rates has been proposed by Swain and Dittmer,[17] *i.e.*

$$\log (k^{A}/k_0^{A}) - \log (k^{A_0}/k_0^{A_0}) = a_{A}b \quad (11)$$

where $a$ is a constant characteristic of compound A and $a = 0$ for the arbitrarily chosen standard compound $A_0$, $b$ is a constant characteristic of the solvent in which the specific rates are denoted by $k$ and $b = 0$ for the arbitrarily chosen standard solvent, 80% aqueous ethanol, in which the specific rates are denoted by $k_0$. Writing one such equation for *t*-butyl chloride and another for *t*-butyl bromide we obtain by difference

$$\log (k^{\mathrm{BuCl}}/k_0^{\mathrm{BuCl}}) - \log (k^{\mathrm{BuBr}}/k_0^{\mathrm{BuBr}}) = b(a_{\mathrm{BuCl}} - a_{\mathrm{BuBr}}) \quad (12)$$

The authors give $a$-values for *t*-butyl chloride and *t*-butyl bromide and $b$-values for 90% ($N_{\mathrm{W}} = 0.311$) and 80% ($N_{\mathrm{W}} = 0.505$) aqueous acetone which lie within the range of solvent composition that we have investigated for both compounds. Using the same $k_0$-values which Grunwald and Winstein used for 80% aqueous ethanol,[18] we obtain from our experimental data values for the left hand side of (12) equal to $-0.495$ and $-0.247$ for 90 and 80% aqueous acetone, respectively, to be compared with $-0.05$ and 0.00 as calculated from the Swain–Dittmer constants. Indeed, equation 11 cannot hold for both *t*-butyl chloride and *t*-butyl bromide when $b$ is a constant for a given solvent since, as we have already noted above, $k^{\mathrm{BuCl}}$ (or $k^{\mathrm{BuCl}}/k_0^{\mathrm{BuCl}}$) is about the same in pure ethanol as it is in aqueous acetone of $N_{\mathrm{W}} = 0.32$ whereas $k^{\mathrm{BuBr}}$ (or $k^{\mathrm{BuBr}}/k_0^{\mathrm{BuBr}}$) is about 80% greater in the latter solvent than it is in the former.

Solvolysis rates often depend very strongly on solvent composition. It is experimentally difficult and frequently too tedious for a researcher's purpose to reproduce mixed solvents with high accuracy. Thus in any correlation of such rates taken from different authors or from the same authors at different times, one may quite rightly expect to assign sizeable deviations to experimental errors. For example, where we have attempted to compare our work with results reported in the literature we have found that we must allow for discrepancies of 0.02 to 0.03 unit in $N_{\mathrm{W}}$ in aqueous acetone, whereas an error of 0.026 unit in $N_{\mathrm{W}}$ will produce in the specific rate of solvolysis of *t*-butyl chloride an error of a factor of 1.5.[19] This factor is the average deviation reported for the Swain–Dittmer correlation, and so one might conclude that the correlation fits a large amount of the data treated very nearly within the limits of experimental error. For this reason we point out that two so closely related compounds as *t*-butyl chloride and *t*-butyl bromide show real deviations which are outside the average deviation. Thus, some doubt is cast on the usefulness of the correlation as a basis for theory, but we do not wish to underestimate the value of such correlations in organizing large quantities of information for use in estimating orders of magnitudes of rates.

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[17] C. G. Swain and D. C. Dittmer, THIS JOURNAL, **75**, 4627 (1953).

[18] Data taken from E. D. Hughes, *J. Chem. Soc.*, 255 (1935); L. C. Bateman, K. A. Cooper, E. D. Hughes and C. K. Ingold, *ibid.*, 925 (1940).

[19] The value of reporting solvent compositions in terms of some easily measured rates is illustrated here.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF CALIFORNIA, BERKELEY]

# The Products of Solvolysis of *t*-Butyl Chloride in Aqueous Methanol Solutions[1,2]

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Methods of analyzing for isobutene, methyl *t*-butyl ether and *t*-butyl alcohol in aqueous methanol solutions are described. These methods are then used to determine the fractions of these substances that are produced in the solvolysis of *t*-butyl chloride in aqueous methanol solutions at several compositions and temperatures.

The products of solvolysis of *t*-butyl chloride in aqueous methanol solutions are methyl *t*-butyl ether, *t*-butyl alcohol and isobutene. The purpose of the work presented here has been to determine quantitatively the fractions of the several products at various solvent compositions.

Bateman, Hughes and Ingold[3] determined the ratio of methyl *t*-butyl ether to *t*-butyl alcohol by a fractional distillation method. We have determined these products by a distribution method. The distribution coefficients of methyl *t*-butyl ether and *t*-butyl alcohol between 20 weight per cent. methanol in water and carbon tetrachloride are sufficiently different so that an analysis of each layer for total concentration of *t*-butyl compounds enables one to calculate the proportion in which the two compounds are present. The analysis for *t*-butyl compounds was based on the quantitative precipitation of a complex containing one molecule of isobutene to seven atoms of mercury (in a mercuric salt) and subsequent volumetric determination of mercury in the precipitate. The analytical method was conceived and developed from previously published work.[4–7]

Determinations of the fraction of isobutene

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[1] This work was supported in part by the Office of Naval Research. United States Navy.

