthalpy in a thermal gradient.

An expression for λ_R in terms of the enthalpy changes of the reactions occurring in a vapor has been developed by Butler and Brokaw.[12] For a single association reaction, $n\mathrm{A(g)} \rightleftharpoons \mathrm{A}_n\mathrm{(g)}$, λ_R can be simply expressed as

$$\lambda_R = \left(\frac{pD_{1n}}{RT^2}\right)\left(\frac{\Delta H_n{}^2}{RT}\right)\frac{K_n p_1{}^{n-1}}{(1 + nK_n p_1{}^{n-1})^2} \tag{5}$$

where R is the gas constant, T is the absolute temperature, p is the pressure, D_{1n} is the binary diffusion coefficient, K_n is the equilibrium constant for the association reaction, ΔH_n is the standard enthalpy of association for the reaction, and p_1 is the monomer partial pressure. When there is a large degree of association, the thermal conductivity vs. pressure plots reach a maximum and then fall off with increasing pressure.[8,9] It can be shown that substitution of mole fractions ($x_1 = p_1/p$ and $x_n = p_n/p$) into eq 5 leads to the expression

$$\lambda_R = \left(\frac{pD_{1n}}{RT^2}\right)\left(\frac{\Delta H_n{}^2}{RT}\right)\frac{x_1 x_n}{(x_1 + nx_n)^2} \tag{6}$$

Further, the expression for λ_R has an even simpler form when the mass fractions m_1 and m_n of the two species are used:

$$\lambda_R = \left(\frac{pD_{1n}}{RT^2}\right)\left(\frac{\Delta H_n{}^2}{RT}\right)\frac{m_1 m_n}{n} \tag{7}$$

It can easily be seen that a maximum in λ_R occurs when $m_1 = m_n = 1/2$. This is equivalent to a monomer mole fraction of $n/(n+1)$. Also, if the relatively weak pressure dependences of λ_f and λ_c are neglected, we can deduce from eq 5 that the pressure at which the maximum in λ occurs (denoted $p_{\lambda_{\max}}$) is related to K_n by

$$p_{\lambda_{\max}} = [K_n n^n (n + 1)^{1-n}]^{-1/(n-1)} \tag{8}$$

Since K_n decreases with temperature (for a negative ΔH_n), $p_{\lambda_{\max}}$ will increase with temperature. This effect is observed in the plots for acetic and trifluoroacetic acids (Figures 1 and 2).

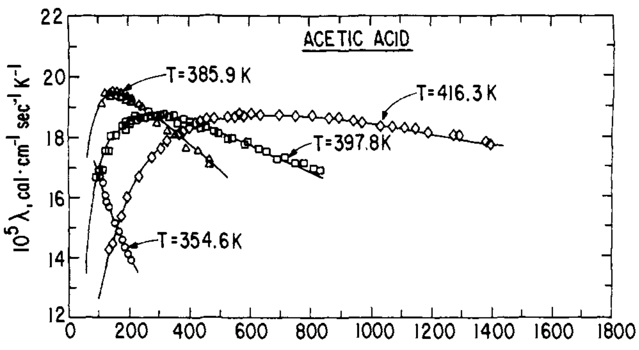


Figure 1. Acetic acid vapor thermal conductivity vs. the total pressure. The solid lines are the best fits to the experimental data using the Butler–Brokaw theory assuming a monomer–dimer model.

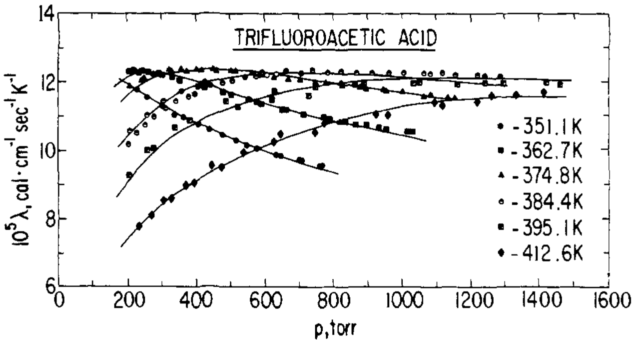


Figure 2. Trifluoroacetic acid vapor thermal conductivity vs. the total pressure. The solid lines are the best fits to the experimental data using the Butler–Brokaw theory assuming a monomer–dimer model.

