nucleation and growth in which a complex ion, probably $Ni(C_2O_4)_2^{=}$, is the rate-determining species. DE is the curve for the equivalent processes determined by the simple ionic species in solution which become predominant under conditions in which the complex ion is unstable.

We represent, in general, the rates of nucleation and growth, respectively, by the equations

$$v_1 = \alpha_1 f_1(C) e^{-E_1/RT}$$
$$v_2 = \alpha_2 f_2(C) e^{-E_2/RT}$$

where α_1 and α_2 are steric factors, $f_1(C)$ and $f_2(C)$ are functions of the concentrations of the species in solution which determine the rates of nucleation and growth, respectively, and E_1 and E_2 are the activation energies. We make two reasonable assumptions

$$\left(\frac{\partial f_1(C)}{\partial C}\right)_T > \left(\frac{\partial f_2(C)}{\partial C}\right)_T \tag{1}$$

and

$$E_1 > E_2 \tag{2}$$

It is possible also that E_2 varies with the surface area of the particles, but the variation is probably small. We shall neglect this factor and also the steric factors.

For the curve AB the concentration of the complex C_c decreases as the concentration of the oxalic acid C_{ox} increases. At A, $v_1 > v_2$ results in a large number of small particles and hence a large surface area. As C_{ox} increases C_c decreases and because of assumption (1) above v_1 decreases more rapidly as C_{ox} increases than does v_2. The surface area will therefore decrease until at B $v_1 \sim v_2$. At higher temperatures, the complex will be less stable, that is, C_c will be smaller, v_1 and v_2 will both be smaller for given concentration conditions than at the lower temperature. Consequently, the curve will not extend to surface areas as large as those at the lower temperature. Further, since $E_1 > E_2$, v_2 will be increased more than v_1 with increasing temperature and the curve will be shallower. Both these facts have been found experimentally.

For the "ionic" curve DE, $v_1 \sim v_2$ at D, but as C_{ox} increases because of assumption (1) v_1 increases more rapidly than v_2. The surface area will therefore increase until at E, $v_1 > v_2$. At higher temperatures because of assumption (2) v_2 will be increased more than v_1 thus giving a shallower curve.

At 20° there is a noticeable tailing-off to a constant area when the concentration of oxalic acid is in marked excess over the nickel sulfate. In general, the ionic concentration function $f(C_i)$, will not depend in a simple way only on the total ionic concentration, but also on the ionic ratio,[4] and the dependence of $f_1(C_i)$ and $f_2(C_i)$ will be different. In consequence it is possible under suitable concentration conditions for v_1 and v_2 to become comparable in magnitude. The concentration conditions at which this state of affairs occurs will depend on the temperature since $E_1 > E_2$ and, in the present case, it appears that the onset of the tailing-off at the higher temperature is displaced to higher concentration values.

It is noticeable that the slopes of the "complex" curves, Figs. 1 and 2, are not in the order of concentration of nickel sulfate. This may be accounted for if, as is most probable, $f(C_c)$ is not a simple function of the concentration of the nickel sulfate and oxalic acid.

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[4] C. W. Davies and A. L. Jones, *Disc. Faraday Soc.*, **5**, 103 (1949).

The Association of Triethylamine and Chloroform

BY GORDON M. BARROW AND E. ANNE YERGER

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The use of chloroform as a solvent for the study of the reactions between acids and bases has an interesting advantage of providing a fairly specific type of solvent interaction. This interaction is mainly the stabilization by the formation of hydrogen bonds, of bases, or negatively charged ions, without the added complications encountered in hydroxylic solvents. For some recent work[1] on acetic acid–triethylamine reactions in chloroform it was necessary to establish the degree of interaction of the solvent with triethylamine itself. The results of this study are reported here.

Experimental

Triethylamine was purified by distillation and was stored over KOH.

Since chloroform has no absorption bands in the infrared spectrum suitable for following the reaction with triethylamine the deuterated compound was prepared. Three grams of deuterium oxide, 99.8%, from the Stuart Oxygen Company was added to a suspension of CaO in freshly distilled chloral according to the method of Truchet.[2] After refluxing for 5 hours a product was taken off at 60–65°. This material was placed over CaO and the liquid was separated by bulb-to-bulb vacuum distillation. Repetition of this step gave 5 cc. of a product whose infrared spectrum indicated a $CDCl_3$ purity of at least 95% and showed no evidence of any impurity other than $CHCl_3$.