[2] This is the second in a series of papers dealing with the solvolysis of *t*-butyl compounds in aqueous organic solvents; see Cropper, Spieth and Olson, THIS JOURNAL, **76**, 6248 (1954).

[3] L. C. Bateman, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 884 (1938).

[4] G. Denigès, *Compt. rend.*, **126**, 1043, 1145, 1277 (1898); *Bull. soc. chim., Paris*, [3] **19**, 384 (1898).

[5] A. Newton and E. J. Buckler, *Ind. Eng. Chem., Anal. Ed.*, **12**, 251 (1940).

[6] A. Lindenberg, *Compt. rend. soc. biol.*, **125**, 135 (1937).

[7] E. M. Marks and D. Lipkin, *J. Org. Chem.*, **3**, 598 (1939).

formed from *t*-butyl chloride were complicated by the following, acid-catalyzed solvolysis of isobutene. Two methods were used for handling this difficulty; the choice of method depended on the relative rates of the two solvolytic reactions. Where isobutene solvolysis was slow compared to *t*-butyl chloride solvolysis, the *t*-butyl chloride reaction was permitted to proceed to completion; then the amount of olefin was determined as a function of time, and the fraction of olefin produced by the first reaction was found by an extrapolation method. Where acid-catalyzed isobutene solvolysis was comparable in rate to *t*-butyl chloride solvolysis, the fraction of isobutene was determined very early in the reaction before the acid concentration had built up appreciably to catalyze the isobutene reaction.

## Experimental Part and Calculations

**Preparation of Materials.**—The preparations of methanol and *t*-butyl chloride have been previously described.[2] Carbon tetrachloride was purified by washing once with concentrated $H_2SO_4$, twice with $NaHCO_3$ solution and once with water. After being dried over anhydrous $CaCl_2$, it was distilled in a 1.0 meter fractionating column. The fraction boiling at 76.2–76.3° at 753.0 mm. was used. The *t*-butyl alcohol was dried with anhydrous $Na_2CO_3$ and $K_2CO_3$ and then refluxed over freshly ignited CaO. The portion which distilled at 82.3° at 757.3 mm. pressure was collected. The alcohol melted at 25.32°. The methyl *t*-butyl ether was prepared by the method of Norris and Rigby.[8] It was twice refluxed over and distilled from sodium wire. The boiling point of the fraction used was 54.8° at 751.5 mm. Isobutene was prepared by the method of Hurd and Spence[9] by refluxing *t*-butyl alcohol over oxalic acid. The gas was dried by passing through a $CaCl_2$ tower and a $P_2O_5$ tower and then collected in a liquid air trap.

Deniges reagent was prepared from 50 g. of HgO, 200 ml. of concentrated $H_2SO_4$ and 1 liter of water according to Lindenberg's method.[6]

**The Analytical Method for *t*-Butyl Alcohol and Methyl *t*-Butyl Ether.**—The analysis for *t*-butyl alcohol and methyl *t*-butyl ether was developed for both $CCl_4$ and 20 weight % methanol–water solutions of these compounds. A weighed sample of either the alcohol or the ether in a sealed glass capsule was introduced into a 150-ml. glass bomb containing either 10 ml. of 20 weight per cent. methanol–water or 5 ml. of $CCl_4$ and a fourfold excess of Deniges reagent with an equal volume of water. The bomb was partially evacuated and sealed off, and then the capsule was broken by shaking. The bomb was placed in water at nearly 100° for 10 minutes. Then it was removed, wrapped in a towel to keep it hot, and placed on a mechanical shaker for 10 minutes. This alternate heating and shaking was repeated two or three times. The bomb was cooled in ice-water. The contents were filtered through a sintered glass crucible and washed with ice-water until the washings gave no test for mercuric ion with ammonium sulfide reagent. The crucible and precipitate were placed in a beaker, treated with 20 to 35 ml. of 70% $HNO_3$ and warmed gently. After solution was complete, the crucible was washed and removed, the mercurous ion was oxidized with nearly saturated $KMnO_4$ solution and the excess $KMnO_4$ was reduced with saturated $Na_2C_2O_4$ solution in ~0.8 *N* $H_2SO_4$. After being diluted to about 200 ml., the solution was titrated for mercuric ion with standard KSCN in the presence of ferric alum indicator. For 25- to 30-mg. samples of ether or alcohol, the amounts of *t*-butyl compound calculated from the analyses agreed with the weights of the samples introduced to ±1.8% in 8 experiments—the possible error in the weight of a sample was 1 to 2%.

**The Distribution Coefficients for *t*-Butyl Alcohol and Methyl *t*-Butyl Ether between $CCl_4$ and 20 Weight % Methanol in Water.**—A small amount of *t*-butyl alcohol or methyl *t*-butyl ether was added to a two-phase system consisting of equal volumes of $CCl_4$ and 20 weight % aqueous methanol in a 250-ml. flask. The mixture was shaken at 25°, and the layers were then permitted to separate. A definite volume of one layer (~5 ml. or ~10 ml.) was removed by air pressure into a stopcock pipet and run into a previously evacuated glass bomb; Deniges reagent and water were used to wash the pipet. The stem of the bomb was sealed off, and the above described procedure for precipitation and analysis was followed.