As was mentioned in the Introduction, the experimental evidence for large amounts of a dimeric species being present in carboxylic acid vapors is quite conclusive. It has also been suggested that some higher polymers may be present in lesser amounts. In order to establish whether the dimer or a higher polymer is causing the enhancement in the thermal conductivities of acetic and trifluoroacetic acids, both sets of data were fit to eq 4 (λ_R given by eq 5) for the cases where dimers, trimers, or tetramers are present. Further, fits in which more than one associated species are assumed to be present (i.e., monomer–dimer–n-mer) were also performed. We now proceed to

Table II. Experimental Thermal Conductivity (cal cm^{-1} s^{-1} K^{-1}) of Trifluoroacetic Acid Vapor as a Function of Pressure at Six Temperatures

T = 351.1 K		T = 362.7 K		T = 374.8 K		T = 384.4 K		T = 395.1 K		T = 412.6 K	
p, Torr	$10^5\lambda$	p, Torr	$10^5\lambda$	p, Torr	$10^5\lambda$	p, Torr	$10^5\lambda$	p, Torr	$10^5\lambda$	p, Torr	$10^5\lambda$
229	11.77	208	12.30	208	11.86	205	10.15	202	9.28	232	7.84
259	11.55	219	12.33	243	12.03	208	10.55	261	10.01	271	8.14
305	11.31	234	12.28	247	12.11	227	10.49	278	10.06	307	8.57
338	11.03	246	12.33	278	12.21	253	10.74	340	10.68	328	8.62
365	10.97	263	12.25	292	12.26	259	11.04	385	10.87	371	9.02
408	10.75	294	12.22	323	12.34	280	10.98	489	11.43	396	9.07
439	10.60	306	12.20	332	12.29	307	11.42	525	11.28	447	9.60
477	10.44	322	12.12	360	12.36	312	11.23	623	11.48	476	9.54
517	10.30	355	12.04	375	12.29	342	11.42	631	11.73	539	9.96
548	10.14	411	11.87	403	12.36	361	11.71	730	11.60	627	10.28
578	10.05	427	11.82	417	12.31	377	11.58	750	11.86	647	10.51
634	9.86	479	11.70	453	12.34	398	11.64	865	11.90	749	10.55
650	9.83	506	11.62	462	12.31	420	11.76	891	11.95	776	10.83
702	9.72	554	11.46	505	12.31	427	11.97	1033	11.94	820	10.83
708	9.70	579	11.39	518	12.31	446	11.58	1052	11.95	924	11.09
764	9.56	593	11.34	566	12.23	479	11.95	1164	11.90	961	11.05
766	9.56	655	11.16	595	12.18	507	12.02	1245	11.95	1097	11.40
		663	11.16	630	12.13	546	12.15	1297	11.94	1119	11.32
		714	11.06	670	12.06	577	12.16	1422	11.95	1223	11.44
		773	10.95	706	12.06	594	12.26	1438	11.90	1262	11.64
		791	10.88	747	11.96	607	12.19	1537	11.90	1335	11.64
		836	10.84	779	11.96	636	12.21	1545	11.91	1415	11.72
		864	10.74	823	11.93	666	12.31	1674	12.09	1456	11.64
		898	10.74	827	11.88	708	12.26	1800	12.09	1543	11.81
		934	10.64	881	11.81	741	12.34			1588	11.68
		961	10.62	896	11.78	785	12.26			1681	12.02
		1018	10.52	945	11.76	823	12.31			1730	11.81
		1033	10.52	952	11.71	869	12.26			1829	12.02
				1005	11.69	914	12.26			1883	11.93
				1065	11.55	962	12.26			1990	12.02
				1085	11.59	1007	12.26			2039	11.98
				1135	11.52	1067	12.26				
				1154	11.50	1084	12.24				
						1120	12.24				
						1148	12.19				
						1222	12.19				
						1242	12.16				
						1288	12.14				

describe the details of the fitting procedure as well as the derivation of expressions for pD_{kl}, λ_f, and λ_c used for each substance.

B. Determination of pD_{kl}, λ_f, and λ_c. Expressions for the binary diffusion coefficients of acetic and trifluoroacetic acids were determined from the gaseous monomer viscosities, η, and the Lennard-Jones potential parameters, ϵ/K and σ, using a procedure described in ref 1b. For acetic acid, the monomer viscosity was experimentally derived by Timrot and Serednitskaya[13] and can be represented by

$$\eta = 0.286T + 3.10\ (\mu\text{P}) \tag{9}$$

For trifluoroacetic acid, no experimental data were found so the viscosity was estimated using the method of Brokaw[14] to be

$$\eta = 0.35T - 2.60\ (\mu\text{P}) \tag{10}$$

The well depth parameters, ϵ/K, for both acids were estimated by Brokaw's method to be 500 and 472 K for acetic and trifluoroacetic acids, respectively. The size parameters for the monomers, σ_1, were estimated by Brokaw's method to be 4.70 and 4.85 Å for acetic and trifluoroacetic acids, respectively.

