ml.) was added and the solution was placed on crushed Dry Ice, whereupon some crystals were formed (75 mg.), m.p. 46–48°. This was subsequently shown to be 4-isopropyl-5-methyl-3-hexenyl *p*-nitrobenzoate (VII) (*vide infra*). The filtrate from these crystals yielded 2.3 g. (70%) of IIIa, b.p. 60–61° at 4 mm., n^{25}D 1.4516, infrared identical with an authentic sample. (2) **90% aqueous dioxane:** The ester (10.43 g., 0.0341 mole) in 250 ml. of solvent was maintained at 60° for 48 hours, then worked up as above. There was obtained 6.4 g. (63%) of VII, m.p. 46–48°.

Anal. Calcd. for $C_{17}H_{23}NO_4$: C, 66.86; H, 7.59; N, 4.58. Found: C, 66.91; H, 7.30; N, 4.49.

From the filtrate, 0.7 g. (13%) of IIIa was isolated. (3) **Absolute methanol:** A preliminary experiment showed that the theoretical PNBA titer was obtained from a solution which had been refluxed 12 hours. In an isolation experiment, 6.57 g. (0.0215 mole) of ester in 300 ml. of absolute methanol was refluxed for 12 hours, then worked up as usual. There was obtained 3.2 g. (81%) of ether, presumably 3-cyclopropyl-3-methoxy-2,4-dimethylpentane (IIIc), b.p. 56° at 4 mm., n^{25}D 1.4338, intense band at 8.93 μ (ether), none at 2.7–3.0 or 5.9–6.3 μ.

Anal. Calcd. for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 78.29; H, 13.03.

(4) **70% methanolic dioxane:** A preliminary experiment showed that after 16.25 hours at 60°, only 34% of the theoretical PNBA titer was obtained, and no additional acid was liberated after 37.5 hours. In an isolation experiment, 5.71 g. (0.0187 mole) of ester in 100 ml. of solvent was maintained at 60° for 36 hours, then worked up as usual. The petroleum ether extracts were concentrated to 50 ml. and cooled in Dry Ice. There was obtained 3.5 g. (61%) of VII, m.p. 46–48° and, from the filtrate, 0.7 g. (22%) of IIIc, infrared spectrum identical with that obtained from solvolysis in absolute methanol.

Structure Proof of 4-Isopropyl-5-methyl-3-hexenyl *p*-Nitrobenzoate (VII). (a) Reduction with Lithium Borohydride.—A solution of 8.0 g. (0.026 mole) of the ester in 50 ml. of tetrahydrofuran was added slowly (no noticeable heat evolved) to 2.2 g. (0.1 mole) of lithium borohydride in 100 ml. of tetrahydrofuran, and the mixture stirred at room temperature for 12 hours, cooled in an ice-bath, 300 ml. of water slowly added and the resulting mixture extracted with several portions of ether. The ether extracts, after drying (Drierite) and removal of the solvent *in vacuo*, left a residue which was taken up in a little petroleum ether and filtered, yielding 3.2 g. (81%) of *p*-nitrobenzyl alcohol, m.p. 91–93° (lit.[24] value 93°). The filtrate was distilled, from which was obtained 3.0 g. (74%) of presumably 4-isopropyl-5-methyl-3-hexenol, b.p. 83° at 5 mm., n^{25}D 1.4505 with infrared bands at 3.0 μ (broad, -OH) and 6.0 μ (weak).

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.91; H, 12.87.

(b) Oxidation of 4-Isopropyl-5-methyl-3-hexenol.—Oxidation of the lithium borohydride reduction product (1 g.) with neutral permanganate (4 g. in 100 ml. of water) at room temperature for four hours gave diisopropyl ketone (0.65 g.) identified by its infrared spectrum and vapor chromatogram.