In two distribution experiments, the ratio, $D_B$, of the concentration of *t*-butyl alcohol in the aqueous methanol layer to the concentration of *t*-butyl alcohol in the $CCl_4$ layer was found to be 6.98 and 6.94—thus, $D_B$, the distribution coefficient for *t*-butyl alcohol was chosen to be 6.96. In two distribution experiments, the ratio, $D_E$, of the concentration of methyl *t*-butyl ether in the aqueous methanol layer to that in the $CCl_4$ layer was found to be 0.0548 and 0.0560—$D_E$, the distribution coefficient for the ether, was chosen to be 0.0554.

**Composition of Products from the Solvolysis of Isobutene.**—A slow stream of isobutene was passed into a flask containing an aqueous methanol solvent of known composition to which a small quantity of concentrated HCl had been added. When the solution was about saturated with isobutene at nearly atmospheric pressure, the flask was stoppered and placed in a 25.00° thermostat for about two weeks. A sample was then withdrawn and the concentration of unreacted olefin was determined by bromination with acidified standard bromide–bromate reagent and titration of the excess bromine iodometrically. Another sample of the reaction mixture was removed, diluted to 20 weight per cent. methanol, and shaken with a volume of $CCl_4$ equal to the volume of the diluted solution. The layers were analyzed according to the above procedure for finding the distribution coefficients. The product composition was calculated on the assumption that the $CCl_4$ layer contained all of the unreacted isobutene. The mole fraction of ether to ether plus alcohol, $R_E$, in the products is

$$F_E = \frac{(1 + D_E)\,[D_B(T_C - I_C) - T_A]}{(D_B - D_E)[T_A + (T_C - I_C)]} \qquad (1)$$

In this equation, $D_E$ and $D_B$ are the distribution coefficients defined above, $T_A$ is the concentration of *t*-butyl compounds in the aqueous methanol layer, $T_C$ is the concentration of *t*-butyl compounds in the $CCl_4$ layer, and $I_C$ is the concentration of isobutene in the $CCl_4$ layer. $I_C$ was calculated from the volume of reaction mixture used in the distribution experiment, the analysis for isobutene concentration in the reaction mixture, and the volume of $CCl_4$ used in the distribution experiment.

**Product Composition of Completely Solvolyzed *t*-Butyl Chloride.**—A 2.0-ml. sample of *t*-butyl chloride was diluted with an aqueous methanol solvent to 250 ml. in a volumetric flask and allowed to react at constant temperature until even the isobutene that was produced had completely solvolyzed.

A.—The product mixtures resulting at 25.0° were analyzed just as were those for isobutene solvolysis. No correction for isobutene concentration was necessary in the calculation; *i.e.*, the mole fraction of ether to ether plus alcohol in the products was given by

$$F_E = \frac{(1 + D_E)(D_B T_C - T_A)}{(D_B - D_E)(T_A + T_C)} \qquad (1')$$

B.—Product analysis experiments on the solvolysis at 20 and 30° were performed several years later with some procedural modifications. The distribution vessel consisted of two glass cylinders, each closed at the top with a ground glass stopper and connected at the bottom through a stopcock by a bridge of thick-walled capillary tubing. Preparation of the distribution mixture was carried out as described for the isobutene solvolysis except that the volume of the $CCl_4$ layer was always 50.0 ml. Its equilibration was conducted in the first cylinder of the distribution vessel with the stopcock closed and the capillary above it filled with mercury to prevent the $CCl_4$ from dissolving the stopcock grease. After equilibration the layers were separated by draining the $CCl_4$ into the second cylinder.

The vessel developed for the precipitation with Deniges reagent was a round bottom, short neck, 50-ml. Pyrex flask flanged at the mouth with a thick rim ground flat across the top. A sample from one of the layers was pipetted into the flask containing Deniges reagent; then 2 disks, cut from $^1/_{16}$ in. silicone rubber sheet, were placed over the

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[8] J. F. Norris and G. W. Rigby, THIS JOURNAL, **54**, 2088 (1932).

[9] C. D. Hurd and L. V. Spence, *ibid.*, **51**, 3561 (1929).

mouth of the flask and these were clamped into position to make an air tight seal by a square brass plate placed over them and screwed at the corners to 2 U-shaped brass plates which encircled the neck beneath the flange. The precipitation and titration procedures were those described above except that $FeSO_4$ was used to reduce the excess $KMnO_4$ prior to titration.