An expression for the binary diffusion coefficient, pD_{kl}, between any two n-mers ($n = k, l$) of the same substance can be obtained from the relation[1b]

$$pD_{kl} = \left(\frac{k+l}{2kl}\right)^{1/2}\left(\frac{\sigma_{11}}{\sigma_{kl}}\right)^2 pD_{11} \tag{11}$$

where pD_{11} is the self-diffusion coefficient of the monomer. Using the viscosity and well-depth data, the pD_{11} for acetic is given by

$$10^5 pD_{11} = 1.255 \times 10^{-3}T^2 + 1.527 \times 10^{-2}T\ (\text{cal cm}^{-1}\ \text{s}^{-1}) \tag{12}$$

The pD_{11} for trifluoroacetic acid is given by

$$10^5 pD_{11} = 8.091 \times 10^{-4}T^2 - 6.010 \times 10^{-3}T\ (\text{cal cm}^{-1}\ \text{s}^{-1}) \tag{13}$$

The σ_{kl} in eq 11 is evaluated by setting $\sigma_k{}^3 = k\sigma_1{}^3$ and $\sigma_{kl} = (\sigma_k + \sigma_l)/2$. Hence, any pD_{kl} for the fitting procedure can be obtained from eq 11.

The frozen thermal conductivity, λ_f, is also somewhat pressure dependent. Mason and Saxena[15] have developed equations which can be used to obtain an expression for λ_f by a procedure described in ref 1b. The expression for the thermal conductivity of a binary mixture of monomers and n-mers is given by

$$\lambda_f = \lambda_1\left[\frac{1}{1 + A_{1n}K_n p_1} + \frac{(\lambda_n/\lambda_1)K_n p_1}{K_n p_1 + A_{n1}}\right] \tag{14}$$

where λ_1 is the monomer thermal conductivity at zero pressure and λ_n is the n-mer thermal conductivity at zero pressure. The A_{1n} and A_{n1} are constants determined from a procedure given in ref 1b and depend on the ratio of monomer to n-mer viscosities and their masses.

For a binary mixture of monomers and dimers the constants A_{12} and A_{21} were determined to have values of 1.705 and 0.6565, respectively, using a dimer to monomer viscosity ratio of $\eta_2/\eta_1 = 0.77$ for both acids on the basis of the work of Timrot and Serednitskaya.[13] The λ_2/λ_1 ratio was determined in a similar manner as in ref 1b except that Hirschfelder's formulation of the Eucken factor, E, was used.[16] This can be written as

$$E = (1 - \delta_f) + 2\delta_f C_p/5R \tag{15}$$

where δ_f was assumed to be equal to 0.667 for both the monomer and dimer of each acid. Using the experimental heat capacity of Weltner[17] for acetic acid and an estimated heat capacity[18] for trifluoroacetic acid, we obtained λ_2/λ_1 ratios of 0.77 and 0.79 for acetic and trifluoroacetic acids, respectively. These values for λ_2/λ_1 lead to decreases (from eq 14) in the total thermal conductivity of ca. 18% over a range of 1 atm for both acids if dimers and monomers are the major species. This is quite small when compared to the 400% increase in thermal conductivity which actually occurs.

For a binary mixture of monomers and trimers the A_{13} and A_{31} coefficients for both acids are 2.122 and 0.5093, respectively, and for a mixture of monomers and tetramers they are 2.482 and 0.4220, respectively. These values were obtained in the same manner as for the monomer and dimer mixture except that the viscosity ratios $\eta_3/\eta_1 = 0.72$ and $\eta_4/\eta_1 = 0.68$ were used. The λ_3/λ_1 ratios used were 0.76 and 0.75 for acetic acid and trifluoroacetic acid, respectively. The λ_4/λ_1 ratios are 0.72 and 0.71 for acetic and trifluoroacetic acid, respectively. Equation 14 leads to decreases of ca. 19 and 23% for the trimer and tetramer, respectively, over 1 atm.

The collisional term, λ_c, arises from the instantaneous transfer of energy between two molecules upon collision.[19] This effect is generally very weakly pressure dependent (ca. 1% of λ_1 at 1 atm pressure). We have estimated (using a procedure described in ref 3) that the magnitude of the λ_c term is negligible compared to the λ_R and λ_f terms and it was thus neglected in the following fits of the data.

C. Fitting the Thermal Conductivity Data to the Theory. In order to determine which polymer (or polymers) causes the enhancement in the thermal conductivity and to obtain thermodynamic data for the association reactions, fits of the data were carried out using a minimization procedure similar to that in ref 1b. All of the isotherms for acetic acid were fit simultaneously to eq 4 with λ_R given by eq 5 (n = 2, 3, or 4) and λ_f given by eq 14 (n = 2, 3, or 4). The fitting parameters were ΔH_n, ΔS_n, and λ_1 (one λ_1 value for each isotherm).