Attempted Preparation of Tricyclopropylcarbinyl *p*-Nitrobenzoate (VIb).—Several attempts to prepare this ester from the lithium alcoholate and *p*-nitrobenzoyl chloride according to the general procedure which was successful for the other esters (*vide supra*) failed over a temperature range from −70° to refluxing pentane. Identifiable products were *p*-nitrobenzoic acid and its anhydride, unchanged alcohol, and a chlorine-containing liquid, b.p. 82° at 3 mm., n^{25}D 1.4998, shown to be 1,1-dicyclopropyl-4-chloro-1-butene (VIII). The infrared showed a carbon-carbon double bond (6.06 μ). The structure follows from the oxidation products.

Anal. Calcd. for $C_{10}H_{16}Cl$: C, 70.37; H, 8.86; Cl, 20.77. Found: C, 70.31; H, 8.90; Cl, 20.79.

Other attempts to prepare the desired ester from the potassium alcoholate and *p*-nitrobenzoyl chloride, from the lithium alcoholate and *p*-nitrobenzoic anhydride, and *via* the method of Brewster and Ciotti[21] all failed.[23]

Oxidation of VIII.—A mixture of 17 g. (0.1 mole) of VIII, 31.6 g. (0.2 mole) of potassium permanganate and 400 ml. of water was stirred for two hours at 0° and 28 hours at room temperature, then filtered and the filtrate extracted with five 70-ml. portions of ether. After drying (magnesium sulfate) and removal of the solvent, there remained 4 g. (40%) of dicyclopropyl ketone, b.p. 65° at 18 mm., infrared spectrum identical with an authentic sample.[18]

The aqueous solution (after ether extraction) was acidified (hydrochloric acid) and again extracted as above. From the residue there was isolated 3 g. (30%) of β-chloropropionic acid, m.p. 38–39° (lit.[25] value 39°). Its infrared spectrum was identical with that of an authentic sample.

Reaction of Tricyclopropylcarbinol (VIa) with Hydrochloric Acid.—To a test-tube containing 10 ml. of ice-cold concentrated hydrochloric acid there was added 5 g. (0.033 mole) of VIa and the mixture was shaken frequently for 30 minutes at 0°. The organic layer and ether extracts of the aqueous layer were combined, dried (potassium carbonate) and distilled, yielding 4.5 g. (80%) of VIII, identical with that obtained from the lithium alcoholate and *p*-nitrobenzoyl chloride.

Hydrolysis of 1,1-Dicyclopropyl-4-chloro-1-butene (VIII).—A mixture of 34 g. (0.2 mole) of VIII and 200 ml. of 10% aqueous potassium carbonate was refluxed with stirring for 24 hours. The organic layer and ether extracts of the aqueous layer were combined, dried (magnesium sulfate) and, after removal of the solvent, gave 27 g. (89%) of VIa, b.p. 71° at 4 mm., infrared spectrum identical with that of an authentic sample.

EAST LANSING, MICH.

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[24] I. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, London, 1953, Vol. 3, p. 645.

[25] Reference 24, Vol. 1, p. 556.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

Solvent Effects in the Solvolyses of Alkyl Bromides in Aqueous Ethanol[1]

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The rates of solvolysis of ethyl, isopropyl and *t*-butyl bromides have been determined at 25.10° in aqueous ethanol containing 24.1 and 1.00% by weight water. Distribution coefficients have been determined for the vapor–liquid equilibria of these same alkyl bromides in the same media at the same temperature. The results are discussed in terms of the Brönsted rate law. A significant fraction of the kinetic solvent effect observed for each alkyl bromide is due to the different activity of the alkyl bromide in the two media.

Introduction

The Brönsted rate law,[2] although fundamental to all chemical rate processes, has been applied only infrequently to organic reactions in spite of its relevance to investigations of kinetic medium effects. This paper is concerned with the application of the Brönsted rate law to the kinetic solvent effects observed in the solvolyses of ethyl, isopropyl and *t*-butyl bromides in aqueous ethanol.