The infrared spectrum of the $CDCl_3$ was obtained on a Baird Associates instrument; for the studies of $CDCl_3$ and triethylamine solutions a Beckman IR-2T instrument with a LiF monochromator was used.

The spectrum of $CDCl_3$, 4% by volume in CCl_4 in a 1-mm. cell, showed some difference compared to that reported by Earing and Cloke.[3] In addition to the $CDCl_3$ absorption bands at 740, 907, 1095 and 2254 cm.$^{-1}$ reported by them, bands also occur at 649(s), 1377(m), 1468(m) and 1805(vw) all of which are attributable to $CDCl_3$. The last three are overtones or combinations of the fundamentals at 365, 649, 740 and 907 cm.$^{-1}$ as assigned by Bernstein, Bordus and Cleveland.[4] The absorptions reported at 991 and 1171 cm.$^{-1}$ were not observed in the freshly prepared $CDCl_3$.

The hydrogen bonding interaction of $CDCl_3$, which is assumed to be no different than that of $CHCl_3$, with triethylamine is most conveniently studied with these reagents in CCl_4 solution. The spectrum of the $CDCl_3$ sample, about 1 molar in a 1.1-mm. cell, was used to determine the coefficient $1/\alpha l$ in the assumed Beer's law relation $C_{CDCl_3} = 1/\alpha l \log I_0/I_{2254\ \mathrm{cm.}^{-1}}$. Using this coefficient the concentrations of free chloroform were calculated from

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[1] G. M. Barrow and E. A. Yerger, THIS JOURNAL, **76**, 5211 (1954).

[2] R. Truchet, *Compt. rend.*, **202**, 1997 (1936).

[3] M. H. Earing and J. B. Cloke, THIS JOURNAL, **73**, 769 (1951).

[4] R. B. Bernstein, A. A. Gordus and F. F. Cleveland, *J. Chem. Phys.*, **20**, 1979 (1952).

the observed optical densities as shown in Table I. (M designates the molarity of the reagent as added to the solution, C the concentration of the component at equilibrium.) Stoichiometry then yields the concentration of the associated $CDCl_3$ from which values of C were obtained for the complex Et_3NDCCl_3. Since these involve a certain scattering, resulting from the subtraction $M_{CDCl_3}-C_{CDCl_3}$, with no noticeable trend, an average value of 2.1 was used to recalculate the amount of dimer present from the observed dimer band. The resulting equilibrium constant, Table I, has the value 0.36 with an average deviation of 0.02.

TABLE I

THE EQUILIBRIUM CONSTANT FOR THE ASSOCIATION OF CHLOROFORM AND TRIETHYLAMINE IN CARBON TETRACHLORIDE

M_{CDCl}	M_{NEt_3}	$\left(\log\frac{I_0}{I}\right)_{2254\text{ cm.}^{-1}}$	$\left(\log\frac{I_0}{I}\right)_{2178\text{ cm.}^{-1}}$	C_{CDCl_3}	$C_{CDCl_3NEt_3}$	K, mole l.
1.25	...	0.415	...	(1.25)	....	..
1.15	0.532	.327	0.638	0.962	0.133	0.35
1.06	1.022	.290	1.16	.853	.242	.36
0.693	0.688	.202	0.562	.595	.117	.36
.346	.334	.106	.150	.312	.0313	.33
.265	.256	.090	.112	.265	.0233	.40
					Av.	0.36

The complex showed a C–D stretching mode, very strong compared to the free C–D band, at 2178 cm.$^{-1}$ representing a shift of 76 cm.$^{-1}$ from that of the free $CDCl_3$. On this basis the expected hydrogen bonding shift of $CHCl_3$ would be about 102 cm.$^{-1}$. This small shift in the presence of the strong base, NEt_3, reflects the weak acidity of the chloroform. This can be compared, for example, to the hydrogen bonding shift of deuteromethanol with various ethers of about 100 cm.$^{-1}$ as reported by Searles and Tamres[5] and to a shift of about 400 cm.$^{-1}$ for the OH band of aliphatic alcohols associated with NEt_3.