The solid lines in Figure 1 are the best fit curves for acetic acid assuming a monomer-dimer binary mixture. The fits are seen to be quite good. The fitting procedure was also carried out assuming monomer-trimer (1-3) and monomer-tetramer (1-4) models. The resulting fits from these models were inadequate. The magnitudes of the maxima in the calculated isotherms deviated significantly from the experimental values. The thermodynamic results for the acetic acid dimer from the (1-2) fit are $-\Delta H_2 = 14.64$ kcal mol^{-1} and $-\Delta S_2 = 35.50$ cal mol^{-1} K^{-1}. Values of the zero-pressure thermal conductivity, equilibrium constants, and dimer mole fractions at saturation are given in Table III for acetic acid.

The possibility that higher polymers are present in the acetic acid vapor in addition to the dimer was also investigated. Addition of either trimers or tetramers to the monomer-dimer model did not improve the fits substantially and thermodynamic parameters for these species had large uncertainties. Hence, it was concluded that the higher polymers make, at most, only very small contributions to λ_R.

The solid lines in Figure 2 are the best fit curves for trifluoroacetic acid assuming a monomer-dimer model. The standard enthalpy and entropy of association for the trifluoroacetic acid dimer are -13.66 kcal mol^{-1} and -36.15 cal mol^{-1} K^{-1}, respectively. The values of λ_1, the equilibrium constants, and the dimer mole fractions at saturation are given in Table III.

Table III. Thermal Conductivity at Zero Pressure (λ_1), Dimerization Equilibrium Constants (K_2), Dimer Partial Pressure (p_2), and Dimer Mole Fraction (x_2) for Acetic Acid and Trifluoroacetic Acid from a Simultaneous Fit of the Thermal Conductivity Data[a]

T, K	$10^5\,\lambda_1$, cal cm^{-1} s^{-1} K^{-1}	K_2, atm^{-1}	p_{sat},[b] Torr	p_2,[c] Torr	x_2[c]
		Acetic Acid			
354.6	2.99	18.39	207	133	0.64
385.9	4.42	3.41	628	349	0.56
397.8	4.31[d]	1.93	914	479	0.52
416.3	5.12	0.85	1570	751	0.48
		Trifluoroacetic Acid			
351.1	3.42	4.00	928	590	0.64
362.7	3.95	2.14	1340	800	0.60
374.8	4.39	1.16	1910	1070	0.56
384.4	4.50	0.73	2490	1320	0.53
395.1	4.56	0.45	3300	1640	0.50
412.6	4.92	0.22	5070	2270	0.45

[a] The results of this fit are $-\Delta H_2 = 14.64$ kcal mol^{-1} and $-\Delta S_2 = 35.50$ cal mol^{-1} K^{-1} for acetic acid and $-\Delta H_2 = 13.66$ kcal mol^{-1} and $-\Delta S_2 = 36.15$ cal mol^{-1} K^{-1} for trifluoroacetic acid. [b] Saturation vapor pressures taken from ref 38 for acetic acid and ref 23 for trifluoroacetic acid. [c] At saturation. [d] The apparent decrease in the λ_1 value at this temperature is an artifact of fitting procedure due to the large extrapolations of the data fits to zero pressure.

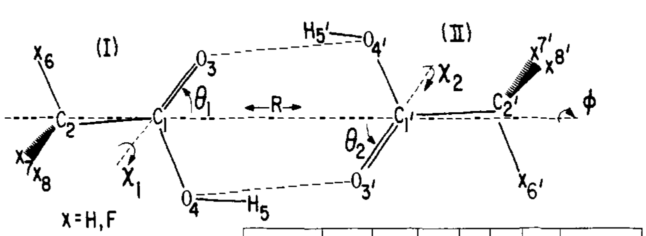
The possibility of higher polymers contributing to the enhancement of the thermal conductivity of trifluoroacetic acid was considered. As in the case of acetic acid, higher polymers contribute only negligible amounts to the thermal conductivity enhancement.

The uncertainty in the calculated ΔH_2 and ΔS_2 for acetic acid was estimated in the same manner as in previous work.[3,4] The resulting total uncertainties for acetic acid are given by $-\Delta H_2 = 14.64 \pm 0.8$ kcal mol^{-1} and $-\Delta S_2 = 35.50 \pm 1.0$ cal mol^{-} K^{-1}. The resulting uncertainties for trifluoroacetic acid are given by $-\Delta H_2 = 13.66 \pm 2.0$ kcal mol^{-1} and $-\Delta S_2 = 36.15 \pm 5.0$ cal mol^{-1} K^{-1}.

