not proceed by the primary mechanism alone. Drops of diethyl phthalate have been identified in the decomposition apparatus, which suggests dissociation according to equation 7

$$ZrCl_4 \cdot C_6H_4(COOC_2H_5)_2 \longrightarrow ZrCl_4 + C_6H_4(COOC_2H_5)_2 \quad (7)$$

It is possible that the ethylene results from the decomposition of the ester, as reported for ethyl benzoate.[5] If this is so, the phthalic acid, resulting from equation 8, would react with any free metal tetrachloride to give hydrogen chloride.

$$C_6H_4(COOC_2H_5)_2 \longrightarrow C_6H_4(COOH)_2 + C_2H_4 \quad (8)$$

$$ZrCl_4 + C_6H_4(COOH)_2 \longrightarrow ZrCl_2(OOC)_2C_6H_4 + 2HCl \quad (9)$$

In the zirconium case only, trace quantities of phthalic anhydride were identified among the decomposition products.

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[5] E. M. Bilger and H. Hibbert, This Journal, **58**, 823 (1936).

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Henry's Law Constants for *t*-Butyl Chloride in Aqueous Methanol Solutions[1]

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Rate equations proposed by various investigators for the solvolysis of *t*-butyl chloride in aqueous methanol solutions involve Henry's law constants for *t*-butyl chloride in those solvents.[2-4] The original determinations of these constants by Halford[5] as quoted by Olson and Halford, admittedly were subject to appreciable errors. We have therefore redetermined the constants as a contribution to the program of limiting the form of the rate equation.

Experimental Part

Two methods were used. In the first method a series of Liebig bulbs, containing *t*-butyl chloride in the solvent under consideration, were connected in series and placed in a thermostat. A known volume of nitrogen was then passed through the bulbs and collected in a large bulb. The bulb was cooled, some water admitted to it, and then sealed. It was then warmed to hydrolyze the chloride, and the resulting acid was titrated. The concentration of the chloride in the last Liebig bulb likewise was determined by completely hydrolyzing a known volume of the solution. In the 100 and 90% methanol solutions, three bulbs were sufficient to saturate the nitrogen so that the composition of the last bulb remained unchanged, but in the 80 and 70% solutions, eight bulbs were needed. No spray could be detected when the effluent gas was admitted to the chamber of an ultra-microscope.

From the known empirical rate equation, the time of mixing and the initial and final times of passage of the gas, an average concentration for the chloride was calculated, *i.e.*

$$N_{av} = N_0\left[\frac{1 - \frac{k}{2}\left\{(t_f - t_0)^2 - (t_i - t_0)^2\right\}}{t_f - t_i}\right]$$

This correction amounted to about 4% in the 70% methanol and to only about 1% in the 80% methanol.

Duplicate runs were made using pure *t*-butyl chloride in the Liebig bulbs. From these data the vapor pressure of pure *t*-butyl chloride at 25° was determined to be 300 mm. A check on this value was found by the following static method. Freshly distilled *t*-butyl chloride was introduced into a flask which was fitted to a manometer and a vacuum line. The liquid was frozen, the system evacuated, and then the liquid was permitted to warm up. This degassing procedure was repeated several times. With the bulb kept somewhat below room temperature, the equilibrium pressure was read. Now a series of seven determinations in a temperature range slightly below room temperature were made, and from the normal boiling point, 50.7°, the equation

$$\ln p = 17.40 - \frac{3487}{T}$$

was found to fit with an average deviation of 0.2%. This agrees with the dynamic determination at 25°. ΔS of vaporization is normal for a non-associated liquid.

The second method was essentially a repetition of Halford's method with some experimental improvements, *e.g.*, the volume of the vapor space was reduced to about 30 ml., a magnetic stirrer was introduced to speed equilibrium, and mercury was interposed between the *t*-butyl chloride and the stopcock.

Results

At 25° the constants obtained by the static method agreed with those obtained by the dynamic method for the 100 and 90% methanol solutions, but slightly lower values were obtained in the more aqueous solvents. Since correction had been applied for the change in concentration because of evaporation and the change due to the change in mole fraction, the most likely cause of error was thought to be the solvolytic reaction; and so the temperature was reduced to 0°. At this temperature, pressures remained constant for long times. In the higher water solvents a pronounced cooling was noticed on the addition of the *t*-butyl chloride.

Plots of log $(p/N)_{BuCl}$ *vs.* volume per cent. of water in the solvent are practically straight lines for both sets of data. If the point for pure methanol at 0° is superimposed on the point for pure methanol at 25°, a rotation of about 3.5° makes the two curves coincide. This permits an easy and precise extrapolation of the 25° curve.

The steeper slope of log (p/N) *vs.* volume per cent. of water for the 0° data is consistent with the cooling mentioned above, for

$$\frac{\partial \log (p/N)_{BuCl}}{\partial T} = \frac{H^* - \bar{H}}{RT^2}$$

Since $H^* - \bar{H}$ decreases as the water content increases and since H^* is constant, $\bar{H}$ must increase.

The results are collected in the Table I.

TABLE I

Methanol, vol. %	log P/N	t, °C.	Methanol, vol. %	log P/N	t, °C.
100	3.350	25	100	2.634	0[a]
90.17	3.697	25	70.5	3.951[b]	0
80.09	4.043	25	60.5	4.292	0
70.45	4.390	25	49.5	4.723	0

[a] We are indebted to Mr. Hultgren of this Laboratory for making the measurements at 0°. [b] Probably several per cent. high. Neglected in drawing line.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND
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[1] This work was supported in part by the Office of Naval Research, United States Navy.

[2] A. R. Olson and R. Halford, This Journal, **59**, 2644 (1937).

[3] P. Bartlett, *ibid.*, **61**, 1630 (1939).

[4] S. Winstein, *ibid.*, **61**, 1635 (1939).

[5] R. Halford, Ph.D. thesis, University of California, Berkeley, 1938.