1029. *Investigation of Aliphatic Ester–Alcohol Hydrogen Bonding by Infrared Spectroscopy: Determination of Equilibrium and Thermodynamic Constants.*

By H. F. Smith and A. S. Rosenberg.

Hydrogen bonding between octan-1-ol and hexyl hexanoate has been studied by infrared spectroscopy, the equilibrium constant (K_e) being determined at 21·7°, 39·3°, and 51·8° and thence ΔH and ΔS are found to be 2·21 kcal./mole and $-7{\cdot}8$ e.u./mole, respectively.

The hydroxy–carbonyl groups of an alcohol–ester system form hydrogen bonds, in an equilibrium $E + A \rightleftharpoons C$, where E = ester, A = alcohol monomer, and C = hydrogen-bonded complex, the equilibrium constant being $K = [C]/[E][A]$. If we assume the complex to be formed by reaction of one molecule each of alcohol and ester, [C] may be expressed as $[E]_s - [E]$, where $[E]_s$ is the stoicheiometric ester concentration. Therefore, we can write

$$K[A] = ([E]_s/[E]) - 1. \qquad (1)$$

The stoicheiometric ester concentration is the amount of ester originally added to the system. The actual ester concentration, [E], is that remaining after hydrogen-bonding equilibrium is reached. $[E]_s$ and [E] are related to the "actual" * and "apparent" † extinction coefficient, ε and ε_a, by the expression $[E_s]/\varepsilon = [E]/\varepsilon_a$, so that we can rewrite equation (1) as

$$K[A] = (\varepsilon/\varepsilon_a) - 1. \qquad (2)$$

Now, ε and ε_a are determined from the carbonyl stretching bands of esters in a non-hydrogen bonding and in a hydrogen-bonding environment, respectively. The alcohol monomer concentration, [A], may be determined from the hydroxyl monomer stretching band close to 3650 cm.$^{-1}$. Mecke[1] has shown the infrared method to be reliable for determining mole fractions of free and hydrogen-bonded alcohols in carbon tetrachloride solution, finding good agreement between the mole fraction of free methanol in carbon tetrachloride determined by infrared spectroscopy and by vapour-pressure measurements.

In our work, we have assumed that the hydrogen-bonded alcohol dimer and polymers

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* Carbonyl extinction coefficient determined in absence of alcohol.

† Carbonyl extinction coefficient determined in presence of alcohol.

[1] Mecke, *Discuss. Faraday Soc.*, 1950, **9**, 161.

are cyclic. We have assumed also that only the monomer alcoholic hydroxyl participates in alcohol–ester hydrogen-bonding, though there is still debate whether this is the case.[2]

Since we determined the alcohol monomer concentration by measurement of the monomer hydroxyl stretching band's intensity, it could be argued that equilibrium constants determined in this manner are in error because there will be some open-chain alcohol aggregates having terminal hydroxyl groups that absorb in this region. Kuhn[3] and Ingraham *et al.*[4] have studied aromatic and aliphatic dihydroxy-compounds at high dilution to show that a terminal hydroxyl group will absorb close to the frequency of the monomer hydroxyl. Smith and Creitz[5] have assigned to the monomer hydroxyl groups a stretching frequency of 3650 cm.$^{-1}$ and to the terminal hydroxyl group of a polymeric alcohol chain a stretching frequency of 3623 cm.$^{-1}$. Pimentel and McClellan[2] conclude that the intensity of absorption at the monomer alcohol's stretching frequency will not be proportional to the monomer hydroxyl concentration unless the associated alcohols form cyclic structures, eliminating terminal hydroxyl groups. Van Thiel, Becker, and Pimentel,[6] using their ingenious matrix-isolation technique, were able to show that methanol existed as cyclic dimers, trimers, and tetramers trapped in solid nitrogen. Becker *et al.*[7] have reported good nuclear magnetic resonance evidence to support the theory that primary alcohols form cyclic dimers at low concentrations.