IV. Discussion

The experimental thermal conductivity data for both acids exhibit very large enhancements due to the dimerization reaction. At the highest portions of the isotherms in Figures 1 and 2 the thermal conductivities are generally about three to five times their zero-pressure values obtained from the fitting procedure (Table III). It is noteworthy that these substances, with relatively large molecular weights, have thermal conductivities comparable to those of the light inert gases He and Ne. The largest thermal conductivity observed for acetic acid is ca. 23% greater than that of Ne. Overall, the thermal conductivity of trifluoroacetic acid is less than that of acetic acid owing to its smaller enthalpy of association, but it is nevertheless quite high.

The theoretical fits in Figures 1 and 2 indicate that the Butler-Brokaw theory does quite well in predicting and explaining the enhancement in the thermal conductivity which occurs in vapors exhibiting large amounts of association such as the carboxylic acids. The theory correctly predicts (1) the decrease in the maximum thermal conductivity with increasing temperature, (2) the increasing pressure at which the maximum thermal conductivity occurs with increasing temperature, (3) the leveling off (i.e., the relative constancy) of the thermal conductivity at high pressures, and (4) the rapid rate of in-



	R	θ_1	θ_2	χ_1	χ_2	Ø	E, a.u.
X=H Acetic Acid	3.80 Å	54.5°	54.5°	0°	0°	180°	−449.63921
X=F TFA Acid	3.84 Å	54.2°	54.2°	0°	0°	180°	−1034.36195

Figure 3. The equilibrium geometry of the dimers of acetic acid and trifluoroacetic acid as determined with the STO-3G basis set. The optimized geometrical parameters are given in the inset table.

crease of the thermal conductivity with pressure in the low-pressure region.

There has been only one other study of the gaseous thermal conductivity of a carboxylic acid to our knowledge. This was by Timrot and Makhrov,[20] who measured the thermal conductivity of acetic acid vapor as a function of pressure in the temperature range 25–140 °C using a thermoelectric device in a relative technique with helium and air as calibrating gases. Their data appear to be identical in overall shape (e.g., peak positions) with that of this work. However, at comparable temperatures their thermal conductivity data are consistently ca. 6% lower. This may be due, in part, to their use of Vargaftik's[21] recommended values for the thermal conductivity of He in the calibration procedure. At 350 K, Vargaftik's value for He is ca. 4% lower than the value obtained from eq 1, which could explain most of the discrepancy.

In the plethora of data on acetic acid dimerization acquired over the last 30 years by different methods, most of the values of ΔH_2 reported are between −13.0 and −16.0 kcal mol^{-1}. In a recent comprehensive review of the literature on acetic acid, Chao and Zwolinski[7] arrived at the following thermodynamic data for the dimerization reaction at 373 K: $-\Delta H_2 = 14.92$ kcal mol^{-1}, $-\Delta S_2 = 35.92$ cal mol^{-1} K^{-1}, and $K_2 = 7.73$ atm^{-1}. The results from our thermal conductivity analysis ($-\Delta H_2 = 14.64 \pm 0.8$ kcal mol^{-1}, $-\Delta S_2 = 35.50 \pm 1.0$ cal mol^{-1} K^{-1}, and K_2 (at 373 K) = 6.55 atm^{-1}) are close to their recommended values.

Thermodynamic data for trifluoroacetic acid dimerization are available from vapor-density and NMR investigations. In the vapor-density study by Lundin, Harris, and Nash[22] the following thermodynamic parameters were deduced: $-\Delta H_2 = 14.05$ kcal mol^{-1}, $-\Delta S_2 = 36.5$ cal mol^{-1}, and K_2 (at 373 K) = 1.79 atm^{-1}. The results of another vapor-density study by Taylor and Templeman[23] are in essential agreement with the former study. In the NMR study, Lumbroso-Bader et al.[24] report $-\Delta H_2 = 14.5 \pm 0.6$ kcal mol^{-1}, $-\Delta S_2 = 38.4 \pm 1.4$ cal mol^{-1}, and K_2 (at 373 K) = 1.26 atm^{-1}. Our thermal conductivity analysis yields values for $-\Delta H_2 = 13.66$ kcal mol^{-1}, $-\Delta S_2 = 36.15$ cal mol^{-1} K^{-1}, and $K_2 = 1.26$ atm^{-1} (at 373 K), which are close to these other results. Hence, all of the experimental results indicate that the hydrogen bonds in trifluoroacetic acid dimer are not quite as strong as in the acetic dimer and that there is less dimer present in the vapor.