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[1] Presented at the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April, 1958.

[2] J. N. Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

With respect to the rates of a reaction which takes place in two different solvents, the Brönsted rate law can be put into the form of equation 1,[3] where v represents the rate of reaction; a_A represents the activity, relative to a common standard state, of the substrate, A; the numerical subscripts identify the solvents; and F is a factor which includes the activity coefficients, relative to a common standard state, of the critical complex in the two media, and which may also include other terms, depending on the molecularity of the reaction.

$$(v)_1/(v)_2 = [(a_A)_1/(a_A)_2](F) \tag{1}$$

The form of equation 1 is the same for all reactions of first order in A, and, indeed, even for reactions which are composites of several simultaneous reactions of first order in A. In the simplest case of a unimolecular reaction of first order in A—*e.g.*, the solvolysis of an alkyl halide by an SN1 mechanism—F is defined by equation 2, where f^* represents the activity coefficient of the critical complex and the numerical subscripts identify the solvents.

$$F = (f^*)_2/(f^*)_1 \tag{2}$$

In the rather more complex case of two simultaneous bimolecular reactions involving A and two different reagents, B and C—*e.g.*, the solvolysis of an alkyl halide by an SN2 mechanism in aqueous ethanol—F is defined by equation 3.

$$F = [(a_B/f_B^*)_1 + K(a_C/f_C^*)_1]/[(a_B/f_B^*)_2 + K(a_C/f_C^*)_2] \tag{3}$$

In this equation, a_B and a_C represent the activities of B and C, respectively; f_B^* and f_C^* represent the activity coefficients of the critical complexes in reaction with B and C, respectively; K is a constant; and the numerical subscripts identify the solvents.

From equation 1 it can be seen that in any reaction the observed kinetic solvent effect, $(v)_1/(v)_2$, is actually a function of two variables; the activity ratio $(a_A)_1/(a_A)_2$ and the factor F. Of these two variables, only the F-factor is a function of properties which can be identified with the critical complex, for the activity ratio depends only on the ground states of the substrate in the two solvents. Thus, if the kinetic solvent effect is to be used to define mechanism, or to specify the nature of the critical complex, it is necessary to make a correction for the activity ratio, or to demonstrate that it can be ignored safely.

This limitation on the relationship between kinetic solvent effects and mechanism has been recognized, at least implicitly, for some time.[4,5] However, probably due to experimental difficulties in establishing substrate activities, it is customary to ignore this limitation in discussions of kinetic solvent effects[6] although the few existing data[5,7] indicate that the activity ratio of equation 1 may be large.

Results

For volatile organic compounds, it is convenient[5,7] to identify activity in solution with fugacity in the vapor which is in equilibrium with the solution. On the basis of the usual assumption that the vapor behaves as an ideal gas, equation 1 can be written as equation 4, where p_A represents the partial pressure of the substrate, A, above the solution.

$$(v)_1/(v)_2 = [(p_A)_1/(p_A)_2](F) \tag{4}$$

For this research, it is convenient to define a distribution coefficient, D, as the ratio of the equilibrium vapor density of the substrate in the vapor phase to its concentration in solution; *i.e.*, by equation 5, where n/V is the density in moles per liter of the substrate in the vapor phase, and C is its concentration in moles per kg. of solvent in the solution.

$$D = (n/V)(1/C) \tag{5}$$

When the rate of reaction is written as first order in substrate, and with the aid of the perfect gas law, equation 4 can be simplified to equation 6. In this equation, k represents the specific first-order or pseudo first-order rate constant for reaction; D represents the distribution coefficient for the substrate; and the numerical subscripts identify the solvents. Equation 6 is the form of the Brönsted rate law which is employed in this investigation.

$$k_1/k_2 = (D_1/D_2)(F) \tag{6}$$

The solvent effects studied in this investigation are those associated with the solvolyses of ethyl, isopropyl and *t*-butyl bromides at 25.10° in aqueous ethanol. Specific first-order rate constants were obtained for the development of acid from these bromides in solvents containing 24.1 and 1.00% by wt. water. The distribution coefficients necessary for analysis of the data by equation 6 were obtained by measurements of the vapor densities of the bromides over solutions in the same two solvents. The data obtained are recorded in Table I along with derived data and appropriate literature data on *n*-butyl bromide and *t*-butyl chloride.