Unlike the condition in earlier experiments, the volume of the $CCl_4$ layer, $V_C$, was always somewhat different from the volume of the aqueous methanol layer, $V_A$, so that the mole fractions of ether to ether plus alcohol in the products were calculated from the equation

$$F_E = \frac{(D_E + V_C/V_A)(D_BT_C - T_A)}{(D_B - D_E)(T_A + T_CV_C/V_A)} \qquad (1'')$$

Each value of $F_E$ at 25° was obtained from a single distribution experiment, and each value at 20 and 30° was obtained from two to four distribution experiments. At least two analyses were performed on each layer and the precision of these analyses fell around ±1.3% whereas the poorest precision obtained was ±2.8%. Errors in the concentrations of *t*-butyl compounds in the separate layers introduce smaller errors, percentagewise, into $F_E$ so that the error in $F_E$ permitted by the sum of the average deviations found for the concentrations in the two layers lies at about ±1.3% with a maximum of ±2.5%.

**Fraction of Isobutene Formed during the Solvolysis of *t*-Butyl Chloride.**—For the determination of olefin formed during the solvolysis of *t*-butyl chloride, sample bulbs of the reactant in aqueous methanol like those described previously were used.[2]

Quantitative analysis for isobutene was performed by bromination in the presence of a known amount of bromine and titration of the excess bromine iodometrically. A sample bulb containing isobutene to be analyzed was introduced into a 500-ml. thick-walled erlenmeyer flask fitted with a ground glass stopper and containing a known amount of standard bromide–bromate reagent in approximately 300 ml. of ice-cold water. Then, about 25 ml. of approximately 6 *N* HCl was added to the solution, and the flask was immediately stoppered and returned to the ice-bath where the solutions were mixed by swirling. The production of bromine under these conditions is slow so that the solution was allowed to stand for 15 to 30 minutes after which time the bulb was shattered by shaking. Vigorous shaking was continued for one minute. (When rates were such that solvolytic reactions could not be considered quenched on introduction of the bulb into an iced solution, the bromine solution was made first and the bulb introduced quickly to avoid bromine loss.) The excess bromine was titrated in the usual manner. Preliminary experiments showed that methanol, *t*-butyl alcohol, methyl *t*-butyl ether and the Tygon caps did not interfere with the bromine titration result whereas *t*-butyl chloride reacted somewhat with bromine under these conditions. The *t*-butyl chloride interference was eliminated from estimations of isobutene in the presence of *t*-butyl chloride by an additional step in the procedure. After bromine production was complete, the flask was turned in an ice–salt-bath until the bromine solution became a mush of ice; then the bulb was shattered by shaking, and following 30 seconds of very vigorous shaking, the solution was immediately titrated.

**A.**—In solvents where the solvolysis of *t*-butyl chloride was rather fast compared to the acid-catalyzed solvolysis of isobutene, the olefin was measured as a function of time after the *t*-butyl chloride reaction was complete. Then, these data were treated by an extrapolation method to yield the fraction of olefin actually produced during the *t*-butyl chloride solvolysis. The extrapolation method was developed in the following manner.

For the reactions occurring in solution the rate laws

$$-\frac{d(\mathrm{BuCl})}{dt} = k(\mathrm{BuCl}) \text{ and,} \qquad (2)$$

$$\frac{d(\mathrm{O})}{dt} = k_\mathrm{O}(\mathrm{BuCl}) - k_s(\mathrm{O})(\mathrm{HCl}) \qquad (3)$$

can be written where (BuCl), (O) and (HCl) are the moles per liter of *t*-butyl chloride, olefin and hydrochloric acid, respectively, at time, *t*, $k$ = specific rate constant for the production of HCl from *t*-butyl chloride, $k_\mathrm{O}$ = specific rate constant for the production of olefin from *t*-butyl chloride, and $k_s$ = second-order specific rate constant for the solvolysis of isobutene. Two useful definitions are: $f'_\mathrm{O}$ = (O)/(HCl) = the fraction of olefin *existing* in the products of *t*-butyl chloride solvolysis; and, $f_\mathrm{O} = k_\mathrm{O}/k$ = the fraction of olefin *formed* by the solvolysis of *t*-butyl chloride. The notation can be simplified by writing $\alpha$ for the initial concentration of *t*-butyl chloride (or the final concentration of HCl) and $x$ for the concentration of *t*-butyl chloride so that $(\alpha - x)$ is the concentration of HCl at time, *t*.

By appropriate substitutions the two differential equations can be solved to yield an expression for the measured quantity, $f'_\mathrm{O}$, *i.e.*

$$\ln f'_\mathrm{O} = \ln f_\mathrm{O} + (\alpha k_s/k - 1)\ln \alpha - \ln(1 - e^{-kt}) - \frac{\alpha k_s e^{-kt}}{k} - \alpha k_s t + \ln\left[\frac{\alpha^{(1 - \alpha k_s/k)} - x^{(1 - \alpha k_s/k)}}{(1 - \alpha k_s/k)} + \left(\frac{k_s}{k}\right) \times \frac{\alpha^{(2 - \alpha k_s/k)} - x^{(2 - \alpha k_s/k)}}{(2 - \alpha k_s/k)} + \left(\frac{k_s}{k}\right)^2 \times \frac{\alpha^{(3 - \alpha k_s/k)} - x^{(3 - \alpha k_s/k)}}{2!\,(3 - \alpha k_s/k)} + \ldots\right] \qquad (4)$$