The possibility that a higher polymer exists in the acetic acid vapor concurrently with the dimer has been investigated in several studies. In a vapor-density study Johnson and Nash[25] found a trimer having $-\Delta H_3 = 22.7$ kcal mol^{-1} and $-\Delta S_3$ −85.26 cal mol^{-1} K^{-1}. Inclusion of a trimer having these values for the thermodynamic parameters in the thermal conductivity monomer-dimer fit did not affect the overall fit significantly, indicating a negligible contribution of the trimerization reaction to λ_R. Thus, we cannot rule out these thermodynamic parameters for the trimer solely on the basis of the thermal conductivity data. The amount of trimer present in the vapor as predicted by the above results is very small compared to the amount of dimer. For example, at 1 atm the mole fraction of trimer is less than 2×10^{-7}. Ritter and Simons[26] report a tetrameric species in acetic acid vapor having thermodynamic parameters $-\Delta H_4 = 6.75$ kcal mol^{-1} and $-\Delta S_4 = 26.9$ cal mol^{-1} K^{-1} from a vapor-density study. A monomer-dimer-tetramer fit of the thermal conductivity data gave similar results ($-\Delta H_4 = 8.0$ kcal mol^{-1} and $-\Delta S_4 = 26.9$ cal mol^{-1} K^{-1}) with a slightly better standard deviation than the monomer-dimer fit. However, the uncertainties in ΔH_4 and ΔS_4 are very large, possibly of the order of the numbers themselves, and are not reliable. This is due to the small contribution to λ_R from the tetrameric reaction (tetramer mole fraction at 1 atm is less than 8×10^{-4}). These results indicate that the amount of trimer and tetramer present in acetic acid vapor is extremely small and that the dimer is by far the dominant associated species in the vapor.

Table IV. Monomer Geometries for Acetic and Trifluoroacetic Acids[c]

geometrical parameter	acetic acid[a] (X = H)	trifluoroacetic acid[b] (X = F)
r(C—X)	1.102	1.36
r(C—C)	1.520	1.52
r(C=O)	1.214	1.22
r(O—H)	0.97	0.96
r(C—O)	1.364	1.36
∠C—C—X	109.5	109.5
∠C—C=O	126.6	120.0
∠C—C—O	110.6	120.0
∠C—O—H	107.0	109.5

[a] Taken from the electron diffraction work of Derissen (ref 29). H-O-C-C trans; H-C-C-O trans. [b] Taken from a standard molecular model of Pople and Gordon (ref 34). H-O-C-C trans; F-C-C-O trans. [c] Bond distances in ångstroms and angles in degrees.

V. Quantum-Mechanical Calculations

Along with our experimental investigations into gas-phase association reactions, we have found ab initio molecular orbital calculations to be helpful in understanding the nature of these processes. In the present case of acetic and trifluoroacetic acids, as in previous studies,[2,4] the lowest energy dimeric structures were determined using standard LCAO-SCF methods. The minimal STO-3G basis set,[27] which has given reasonable results for structures and binding energies of other hydrogen-bonded complexes,[28] was employed. Stable dimer geometries were found by a systematic search of the intermolecular potential surface while holding the monomer geometry fixed. The intermolecular angles were optimized to ±2° and the hydrogen bond lengths were optimized to ±0.02 Å. The binding energy for a dimer is obtained by subtracting the sum of the monomer energies from the total energy of the dimer.

A. Acetic Acid. The experimental acetic acid monomer geometry of Derissen[29] was used in the dimer calculations and is given in Table IV. The experimental monomer structure has the hydroxyl hydrogen and one of the methyl hydrogens both cis to the carbonyl oxygen (see Figure 3). This rotational configuration was also found to be most stable in several calculations with the STO-3G basis set. The STO-3G energy of this acetic acid monomer is −224.808 00 au.

The acetic acid dimer structure was arranged in a cyclic configuration with the carboxylic acid group of each monomer acting as both a proton acceptor (via C=O) and a proton donor (via O—H) as shown in Figure 3. This structure is similar to what has been found in several experimental studies.[29,30] The positions of the two monomer molecules relative to each other in the cyclic dimer were specified by six intermolecular pa-

Table V. Energies of Various Rotational Isomers of Trifluoroacetic Acid

isomer	dihedral angles,[a] deg $\angle FC_2C_1O_4$	dihedral angles,[a] deg $\angle C_2C_1O_4H_5$	total energies, au[b]	rel energies, kcal mol^{-1}
a	0	60	−517.158 36	6.86
b	180	120	−517.158 67	6.66
c	180	60	−517.158 79	6.59
d	180	0	−517.165 08	2.64
e	180	150	−517.165 48	2.39
f	0	0	−517.167 14	1.34
g	0	180	−517.169 02	0.17
h	180	180	−517.169 29	0.0

[a] See Figure 3; standard model geometry used (Table IV). [b] 1 au = 627.5 kcal mol^{-1}.