In the media studied, the kinetic solvent effects (row 3, Table I) increase in the order, ethyl bromide < isopropyl bromide < *t*-butyl bromide, as expected.[8] The activity ratios (row 6, Table I) increase in the same order, but much more slowly; as a result, the F-factors (row 7, Table I) also increase in the same order.

Discussion

The purpose of this work was an evaluation of the contribution of varying substrate activity to the kinetic solvent effects observed in the reactions of simple organic compounds in common solvents. A comparison of the activity ratios (row 6) with the kinetic solvent effects (row 3) in Table I, shows that varying substrate activity accounts for a significant fraction of the kinetic solvent effect observed in each of the three systems studied. These data, together with existing literature data,[5,7]

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[3] See, for example, R. Livingston in A. Weissberger, "Technique of Organic Chemistry," Vol. VIII, Interscience Publishers, Inc., New York, N. Y., 1953, p. 15 ff.

[4] P. D. Bartlett, THIS JOURNAL, **61**, 1630 (1939); S. Winstein, *ibid.*, **61**, 1635 (1939); L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 174, 175; for a recent summary, see S. Winstein and A. H. Fainberg, *ibid.*, **79**, 5937 (1957).

[5] E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

[6] *E.g.*, C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 345 ff.

[7] (a) A. R. Olson and R. S. Halford, THIS JOURNAL, **59**, 2644 (1937); (b) M. L. Bird, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 255 (1943).

[8] S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951).

TABLE I

KINETIC, THERMODYNAMIC AND DERIVED DATA FOR ALKYL HALIDES IN AQUEOUS ETHANOL AT 25.10°[a]

	EtBr	*i*-PrBr	*t*-BuBr	*n*-Bu-Br[e]	*t*-Bu-Cl[f]
$k_{24.1\%}$[b]	3.94×10^{-8}	4.8×10^{-8}	3.66×10^{-4}		
$k_{1\%}$[b]	6.4×10^{-9}	4.7×10^{-9}	5.4×10^{-6}		
$k_{24.1\%}/k$	6.2	10.2	68	5.0	41
$D_{24.1\%}$[c]	0.0105	0.0060	0.0046		
$D_{1\%}$[c]	0.0047	0.0022	0.00131		
$D_{24.1\%}/D_{1\%}$	2.2	2.7	3.5	4.2	10
F[d]	2.8	3.8	19	1.2	4.1

[a] The variation in temperature is ±0.02°. 1% refers to a solvent containing 0.0100 ± 0.0002 g. water/g. solvent; 24.1%, to a solvent containing 0.241 ± 0.003 g. water/g. solvent. [b] Specific first-order rate constants for the production of acid; the units are sec.$^{-1}$. Each value is the average of at least three determinations with an average deviation of *ca.* ±2%. [c] Distribution coefficients for the distribution of the alkyl halide between the vapor and liquid phases; the units are moles/l. (in the vapor phase)/moles/kg. of solvent (in the liquid phase). Each value is the average of at least three determinations, the average deviation being *ca.* ±5% except for *t*-butyl bromide in the 24.1% solvent where it is ±20%. [d] The ratio of rows 3 and 6; see text. [e] Interpolated from data in ref. 7b; the temperature is 75.1°. [f] Interpolated from data in ref. 7a.

suggest that *the effect of medium upon substrate activity should not be ignored in any discussion of kinetic solvent effects.*