EXPERIMENTAL

Materials.—The aliphatic ester and alcohol used in this study were n-hexyl hexanoate and octan-1-ol, prepared in our laboratories and shown by gas chromatography to have purities of >99 mole %. Carbon tetrachloride (Mallinckrodt Analytical Reagent grade), dried and stored over calcium hydride, was used as solvent (the hydride removed all the water).

Spectral measurements were made on a Perkin-Elmer model 221G infrared spectrophotometer. Temperature-control was maintained by an air-bath surrounding the infrared sample cell. This bath consisted of an insulated box, with sodium chloride windows for transmission of infrared radiation, a cooling coil, and a heating element controlled by a thermal regulator, as well as a circulating fan and a cell holder. Temperature control was within $\pm 0{\cdot}2°$.

The sample cells used were of standard Perkin-Elmer design calibrated by measurement of the diffraction pattern or by direct comparison with a cell calibrated by diffraction measurement.[8]

Technique.—The alcohol–ester solutions in carbon tetrachloride were examined at 21·7°, 39·3°, and 51·8°, the same series at each temperature, four measurements being made at each temperature. These were: (1) extinction coefficient for the carbonyl stretching band of hexyl hexanoate, (2) the extinction coefficient for the monomeric hydroxyl stretching band of octan-1-ol, (3) the apparent extinction coefficient of the carbonyl stretching band of hexyl hexanoate in the various solutions containing octan-1-ol, and (4) the alcohol monomer concentration of these different solutions. From these measurements the equilibrium constant for the hydrogen-bonding at each temperature was calculated by using equation (2).

Using the equation

$$\Delta F = \boldsymbol{R}T \ln K_e - \Delta H - T\Delta S,$$

rearranged to give

$$\ln K_e = -\Delta H/\boldsymbol{R}T + \Delta S/\boldsymbol{R},$$

we calculated H and S for the two systems. By plotting ln K against $1/T$, we obtained a curve of slope $-\Delta H/\boldsymbol{R}$ and intercept $\Delta S/\boldsymbol{R}$.

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[2] Pimentel and McClellan, "The Hydrogen Bond," Freeman and Company, 1960, p. 97, San Francisco.

[3] Kuhn, *J. Amer. Chem. Soc.*, 1954, **76**, 4323; 1952, **74**, 2492.

[4] Ingraham, Corse, Bailey, and Still, *J. Amer. Chem. Soc.*, 1952, **74**, 2297.

[5] Smith and Creitz, *J. Res. Nat. Bur. Stand.*, 1951, **46**, 145.

[6] Van Thiel, Becker, and Pimentel, *J. Chem. Phys.*, 1957, **27**, 486.

[7] Becker, Liddel, and Shoolery, *J. Mol. Spectroscopy*, 1958, **2**, 1.

[8] Lord, McDonald, and Miller, *J. Opt. Soc. Amer.*, 1952, **42**, 149.

RESULTS AND DISCUSSION

The absorbance values for the carbonyl stretching bands of hexyl hexanoate and carbon tetrachloride appear in Table 1. A linear relation is evident when these are plotted against ester concentration. The resulting extinction coefficients (ε) are: at 21·7°, 55·84 ± 0·25; at 39·3°, 54·70 ± 0·19; at 51·7°, 54·09 ± 0·10 mole^{-1} mm.$^{-1}$.

TABLE 1.

Intensity of carbonyl stretching band at various temperatures, given as absorbance (l = 0·0859 mm.).

[Ester] (M)	0·02314	0·03678	0·05741	0·08030	0·09683
At 21·7°	0·1086	0·1752	0·2856	0·3890	0·4626
At 39·3°	0·1099	0·1729	0·2704	0·3806	0·4519
At 51·7°	0·1058	0·1717	0·2681	0·3724	0·4502

TABLE 2.

Intensity of hydroxyl monomer stretching band at various temperatures, given as absorbance (l = 1·081 mm.).