rameters (Figure 3). These are R, the intermolecular distance; θ_1 and θ_2, the $C_{1'}C_1O_3$ and $C_1C_{1'}O_{3'}$ angles, respectively; χ_1 and χ_2, the angles of rotation of the molecules about the $C_1{=}O_3$ and $C_{1'}{=}O_{3'}$ bonds respectively; ϕ, the angle of rotation of molecule II about the $C_1C_{1'}$ axis. The two acetic acid monomers were initially arranged to form two parallel O-H···O hydrogen bonds with the CO_2H planes of each monomer being coplanar. This configuration, illustrated in Figure 3, corresponds to $\chi_1 = \chi_2 = 0$ and $\phi = 180°$. The energy of the dimer was minimized with respect to the six intermolecular parameters. The results are given in the inset table of Figure 3. The dimer structure is found to have a symmetric and planar cyclic structure with nearly linear O-H···O bonds. The O-H bonds are rotated outward by 1.5° from the O···O intermolecular line which is close to the 1° rotation found by Del Bene and Kochenour in an STO-3G study of the formic acid dimer.[31] The C_1-C_2 and $C_{1'}$-$C_{2'}$ bonds make angles of 1° (in counterclockwise directions) with the intermolecular axis ($C_1C_{1'}$). The O···O bond distance is 2.60 Å compared to the experimental result of 2.68 Å.[29]

The binding energy of the acetic acid dimer is −14.57 kcal/mol. The use of an optimized monomer geometry and allowance for the distortion of the monomer unit in the dimer could change this result to some extent. In the case of the formic acid dimer, Del Bene and Kochenour[31] found that allowing the monomer to distort from its optimized geometry resulted in a binding energy that was more negative by 2.7 kcal mol^{-1}. These theoretical results also have uncertainties due to the use of the minimal basis set and neglect of electronic correlation energy. It is difficult to place any definite uncertainties on the binding energy or geometry results from these sources of error. However, it has been generally found that (in comparison with larger basis set calculations and experiment) the STO-3G basis set gives reasonable binding energies and geometries for most hydrogen-bonded complexes.[32] Also, correlation energy has been found to change the binding energy of the water dimer by only 1 kcal mol^{-1}.[33] Hence, we believe that the geometries and binding energies for the acetic and trifluoroacetic acid dimers are reliable enough to obtain useful information on the hydrogen bonding in these systems.

B. Trifluoroacetic Acid. A standard experimental model[34] was used for the bond lengths and angles of the trifluoroacetic acid monomer. These are given in Table IV. Various rotational configurations of the monomer are possible depending on the orientations of the O-H and CF_3 groups. Rotation of the CF_3 group about the C-C bond leads to cis and trans forms ($FC_2C_1O_4$ dihedral angles of 0 and 180°, respectively) while rotation of the hydroxyl hydrogen about the C-O bond leads to configurations described by the $C_2C_1O_4H_5$ dihedral angle. The STO-3G energies of the most likely configurations were calculated and are given in Table V. The most stable structure was the trans form with a $C_2C_1O_4H_5$ dihedral angle of 180° as illustrated in Figure 3. This configuration is identical with the experimental acetic acid monomer geometry. In contrast to similar STO-3G calculations on 2,2,2-trifluoroethanol[2] the lowest energy trifluoroacetic acid monomer does not contain an intramolecular hydrogen bond.

Using the most stable trifluoroacetic acid isomer (structure h, Table V) the geometry of the dimer was optimized with the same intermolecular parameters as in the case of the acetic acid dimer (see Figure 3). The optimized parameters are given in the inset table of Figure 3. The optimized trifluoroacetic acid dimer geometry is similar to that of acetic acid dimer with hydrogen bonds that are also nearly linear. The O-H bonds are rotated 0.9° outward from the O···O intermolecular line. The hydrogen-bond distance (O-H···O) is 2.58 Å, which is slightly shorter than the 2.60 Å for the same distance in the acetic acid dimer. A 1944 electron diffraction study[30] of both dimers found the O-H···O bond distances to be 2.76 ± 0.06 Å. The STO-3G binding energy of the equilibrium trifluoroacetic acid dimer is −14.66 kcal mol^{-1}. This value is more negative by 0.09 kcal mol^{-1} than the corresponding value for the acetic acid dimer.

