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]

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

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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).

band maximum optical density by drawing each carbonyl absorption as a symmetric band.

The results of a set of experiments for carbon tetrachloride are given in Table I, while those for chloroform are in Table II. Values of

$$\alpha_{(\mathrm{HOAc})_2} = \frac{1}{C_{(\mathrm{HOAc})_2}\, l} \log \frac{I_0}{I}$$

where obtained from the intensities using the 0.034 mm. cell by extrapolation to high concentration and by correcting for the small amount of monomer present on the basis of an approximate equilibrium constant. A value for $\alpha_{(\mathrm{HOAc})}$ was then obtained from the results for the more dilute solutions from log I_0/I for the monomer and the monomer concentration as obtained from the stoichiometry.

TABLE I

THE EQUILIBRIUM CONSTANT FOR THE REACTION $2\mathrm{HOAc} \rightleftharpoons (\mathrm{HOAc})_2$ IN CARBON TETRACHLORIDE

Cell length, mm.	M_{HOAc}	$\left(\log \frac{I_0}{I}\right)_{(\mathrm{HOAc})_2}$	$\left(\log \frac{I_0}{I}\right)_{\mathrm{HOAc}}$	$C_{(\mathrm{HOAc})_2}$	C_{HOAc}	K, mole^{-1} l.
0.034	0.170	0.422	...	0.081	......	..
	.100	.250	...	.050	......	..
	.050	.128	0.01	.025	0.005	1000
0.250	.050	.814	.068	.0211	.0044	1090
	.025	.434	.047	.0113	.0030	1250
	.010	.160	.026	.0041	.0017	1420
1.10	.010	.690	.112	.0041	.0017	1420
	.005	.328	.072	.00190	.00105	1720
	.0025	.168	.050	.0099	.00074	1810
20.6	.00056	.442	.324	.000139	.000253	2170
	.00028	.180	.208	.000057	.000163	2150
	.000112	.054	.103	.0000170	.000080	2650

TABLE II

THE EQUILIBRIUM CONSTANT FOR THE REACTION $2\mathrm{HOAc} \rightleftharpoons (\mathrm{HOAc})_2$ IN CHLOROFORM

Cell length, mm.	M_{HOAc}	$\left(\log \frac{I_0}{I}\right)_{(\mathrm{HOAc})_2}$	$\left(\log \frac{I_0}{I}\right)_{\mathrm{HOAc}}$	$C_{(\mathrm{HOAc})_2}$	C_{HOAc}	K, mole^{-1} l.
0.034	0.349	0.820	(0.073)	0.147	(0.040)	(90)
	.174	.370	(.036)	.066	(.020)	(160)
0.095	.070	.428	.074	.0275	.0147	130
	.035	.204	(.050)	.0131	.010	130
1.00	.01395	.614	.309	.00374	.00583	110
	.00698	.267	.192	.00163	.00362	120
	.00279	.078	.098	.000475	.00185	140
20.4	.000558	.178	.493	.000053	.000455	260
	.000186	.040	.182	.000012	.000168	420

The equilibrium constants for CCl_4 solutions are satisfactorily constant, changing by about a factor of two for concentrations differing by a factor of about 500. This difference is greater than can be accounted for by errors in solution concentrations or determinations of optical densities or cell thicknesses.

All values are lower than the results of Harris and Hobbs[1] who give, for the dimerization equilibrium, the values 5,550 and 3,200 for concentrations in the ranges of about 0.003–0.07 *M* and 0.00025–0.0025 *M*, respectively. The latter constant is considered more reliable and it appears from the present results that the dependence of the equilibrium constant on concentration is the reverse of that indicated by the less reliable value of Harris and Hobbs.

The equilibrium constants in chloroform are likewise satisfactorily constant except at high dilutions and this deviation, as previously suggested, can be attributed to interaction with impurities in the chloroform.

The principal chloroform association with acetic acid occurs through hydrogen bonding to the monomer carbonyl. If all of the interaction is attributed to this and the dimer is considered unaffected in the chloroform, one calculates for the reaction

$$\mathrm{HOAc} + \mathrm{HCCl_3} \rightleftharpoons \mathrm{HOAc \cdot HCCl_3}$$

the equilibrium constant of about 0.2, representing a lower limit, which can be compared with association constants of alcohols of about 1.5 as reported by Coggeshall and Saier[2] or with that for the association of chloroform with triethylamine of 0.36 determined by Barrow and Yerger.[3]

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[2] N. D. Coggeshall and E. L. Saier, THIS JOURNAL, **73**, 5414 (1951).

[3] G. M. Barrow and E. A. Yerger, *ibid.*, **76**, 5247 (1954).

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

Observations on the Rare Earths. LXIII.[1] The Preparation of Anhydrous Rare Earth Metal Nitrates

BY THERALD MOELLER AND VICTOR D. AFTANDILIAN

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The literature records no general procedure for the preparation of anhydrous rare earth metal nitrates. It is true that reaction of fused ammonium nitrate with lanthanum oxide yields the anhydrous nitrate,[2] but with neodymium only the compound $Nd(NO_3)_3 \cdot NH_4NO_3$ could be obtained under comparable conditions, and attempts to remove excess ammonium nitrate by thermal decomposition gave a basic neodymium nitrate.[2] All attempts at dehydration of hydrated nitrates have yielded basic products.

Reaction of liquid dinitrogen(IV) oxide with metal carbonates or oxides to yield anhydrous nitrates was probably first noted by Oswald,[3] who obtained sodium nitrate in this fashion. Subsequent studies[4-9] have shown the method to be a general one, the reactions proceeding most readily in closed containers at elevated temperatures and resultant high nitrogen(IV) oxide pressures.[8,9] Even under the most drastic conditions reported (87°, 14.5 atm.),[8,9] a number of instances of slow

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[1] For the preceding communication in this series, see T. Moeller and P. A. Zimmerman, THIS JOURNAL, **75**, 3940 (1953).

[2] L. F. Audrieth, E. E. Jukkola and R. E. Meints with B. S. Hopkins, *ibid.*, **53**, 1805 (1931).

[3] M. Oswald, *Ann. chim.*, [9] **1**, 32 (1914).

[4] E. Briner, J. B. Lugrin and R. Monnier, *Helv. Chim. Acta*, **13**, 64 (1930).

[5] G. Boh, *Ann. chim.*, [11] **20**, 421 (1945).

[6] C. C. Addison, J. Lewis and R. Thompson, *J. Chem. Soc.*, 2829, 2838 (1951).

[7] C. C. Addison and J. Lewis, *ibid.*, 2833 (1951); 1319 (1953).

[8] G. Gibson and J. J. Katz, THIS JOURNAL, **73**, 5436 (1951).

[9] J. R. Ferraro and G. Gibson, *ibid.*, **75**, 5747 (1953).