$[\text{Alcohol}]_s$ (M)	0·00857	0·01190	0·01431	0·02766	0·03448
At 21·7°	0·0543	0·0717	0·0908	0·1579	0·2037
At 39·3°	0·0523	0·0697	0·0817	0·1593	0·1970
At 51·6°	0·0445	0·0641	0·0777	0·1520	0·1889

The absorbance values for the alcohol monomer band in carbon tetrachloride solutions of octan-1-ol are listed in Table 2 and give the extinction coefficients (ε): at 21·7°, 5·459 ± 0·026; at 39·3°, 5·317 ± 0·032; at 51·6°, 5·055 ± 0·026 mole^{-1} mm.$^{-1}$. A plot of the absorbance against alcohol concentration at each temperature shows excellent linearity.

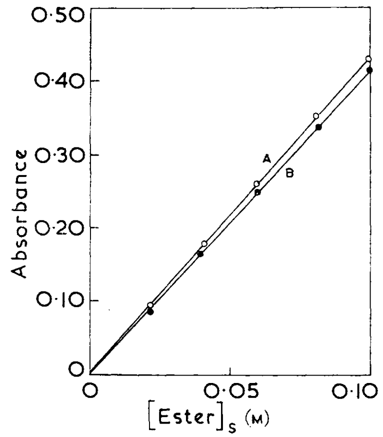

FIG. 1.

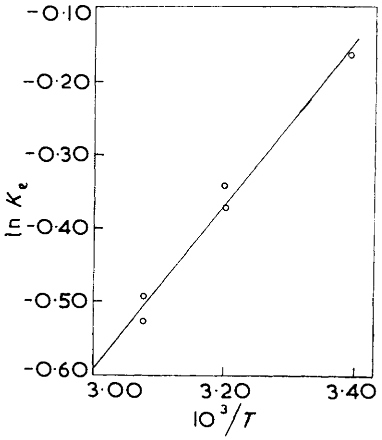

FIG. 2.

FIG. 1. A plot of absorbance (l = 0·0859 mm.) at 1720 cm.$^{-1}$ against concentration of hexyl hexanoate in octan-1-ol–carbon tetrachloride solutions at 39·3°.

$[\text{Alcohol}]_s$ = (A) 0·1274M, (B) 0·2549M.

FIG. 2. A plot of ln K_e against $10^3/T$, where K_e = equilibrium constant, and T is in °K.

Tables 3 and 4 and Fig. 1 show the intensities of the carbonyl stretching band of hexyl hexanoate in carbon tetrachloride–octan-1-ol solutions. The absorbance of the ester-carbonyl group at five concentrations is essentially constant with respect to temperature.

The alcohol monomer concentration of the ester alcohol solution are listed in Table 5, as calculated from the coefficients listed in Table 3. From all of these results, the equilibrium constants for the reaction, Alcohol + Ester $\rightleftarrows$ Complex, were calculated and are listed in Table 6. By plotting $\ln K$ against $1/T$, we obtained a line with a slope of $+1110 \pm 70$ and an intercept of $-3{\cdot}9 \pm 0{\cdot}3$ (cf. Fig. 2). Since the slope may be defined as $-\Delta H/\boldsymbol{R}$ and the intercept as $\Delta S/\boldsymbol{R}$, the changes in enthalpy and entropy of the system were determined as —2·2 kcal./mole and —7·8 e.u./mole, respectively.

TABLE 3.

Intensity of carbonyl stretching band of hexyl hexanoate in octan-1-ol solution, given as absorbance (l = 0·0859 mm.).