The charge distributions in the acetic acid and trifluoroacetic acid monomers can give some insight into the interactions taking place in both dimers. The Mulliken population analysis for both species is given in Table VI. When the $-CH_3$ group in acetic acid is replaced by the electron-withdrawing $-CF_3$ group, the oxygen in the C=O group becomes less negative by 0.035 e$^-$ while the hydrogen in the O—H group becomes more positive by 0.027 e$^-$. Thus, from purely electrostatic arguments (assuming that the binding energy is the result of interaction between the carbonyl oxygen and the hydroxyl hydrogen), it is difficult to predict which dimer would be more stable. The results of the STO-3G calculations indicate that the more positive hydrogen may be dominant and results in the trifluoroacetic acid dimer being slightly more stable than the acetic acid dimer. However, this is not conclusive because of the incomplete geometry optimization.

C. Comparison of the Theoretical Binding Energy with the Experimental Enthalpy of Association for Both Dimers. The theoretical binding energy ΔE_{el} is related to the experimental enthalpy of association by[2,35]

$$\Delta H_2 = \Delta E_{el} + \Delta E_{vib} - 4RT \qquad (16)$$

where ΔE_{vib} is the change in vibrational energy upon dimerization and can be calculated from

$$E_{vib} = (1/2)h \sum_i v_i + \sum_i hv_i/(e^{hv_i/RT} - 1) \qquad (17)$$

where h is Planck's constant and v_i are the fundamental vibrational frequencies. The vibrational frequencies of the acetic acid monomer and dimer were assigned by Chao and Zwolinski[7] and have been used to calculate ΔE_{vib} for acetic acid at 373 K. The contribution from the intramolecular vibrations is 0.15 kcal mol^{-1}. The six new intermolecular vibrations (196, 188, 115, 110, 67, and 47 cm^{-1}) contribute 4.54 kcal mol^{-1}

Table VI. Mulliken Population Analysis for the Monomers of Acetic and Trifluoroacetic Acids[a] (X_3CCOOH)

	C_1	C_2	O_3	O_4	H_5	X_6	X_7, X_8
X = H	5.677	6.196	8.275	8.307	0.786	0.921	0.919
X = F	5.716	5.569	8.240	8.301	0.759	9.133	9.141

[a] Refer to Figure 3 for atom numbering.

to ΔE_{vib}. Thus, the enthalpy of association for the acetic acid dimer calculated from eq 16 using the theoretical ΔE_{el} is -12.85 kcal mol^{-1}.

For trifluoroacetic acid the intermolecular frequencies (233, 180, 197, 146, 109, and 86 cm^{-1}) of Redington and Lin[36] give a contribution to ΔE_{vib} of 4.60 kcal mol^{-1}. The intramolecular frequencies for trifluoroacetic acid dimer have not been measured so their contribution to ΔE_{vib} is assumed to be the same as that for acetic acid (0.15 kcal mol^{-1}). Thus, using eq 16, the enthalpy of association for trifluoroacetic acid dimer is -12.88 kcal mol^{-1}. The intermolecular frequencies of Redington and Lin[36] are consistently higher than the corresponding acetic acid frequencies. Slutsky and Bauer[37] have shown through a normal coordinate analysis that the intermolecular vibrational frequencies of trifluoroacetic acid dimer should be *lower* than those of the acetic acid dimer because of the larger mass of the trifluoroacetic acid molecule. Use of the intermolecular frequencies of Slutsky and Bauer for trifluoroacetic acid dimer in eq 16 instead of those of Redington and Lin gives a ΔH_2 of -12.92 kcal mol^{-1}.

The enthalpy of association calculated from the theoretical binding energy becomes slightly *more* negative with the replacement of the -CH_3 group by the -CF_3 group. The experimental results indicate the opposite effect. This discrepancy may be due to uncertainties already discussed in either the theoretical or experimental numbers. Despite this, the values of ΔH_2 calculated from the theoretical binding energies are relatively close to the experimental enthalpies of -14.64 and -13.66 kcal mol^{-1} for acetic and trifluoroacetic acids, respectively.

VI. Conclusions

From this experimental and theoretical investigation into the properties of acetic and trifluoroacetic acid vapors we reach the following conclusions:

(1) Both acids have remarkably enhanced thermal conductivities in the vapor, approaching or exceeding that of neon gas at most pressures.

(2) A monomer-dimer model is consistent with the experimental data. The best fit thermodynamic results for the dimerization reactions are $-\Delta H_2 = 14.64 \pm 0.8$ kcal mol^{-1} and $-\Delta S_2 = 35.50 \pm 1.0$ cal mol^{-1} K^{-1} for acetic acid and $-\Delta H_2 = 13.66 \pm 2.0$ kcal mol^{-1} and $-\Delta S_2 = 36.15 \pm 5.0$ cal mol^{-1} K^{-1} for trifluoroacetic acid.

(3) Ab initio molecular orbital calculations have determined equilibrium geometries for the dimers of both acids. The geometry for the acetic acid dimer is consistent with the experimental results. The enthalpies of association calculated from the theoretical binding energies are reasonably close to the experimental values.

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