As a comparison for the equilibrium constant of $CHCl_3$ and NEt_3, data are presented in Table II for the association constant of ethyl alcohol and NEt_3. These measurements of the optical density of the 3630 cm.$^{-1}$ OH band were made with CCl_4 solutions in a 20-mm. cell using the Beckman IR-2T instrument with a LiF monochromator. The resulting constant, 2.9, is about eight times that for the $HCCl_3$, NEt_3 association.

TABLE II

THE EQUILIBRIUM CONSTANT FOR THE ASSOCIATION OF ETHYL ALCOHOL AND TRIETHYLAMINE IN CARBON TETRACHLORIDE

M_{EtOH}	M_{NEt_3}	$\left(\log\frac{I_0}{I}\right)_{OH}$	C_{EtOH}	$C_{EtOH.\,NEt_3}$	K, mole^{-1} l.
0.0040	...	0.380	0.0040	.....	..
.0016	...	.158	.00166	.....	..
.0040	0.016	.360	.00380	0.00020	3.3
.0040	.040	.342	.00360	.00040	2.8
.0040	.20	.250	.00263	.00132	2.5
				Av.	2.9

The interaction of chloroform is sufficiently weak so that in a triethylamine solution dimerization is far from complete. This fact is useful in explaining the interactions of the solvent $CHCl_3$ with the species formed in the neutralization of acetic acid with triethylamine.[1]

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[5] S. Searles and M. Tamres, THIS JOURNAL, **73**, 3704 (1951).

The Dimerization of Acetic Acid in Carbon Tetrachloride and Chloroform

BY GORDON M. BARROW AND E. ANNE YERGER

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Recent studies in this Laboratory on the reactions of triethylamine with acetic acid required data on the dimerization of acetic acid in carbon tetrachloride and chloroform. Since these investigations were started a value of the equilibrium constant in carbon tetrachloride has been reported by Harris and Hobbs.[1] Our results for the dimerization constant are somewhat lower than they obtained. Furthermore, the question raised by them concerning the concentration dependence of the equilibrium constant is removed.

The carbon tetrachloride was reagent grade, dried over P_2O_5, and distilled through a 30-cm. packed column. In the earlier experiments chloroform which had been dried over Drierite and $CaCl_2$ and distilled immediately before use was used. With such a procedure, however, the equilibrium constants obtained for the acetic acid dimerization for acetic acid less than about 0.005 M showed a very large concentration dependence. For example, although a fairly constant value for the equilibrium constant of about 150 was obtained for acetic acid concentrations between 0.3 and 0.01, in the more dilute solutions of 0.001 and 0.0005 M constants of 470 and 760 resulted. Values higher than these latter results were obtained for old or less carefully distilled chloroform.

Subsequent measurements were made with chloroform which had been washed several times with sulfuric acid and with water, dried over $CaCl_2$ and Drierite and finally distilled in a nitrogen atmosphere. The results then obtained, as shown in Table II, are constant to a greater acetic acid dilution than in the previously prepared chloroform indicating that the difficulties at these dilutions are probably due to some contaminant interfering with the equilibrium.

The acetic acid was prepared by adding the appropriate amount of acetic anhydride to J. T. Baker analyzed reagent grade acetic acid to give the anhydrous material. The refractive index, $n^{20}D$, was found to be 1.3719.

The monomer and dimer concentrations were determined from the optical densities, log I_0/I, at the absorption maximum, of the respective carbonyl absorption bands. All measurements were made with a Beckman IR-2T instrument with either a NaCl or a LiF monochromator. For the CCl_4 measurements a set of cells was used with cell thickness of 0.034, 0.250, 1.10 and 20.6 mm., as measured by the interference effect for the two smaller cells and directly measured for the thicker cells. For the $CHCl_3$ solutions, cells of thickness of 0.034, 0.095, 1.00 and 20.4 were used. A check on the cell thicknesses, and on deviations from Beer's law was obtained by studying the carbonyl absorption of methyl ethyl ketone in these cells with the instrument settings used for the acetic acid spectra. Deviations from Beer's law under these were not appreciable and the use of a number of different cell thicknesses eliminated the introduction of a regular effect which would lead to an erroneous value of the equilibrium constant. The overlap of the two bands was small and was allowed for in determinations of

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[1] J. T. Harris and M. E. Hobbs, THIS JOURNAL, **76**, 1419 (1954).