When the solvolysis of *t*-butyl chloride is complete, $x = 0, f'_\mathrm{O} = (\mathrm{O})/\alpha$, and $e^{-kt} = 0$, so that equation 4 becomes

$$\ln f'_\mathrm{O} = \ln f_\mathrm{O} + \ln\left[\frac{1}{(1 - \alpha k_s/k)} + \left(\frac{\alpha k_s}{k}\right) \times \frac{1}{(2 - \alpha k_s/k)} + \left(\frac{\alpha k_s}{k}\right)^2 \times \frac{1}{2!(3 - \alpha k_s/k)} + \ldots\right] - \alpha k_s t \qquad (5)$$

The series expressed in brackets is a constant for a given run, so that the first order disappearance of olefin in $\alpha M$ HCl is observed after the solvolysis of $\alpha M$ *t*-butyl chloride is complete. By extrapolation of this straight line, *i.e.*, ln (O)/$\alpha$ *vs.* *t*, back to zero time (*i.e.*, the time of mixing the *t*-butyl chloride solution), one obtains an intercept, $\ln f^*_\mathrm{O}$, which is expressed by the equation

$$\ln f^*_\mathrm{O} = \ln f_\mathrm{O} + \ln\left[\frac{1}{(1 - \alpha k_s/k)} + \left(\frac{\alpha k_s}{k}\right) \times \frac{1}{(2 - \alpha k_s/k)} + \left(\frac{\alpha k_s}{k}\right)^2 \times \frac{1}{2!(3 - \alpha k_s/k)} + \ldots\right] \qquad (6)$$

Values of $k_s$ were obtained from the slope of the plot, $\ln f'_\mathrm{O}$ *vs.* *t*, and values of $f^*_\mathrm{O}$ were obtained from the intercept. The series expressed in brackets always converged rapidly because $\alpha k_s/k$ was always considerably less than unity, so that values of $f_0$, the fraction of olefin actually formed during the solvolysis of *t*-butyl chloride, could readily be calculated from equation 6.

In each of the solvents at 30.0° where the extrapolation method was useful for determining the olefin fraction, 2 to 5 runs, consisting of 6 to 10 bulbs each, were made. The initial concentration of *t*-butyl chloride was varied from one run to the next through a range from 0.05 to 0.2 *M*. The precision of the several resulting values of $f_0$ for a given solvent fell around ±2.0% whereas the poorest precision was ±2.7%. A single run was made in each solvent at 24.8°.

B.—In solvents of lower water concentration ($N_w \leqq 0.25$), where the solvolysis of *t*-butyl chloride is comparable in rate to the acid-catalyzed solvolysis of isobutene, the concentration of isobutene was measured during the *t*-butyl chloride reaction. The solvolysis of isobutene is no longer first order with respect to HCl in solvents of low water concentration so that measurements of the olefin fraction during the course of the *t*-butyl chloride reaction could not be treated analytically by equation 4. Thus, in the absence of a complete kinetic investigation of isobutene solvolysis, it was necessary to measure the olefin fraction so early in the *t*-butyl chloride reaction that the HCl concentration had not built up appreciably to catalyze the olefin solvolysis. In these cases the fraction of olefin produced was given by the ratio of olefin to hydrochloric acid. For some runs, both the hydrochloric acid and the olefin were measured—for other runs, the hydrochloric acid concentration at a given time was calculated from the specific rate constants obtained by the equation of Cropper, Spieth and Olson.[2]

In each of the solvents, where olefin fractions were determined during *t*-butyl chloride solvolysis, 1 to 4 runs, comprising 7 to 18 individual analyses, were made. The initial concentration of *t*-butyl chloride was varied from one run to the next through a range from 0.1 to 0.2 *M*. The precision of the resulting $f_0$ values for a given solvent fell around ±1.5% whereas the poorest precision was ±2.9%.

C.—Olefin fractions in the products of basic solvolysis of *t*-butyl chloride were also determined. The base, by preventing the formation of acid, eliminated the solvolytic reaction of isobutene. To check that the base does not change the course of the *t*-butyl chloride reaction it is not enough merely to check the rate of *t*-butyl chloride solvolysis because, since the fraction of olefin formed in these solutions is always less than 0.2, a base-catalyzed olefin elimination which might affect the over-all rate by only 1% would change the olefin fraction by more than 5%.

Olefin fractions found in the products of solvolysis of *t*-butyl chloride in 0.05 *M* NaOH (and also in 0.15 *N* NaOH in solvents having $N_w \geqq 0.25$) agreed with those found in acid solutions. For each solvent of a given water–methanol composition 3 to 12 analyses were made and the precision fell around ±1.5% whereas the poorest precision found was ±2.7%.

A few experiments in 0.3 and 0.6 *M* NaOH indicated that, although olefin fractions are insensitive to small concentrations of base, they increase more rapidly than linearly with base concentration in more strongly basic solutions. Thus, in the absence of a complete kinetic and product composition study of the alkaline solvolysis of *t*-butyl chloride, the olefin analyses in dilute base can be considered only as confirmatory for the results in acid solution and cannot stand alone.