Unfortunately, there appears to be no structural regularity in the variation of substrate activity with medium. Ethyl bromide and *n*-butyl bromide, being primary alkyl bromides, might be expected to respond similarly to solvent changes; and, indeed, their kinetic solvent effects are similar. However, in the case of ethyl bromide, the kinetic solvent effect is composed of roughly equal contributions from the activity ratio and the *F*-factor, while in the case of *n*-butyl bromide, the kinetic solvent effect is virtually completely defined by the activity ratio. (Note, however, the different temperatures involved in the two cases.) At the other extreme of structure, *t*-butyl bromide and *t*-butyl chloride, being *t*-butyl halides, might be expected to respond similarly to solvent changes. Here, again, the kinetic solvent effects are similar, but with *t*-butyl bromide the major portion of the kinetic solvent effect is due to the *F*-factor, while with *t*-butyl chloride, the major portion of the kinetic solvent effect is due to the activity ratio.

The use of the Brönsted rate law permits the isolation of that part of the kinetic solvent effect, the activity ratio, which must be excluded from any discussion of kinetic solvent effect and mechanism. However, the remainder of the kinetic solvent effect, the *F*-factor, is simply related to properties of the critical complex only in the case of a unimolecular reaction, in which case it is defined by equation 2. It seems highly probable that the solvolysis of *t*-butyl bromide in aqueous ethanol is a unimolecular carbonium ion reaction. If so, the magnitude of the *F*-factor indicates that the critical complex is more stable in the solvent containing 24.1% by wt. water than in the solvent containing 1.00% by wt. water by a factor of *ca.* 19. No such simple analysis of the *F*-factors is possible with ethyl and isopropyl bromides, where the most probable definitions of the *F*-factors are, respectively, equation 3, and some linear combination of, or some expression intermediate between, equations 2 and 3.

Experimental

Materials.—The alkyl bromides were redistilled commercial products, and were free from impurities which could be detected by vapor-phase chromatography.

Solvents.—Solvent was prepared on a weight basis from redistilled commercial ethanol (benzene-free by ultraviolet analysis) and distilled water. Batches of solvent were prepared as needed for each kinetic run and for each vapor density determination. The final water concentrations were always checked by Karl Fischer titrations. The 1.00% water-in-ethanol solvent contained 0.0100 ± 0.0002 g. water/g. of solvent, and the 24.1% water-in-ethanol solvent, 0.241 ± 0.003 g. water/g. of solvent.

Kinetic Measurements.—For a kinetic run involving ethyl or isopropyl bromide, a weighed amount of the alkyl bromide was mixed with a weighed amount of solvent, and aliquots were sealed in glass ampoules which were immersed in the constant temperature bath. At appropriate time intervals, ampoules were removed from the bath, the contents (*ca.* 10 ml.) were transferred to serum bottles which contained 10 ml. of hexane and 20 ml. of water, the bottles were shaken vigorously to extract the organic bromide into the hexane layer, and the two-phase systems were titrated with standard sodium hydroxide to the brom thymol blue end-point. All analyses were on a weight basis. Because of the long half-lives of these reactions, they were followed only to *ca.* 4% reaction in the 1.00% water-in-ethanol solvent, and to *ca.* 10% reaction in the 24.1% water-in-ethanol solvent. Within each run, rate constants were calculated from the equation, $k = [\Delta(\mathrm{H}^+)/\Delta t][1/(\mathrm{RBr})]$, where $\Delta(\mathrm{H}^+)$ is the change in acid concentration over the time interval, Δt, and (RBr) is the concentration of alkyl bromide taken as the initial concentration of alkyl bromide minus the concentration of acid in the middle of the interval. The intervals $\Delta(\mathrm{H}^+)$ and Δt were read from a smooth curve drawn through the points of a large-scale plot of the acid concentration (corrected for the solvent blank) *vs.* time. The rate constant for each kinetic run was taken as the average of from six to twelve values calculated in this manner from successive, equal, intervals, $\Delta(\mathrm{H}^+)$, which in no instance exceeded 1% reaction. A typical kinetic analysis is reproduced in Table II.