	0·12744M-Alcohol									
[Ester]$_s$ (M)	0·02177	0·04098	0·05943	0·08030	0·09933	0·02133	0·03890	0·05925	0·08135	0·09971
At 21·7° ...	0·0920	0·1772	0·2574	0·3500	0·4350	0·0892	0·1658	0·2519	0·3487	0·4242
At 39·3° ...	0·0934	0·1778	0·2596	0·3518	0·4301	0·0860	0·1658	0·2494	0·3379	0·4166
At 51·7° ...	0·0934	0·1784	0·2579	0·3456	0·4317	0·0892	0·1632	0·2467	0·3373	0·4145

TABLE 4.

Apparent carbonyl stretching band extinction coefficients for solutions of ester in alcohol–carbon tetrachloride.

	ε_a (mole^{-1} mm.$^{-1}$)		
[Alcohol]$_s$ (M)	21·7°	39·3°	51·8°
0·1274	50·71 ± 0·16	50·63 ± 0·14	50·41 ± 0·12
0·2549	49·60 ± 0·11	48·63 ± 0·21	48·39 ± 0·07

Conclusions.—The extinction coefficients of the ester-carbonyl stretching band seem to indicate that the molar absorptivity of hexyl hexanoate in carbon tetrachloride is a function of temperature. However, it may be shown that this variation results from changes in the density of the solution. Using the absorptivity data obtained at 51·7° as reference point, we calculated the changes in the extinction coefficient expected solely from density changes at 39·3° and 21·7°, after determining the ratio of the density of the solutions at 51·7° and 39·3°, and at 51·7° and 21·7°, which we found to be 1·016 and 1·038, respectively; these are the same as the ratios of the extinction coefficients at these temperatures, namely, 1·011 and 1·032, respectively.

TABLE 5.

Actual alcohol monomer concentrations in alcohol–ester–carbon tetrachloride solutions.

	Actual alcohol monomer concn. (M)		
[Alcohol]$_s$ (M)	21·6°	39·3°	51·8°
0·1274	0·1013	0·1134	0·1206
0·2549	0·1490	0·1801	0·2011

TABLE 6.

Equilibrium constants for alcohol–ester complex formation at various temperatures.

	K (mole^{-1})		
[Alcohol]$_s$ (M)	21·7°	39·3°	51·8°
0·1274	1·088	0·708	0·605
0·2549	0·854	0·694	0·586

This conclusion does not seem applicable in the case of the ester in alcohol–carbon tetrachloride solution. In this case we observed that the extinction coefficient remained constant with variation of temperature. This is probably because complex formation is more complete at the lower temperature, which tends to decrease the free-carbonyl concentration and offset the effective increase due to a rise in density.

Moreover, even if the molar absorptivity of the ester were not constant, the conclusions of this paper would not be obviated. We have used the ratio of the actual to the apparent extinction coefficient, both being measured at the same temperature. This procedure will cancel out the effect of any absorptivity change with temperature.

This leaves the effect of alcohol dimer, trimer, and tetramer structure on the equilibrium constants to be considered. We assumed these compounds to be cyclic, for which, generally, there is good evidence. Higher polymers probably will not cyclize, but we believe this to be inconsequential in our work because the [A] term of the equilibrium constant equation includes all hydroxyl groups which are free and capable of hydrogen bonding with the ester-carbonyl group not only monomer hydroxyl.

Terminal hydroxyl groups of open-chain alcohol polymers should surely be able to form hydrogen bonds with the ester-carbonyl group. There might be a slight decrease in hydrogen-bonding ability of terminal hydroxyl compared with monomer hydroxyl, owing to steric factors or slight changes in the dipole nature of the hydroxyl group terminating a polymer chain. This decrease must be quite small since the monomer hydroxyl and the terminal hydroxyl of open polymeric chains absorb within 25 cm.$^{-1}$ of each other. Therefore, if the polymeric alcohols exist as open chains, we must consider it fortuitous that their terminal hydroxyl groups absorb in the same region as the monomer's because, in so doing, our [A] term in the equilibrium constant expression, becomes more valid and the equilibrium and thermodynamic constants more meaningful.

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Research and Development Department,
Continental Oil Company, Ponca City,
Oklahoma, U.S.A.

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