## Results

The results of the distribution experiments which yielded values of $F_E$, *i.e.*, the fraction: moles of methyl *t*-butyl ether to moles of ether plus moles of *t*-butyl alcohol, for the solvolysis of isobutene and the complete solvolysis of *t*-butyl chloride are collected in Table I.

TABLE I

THE FRACTION OF ETHER TO ETHER PLUS ALCOHOL IN THE PRODUCTS

| $N_W$ | Temp., °C. | $F_E$ Found | Calcd. | Δ, % |
|---|---|---|---|---|
| | | Isobutene | | |
| 0.489 | 25.0 | 0.473 | 0.445 | +6.3 |
| .364 | 25.0 | .580 | .565 | +2.6 |
| .206 | 25.0 | .813 | .741 | +9.7 |
| | | *t*-Butyl chloride | | |
| 0.463 | 20.0 | 0.453 | 0.464 | −2.4 |
| .354 | 20.0 | .574 | .576 | −0.4 |
| .250 | 20.0 | .690 | .691 | −0.1 |
| .156 | 20.0 | .810 | .801 | +1.1 |
| .486 | 25.0 | .445 | .441 | +0.9 |
| .359 | 25.0 | .566 | .571 | −0.9 |
| .197 | 25.0 | .765 | .752 | +1.7 |
| .443 | 30.0 | .496 | .484 | +2.5 |
| .354 | 30.0 | .578 | .576 | +0.4 |
| .250 | 30.0 | .687 | .691 | −0.6 |
| .156 | 30.0 | .804 | .801 | +0.4 |

Within the limits of experimental error, values of $F_E$ at 20, 25 and 30° for *t*-butyl chloride fall on the same smooth curve and may be expressed by the one parameter empirical equation

$$F_E = \frac{0.745N_A}{0.745N_A + N_W} \qquad (7)$$

The fourth column of Table I shows values of $F_E$ calculated from this equation. The last column shows the percentage deviations of the experimental from the calculated values.

The experimental values of $F_E$ obtained from isobutene solvolysis are everywhere higher than those calculated from the equation fitted to the *t*-butyl chloride data. Because of the correction for remaining isobutene which was necessary in the experiments on isobutene solvolysis, the results for this reaction are less reliable than those for the *t*-butyl chloride reaction, and it is not possible to decide whether this deviation is real.

If we designate by $F'_E$ the mole fraction of ether to ether plus alcohol produced directly during the solvolysis of *t*-butyl chloride, then $F_E$ found in the complete solvolysis of *t*-butyl chloride is the weighted average of $F'_E$ and $F_E$ found in the solvolysis of isobutene. Since the fraction of isobutene formed from *t*-butyl chloride is always less than 0.2, a 10% difference between $F'_E$ and $F_E$ from isobutene would cause less than 2% difference between $F'_E$ and $F_E$ from *t*-butyl chloride. Thus, equation 7 probably represents $F'_E$ to between one and two %. (Bateman, Hughes and Ingold[3] obtained values of $F'_E$ at 25° for mole fractions of water equal to 0.164, 0.284 and 0.490 which differ from our calculated values by +4.7, +4.0 and −9.4%, respectively. Since these authors' values of $F'_E$ are in qualitative agreement with ours, it is worthwhile to pursue their results for *t*-butyl chloride in aqueous ethanol to show that an equation of the form of 7 also applies to the ethyl *t*-butyl ether fractions for which the adjustable parameter is about 0.4.)

If the temperature coefficient of $F'_E$ actually is zero, then the heat of activation for the process in which methyl *t*-butyl ether is formed is equal to the heat of activation for the process in which *t*-butyl alcohol is formed. Although no trend in $F'_E$ between 20 and 30° is found from our data, certainly a 1% change in $F'_E$ between 20 and 30° could not be detected. Such a change, *i.e.*, 0.1% per degree, would correspond to a difference in heats of activation of about 900 cal. at $N_W = 0.156$ and about 300 cal. at $N_W = 0.486$.

Values of $f_0$, the fraction of the total rate that produced olefin during the solvolysis of *t*-butyl chloride in various methanol–water solvents, are collected in Table II. Values for the fraction of isobutene found in the products of basic (0.05 to 0.15 *M* NaOH) solvolysis of *t*-butyl chloride in solutions of various methanol–water compositions at 30.00° are collected in Table III.

TABLE II

THE FRACTION OF ISOBUTENE FORMED IN THE SOLVOLYSIS OF *t*-BUTYL CHLORIDE IN AQUEOUS METHANOL WHEN THE SOLUTION IS INITIALLY NEUTRAL

| $N_W$ | $f_0$ |  | Δ,% |
|---|---|---|---|
|  | Found | Calcd. |  |
|  | $t = 30.0°$ |  |  |
| 0.501[a] | 0.144 | 0.145 | −0.7 |
| .496[a] | .144 | .146 | −1.4 |
| .370[a] | .167 | .165 | +1.2 |
| .368[a] | .160 | .165 | −3.0 |
| .253 | .182 | .180 | +1.1 |
| .249 | .179 | .181 | −1.1 |
| .124 | .194 | .193 | +0.5 |
| .123 | .194 | .193 | +0.5 |
| .066 | 202 | .196 | +3.1 |
| .065 | .192 | .196 | −2.0 |
|  | $t = 24.80°$ |  |  |
| 0.501[a] | 0.135 | 0.135 | 0.0 |
| .368[a] | .156 | .153 | +2.0 |
| .249 | .167 | .168 | −0.6 |
| .124 | .182 | .179 | +1.7 |
| .123 | .178 | .179 | −0.6 |
| .065 | .182 | .182 | 0.0 |

[a] Results were obtained by the extrapolation method, whereas the other results were obtained from analyses made early in the *t*-butyl chloride solvolysis.