TABLE II

THE SOLVOLYSIS OF ETHYL BROMIDE IN 24.1% BY WEIGHT AQUEOUS ETHANOL AT 25.10°[a]

Time, sec. $\times 10^{-5}$	Reaction, %	k,[b] sec.$^{-1} \times 10^8$
1.48	1.46	3.80
4.10	2.44	3.84
6.67	3.42	3.94
9.24	4.40	3.97
11.86	5.38	3.92
14.50	6.36	3.95
17.17	7.34	3.93
19.85	8.32	4.01
	Av.	3.92 ± 0.05

[a] The solvent contained 0.244 g. water/g. solvent, and the initial concentration of ethyl bromide was 0.1033 molal. [b] Specific first-order rate constant for the production of acid; calculated from the equation, $k = [\Delta(\mathrm{H}^+)/\Delta t][1/(\mathrm{EtBr.})]$, at successive intervals of 0.98% reaction; see Experimental.

For a kinetic run involving *t*-butyl bromide, a weighed amount of *t*-butyl bromide was added to a weighed amount of solvent contained in a stoppered flask and previously equilibrated in the constant temperature bath. The contents of the flask were mixed quickly, the flask was restored to the constant temperature bath, and aliquots of the solution were removed at appropriate time intervals for analysis of the acid generated in the reaction. For analysis, the aliquot was discharged into an excess of ice-cold acetone, and the resulting solution was titrated immediately to the lacmoid end-point with standard sodium hydroxide. The rate constant was calculated with the aid of the usual integrated form of the first-order rate equation, $\ln[(a)/(a - x)] = kt$, where a is the initial concentration of *t*-butyl bromide, x is the concentration of acid at any time, t, and k is the specific first-order rate constant. The value of k was taken as the slope of the best visual straight line defined by a plot of $\ln[(a)/(a-x)]$ *vs.* t. In the 24.1% water-in-ethanol solvent, where a check was made, the calculated and experimental infinity titers were identical within experimental error. In the 1.00% water-in-ethanol solvent, rates were followed to *ca.* 20% reaction, and in the 24.1% water-in-ethanol solvent, to *ca.* 75% reaction.

No test of the first-order nature of these solvolyses was considered necessary, and all solutions were approximately 0.100 molal in alkyl bromide. The averaged results of the kinetic investigations are given in Table I. All kinetic runs were made in triplicate on solutions involving different batches of solvent, so the uncertainties in the reported rate constants include the uncertainties involved in reproducing the compositions of the solvents.

Vapor Density Measurements and Distribution Coefficients.—With ethyl and isopropyl bromides, the apparatus for the vapor density measurements consisted of a stainless steel bomb and a stainless steel sampler of known volumes. The sampler was fitted at both ends with monel diaphragm valves and could be attached to the bomb or, alternatively, could be integrated into the flow system of a Fisher–Gulf Partitioner. In a vapor density determination, the evacuated sampler was attached to the bomb and an aliquot of a solution of the appropriate alkyl bromide in the appropriate solvent was injected into the bomb through a silicone rubber port. The apparatus was immersed in the constant temperature bath until temperature and vapor equilibria were established, and the valve between the sampler and the bomb was opened for a period of time sufficient for the re-establishment of vapor equilibrium. The valve then was closed, the apparatus was removed from the constant temperature bath, and the sampler was disengaged from the bomb and integrated into the flow system of the vapor-phase chromatography unit. The contents of the sampler were swept into the unit, and the area produced by the alkyl bromide in the resulting chromatogram was recorded. The vapor density corresponding to this area was read from a calibration curve of vapor density *vs.* area established by the same procedure in the same apparatus on the same day. Analyses for ethyl bromide were carried out at 35° on a 10-ft. column of 0.25-in. copper tubing packed with paraffin oil on firebrick. Analyses for isopropyl bromide were carried out at 65° on a composite column consisting of a 10-ft. length of 0.25-in. copper tubing packed with dimethylsulfolane on firebrick, connected in series with a similar piece of tubing packed with paraffin oil on firebrick. Helium was the eluting gas in all cases.