TABLE III

THE FRACTION OF ISOBUTENE FORMED IN THE BASIC SOLVOLYSIS OF *t*-BUTYL CHLORIDE IN AQUEOUS METHANOL AT 30.0°

| $N_W$ | $f_0$ |  | Δ, % |
|---|---|---|---|
|  | Found | Calcd. |  |
| 0.498 | 0.148 | 0.146 | +1.4 |
| .463 | .154 | .151 | +2.0 |
| .434 | .157 | .153 | +2.6 |
| .403 | .161 | .160 | +0.6 |
| .373 | .170 | .164 | +3.7 |
| .368 | .166 | .165 | +0.6 |
| .310 | .173 | .173 | 0.0 |
| .291 | .171 | .176 | −2.8 |
| .248 | .184 | .181 | +1.7 |
| .239 | .178 | .182 | −2.2 |
| .204 | .186 | ,186 | 0.0 |
| .136 | .194 | .192 | +1.0 |
| .086 | .194 | .195 | −0.5 |
| .079 | .198 | .195 | +1.5 |
| .065 | .195 | .196 | −0.5 |
| .060 | .195 | .196 | −0.5 |
| .054 | .195 | .196 | −0.5 |

These olefin fractions conform to the two parameter empirical equation

$$f_0 = \frac{f_0^0}{1 + 1.42N^2{}_W} \qquad (8)$$

where $f_0^0$, the value of $f_0$ in pure methanol, is 0.197 at 30.0° and 0.183 at 24.8°. The third columns of Tables II and III show values of $f_0$ calculated by equation 8. The fourth columns show the percentage deviations of the experimental values from the calculated; these deviations are of the order of the precision with which an experimental value was found (as described in the experimental section). Bateman, Hughes and Ingold[3] obtained values of $f_0$ at 25° for mole fractions of water equal to 0.284 and 0.490, which differ from our calculated values at 24.8° by −21 and −34%, respectively.

A differential equation relating the fractions, *f*, in which the several products, ether (E), *t*-butyl alcohol (B) and olefin (O), are formed to the average heats of activation, $\Delta H^\ddagger$, of the processes in which these products are formed is

$$\frac{RT^2}{(1 - f_0)}\left(\frac{\partial \ln f_0}{\partial T}\right)_{N_W} = \Delta H_0^\ddagger - \frac{f_E\Delta H_E^\ddagger + f_B\Delta H_B^\ddagger}{(1 - f_0)} \qquad (9)$$

The last term of 9 is the weighted average of the heats of activation for ether and alcohol formation and is equivalent to the expression, $F'_E\Delta H_E^\ddagger + (1 - F'_E)\Delta H_B^\ddagger$, which is independent of $f_0$. Because of the experimental constancy of $F'_E$ between 20 and 30°, these heats of activation can differ very little, say a maximum of 300 to 400 cal., from their weighted average, which is now designated by $\Delta H_{E,B}^\ddagger$. Equation 9 can be readily integrated and used to calculate the average difference between the heats of activation of the elimination and substitution reactions, *i.e.*, $\Delta H_0^\ddagger - \Delta H_{E,B}^\ddagger$, in the temperature range 24.8 to 30.0°.

For pure methanol, the calculated value of $\Delta H_0^\ddagger - \Delta H_E^\ddagger$ is 3140 cal., and the solution of equation 9 at $N_W = 0$ is $f_0^0 = 45.1e^{-3140/RT}/(1 + 45.1e^{-3140/RT})$, where 45.1 is the ratio of the frequency factor for the elimination rate to that for the methanol substitution rate. A 1% change in the choice of $f_0^0$ at one temperature would change $\Delta H_0^\ddagger - \Delta H_E^\ddagger$ by about ±400 calories, so that this difference cannot be considered to be determined to better than about 13%.

At $N_W = 0.5$, the calculated value of $\Delta H_0^\ddagger - \Delta H_{E,B}^\ddagger$ is 270 cal. less than that at $N_W = 0$. This small change is an artificial result inherent in the particular choice of empirical fit of the data. The best value of $\Delta H_0^\ddagger - \Delta H_{E,B}^\ddagger$ throughout the entire experimental range is 3000 ± 400 cal.

It is interesting that, if the decrease in $f_0$ between $N_W = 0$ and $N_W = 0.5$ at constant temperature is assigned to a change only in the heat of activation of the elimination reaction relative to that of the substitution reactions, an increase of only about 200 cal. in $\Delta H_0^\ddagger - \Delta H_{E,B}^\ddagger$ is required. Such an increase falls well inside the limits of experimental error, so that the gross behavior described by equation 8 cannot be separated into heat and probability effects.

The form of equation 8 was chosen as the simplest one which describes the change in $f_0$ in the experimental region from $N_W = 0$ to $N_W = 0.5$. Since $f_0$ changes by only about 25% throughout this region, one need not expect the form to be of significance. It was, therefore, interesting to find that in the products of solvolysis of *t*-butyl nitrate at 25.0° in aqueous dioxane as determined by Lucas and Hammett[10] the olefin fractions, which changed by more than a factor of 5 in the experimental region from $N_W = 0.620$ to $N_W = 0.205$, obey an equation of the same form, *i.e.*

$$f_0\,(t\text{-BuNO}_3\text{ in aq. diox. at }25°) = \frac{1}{1 + 26.9N_W^2} \quad (10)$$

Equation 10 is a one parameter equation since, in this solvent system, $f_0^0$, the fraction of olefin formed at $N_W = 0$, must be equal to unity.

In the solvent of composition $N_W = 0.765$, these authors measured olefin fractions at 0.3 and 10.0°. Solution of equation 10 at $N_W = 0.765$ (*i.e.*, outside the 25° experimental range) yields a value of $f_0$ which is compatible with the measurements at lower temperatures; that is, with increasing temperature the rate of the elimination reaction increases relative to that for the substitution reaction, and the increase is accounted for by a difference of about 2500 cal. in the heats of activation of the two reactions.

In their analyses for olefin in the presence of *t*-butyl nitrate, Lucas and Hammett had to correct for the amount of olefin produced during the very rapid hydrolysis of *t*-butyl nitrate in their aqueous analytical solution. They found that 2.99% of the *t*-butyl nitrate was converted to olefin under their experimental conditions, whereas equation 10 predicts 3.58% olefin formation in pure water at 25.0°. (The temperature of their analytical work was not given.)

Interpreted as a conventional concentration function, equation 10 means that the transition state for alcohol formation contains two more water molecules than the transition state for the elimination reaction. Such an interpretation then implies that in the methanol–water system there would be at least four analogous transition states leading to substitution, for every transition state en route to elimination, *i.e.*, one having two additional methanol molecules, one having two additional water molecules, and two others, each of which contained an additional methanol molecule and an additional water molecule. Thus, equation 8 would be an oversimplification.

The rates of solvolysis of *t*-butyl chloride in aqueous methanol which have been presented in a previous paper[2] and the product compositions as presented in this paper will be discussed in a later paper after further pertinent data have been presented.

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[10] G. R. Lucas and L. P. Hammett, THIS JOURNAL, **64**, 1928 (1942).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

# Reduction at the Streaming Mercury Electrode. I. The Limiting Current[1]

BY J. R. WEAVER AND R. W. PARRY

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Solutions of the diffusion problem applicable to steady state reduction at the streaming mercury electrode are presented, with special attention being given to the influence of stream contraction and expansion, and variable liquid velocity. Experimental methods are described for the photographic determination of stream diameter and solution flow. The surface velocity of the stream was calculated from measurements of the charging current. Verification of the theory is shown by experimental measurements of the reduction current for several ions.

The streaming mercury electrode has been used rather extensively in recent years as a substitute for the dropping electrode in certain forms of polarography.[2–6] For rate studies, the streaming electrode has several distinct advantages, chief of which is the higher overvoltage due to the greater current density. In addition, the effect of impurities is minimized by the rapid renewal of the mercury surface, the interfacial area is constant, and in the majority of cases there are no maxima. Disadvantages in its use are the large amount of mercury consumed, the difficulty of obtaining the actual length, radius and surface velocity of the stream, and the variation of the potential drop across the interface on different parts of the electrode caused by variation in the *IR* drop through the solution.

In this paper the results of measurements of the limiting steady-state current at the streaming electrode will be discussed with particular reference to the effects of variable radius and surface velocity. Current–voltage curves will be presented in subsequent papers.

## Theoretical

The fundamental equation for the limiting current at the streaming electrode was derived by Rius, Llopis and Polo[5] as

$$I_d = 4nFC\sqrt{\frac{mLD}{d}} \quad (1)$$

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[1] Abstracted in part from a dissertation submitted by J. R. Weaver to the Horace H. Rackham School of Graduate Studies of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] J. Heyrovsky, *Disc. Faraday Soc.*, **1**, 212 (1947).

[3] (a) A. Rius and J. Llopis, *Anales real soc. Epsan. fis. y quim.*, **42**, 617 (1946); (b) A. Ruis and M. J. Molera, *ibid.*, **43**, 1074 (1947).

[4] A. Rius, J. Llopis and S. Polo, *ibid.*, **45**, [B] 501 (1949).

[5] A. Rius, J. Llopis and S. Polo, *ibid.*, **45**, [B] 1039 (1949).

[6] J. W. Loveland and P. J. Elving, *J. Phys. Chem.*, **56**, 250 (1952).