The vapor density measurements with *t*-butyl bromide were carried out in a glass apparatus. The sampler was fitted with a rubber port and was attached, *via* a large-bore stopcock, to a ground glass joint by which it could be joined to the bomb. The bomb was fitted with a rubber port and with a ground glass joint for connection to the sampler. In operation, the assembled apparatus, with the sampler evacuated and the stopcock closed, was immersed in the constant temperature bath. The sample solution was injected into the bomb through the rubber port, and the whole apparatus was rocked, gently, to aid the establishment of equilibrium between the vapor and the solution. After equilibrium was established, the stopcock was opened, and after the system again had reached equilibrium, it was closed. The sampler was then disengaged from the bomb, 10 ml. of water was injected into the sampler through the rubber port, and the sampler was shaken for a period of time ascertained to be sufficient for the complete hydrolysis of the *t*-butyl bromide. The contents of the sampler were then titrated to the phenolphthalein end-point with standard sodium hydroxide. The moles of base consumed was taken as equal to the moles of *t*-butyl bromide initially present in the sampler, and the vapor density was calculated from this value and the known volume of the sampler. With the 24.1% water-in-ethanol solvent, significant reaction occurred during the measurements. With this solvent, two vapor density measurements were made in succession, and the values obtained were extrapolated back to the time of mixing of the solution to give the approximate vapor density above the solution at 0% reaction. In these cases, no great precision was expected nor obtained; five values so obtained had an average deviation of ±20% from the mean.

All vapor density measurements were made on solutions which were approximately 0.100 molal in alkyl bromide. The distribution coefficients were calculated with the aid of equation 5 from the measured vapor densities and the known compositions of the solutions. The averaged values of the distribution coefficients are given in Table I. Each value represents the average of at least three determinations involving different batches of solvent; hence the uncertainties in the reported distribution coefficients include the uncertainties involved in reproducing the compositions of the solvents.

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CHICAGO 37, ILL.

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

The Solvolysis of *cis*-5-Cyclodecen-1-yl *p*-Toluenesulfonate in Acetic Acid and Ethanol

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Acetolysis of *cis*-5-cyclodecen-1-yl *p*-toluenesulfonate at 20° results in the formation of *ca.* 0.8 equivalent of *p*-toluenesulfonic acid by a clean first-order process. Ethanolysis gives about 0.9 equivalent of acid. The remainder of the *p*-toluenesulfonic acid is liberated at higher temperatures. Since the original *p*-toluenesulfonate was homogeneous this behavior shows that solvolysis is accompanied by rearrangement to a relatively unreactive product. The ratio of rearrangement to solvolysis is not affected by the presence of *p*-toluenesulfonate ion which indicates that the rearrangement is intramolecular. The rearrangement product from the acetolysis liberates *p*-toluenesulfonic acid at a measurable rate at 80°. The kinetic behavior of this material indicates that two rearrangement products (tosylates) are formed. The first-order rate of solvolysis of *cis*-5-cyclodecen-1-yl *p*-toluenesulfonate is larger than that of cyclodecyl *p*-toluenesulfonate by factors of seven for acetolysis and ten for ethanolysis. Rates of acetolysis of the four isomeric 1-decalyl *p*-toluenesulfonates are reported.

Introduction

Kinetic and product studies have shown that in several systems solvolysis involves participation by π-electron-containing substituents one or more carbon atoms removed from the reaction center. Such participation results in anchimeric acceleration[3] in the cholesteryl,[4] *anti*-7-norbornenyl,[5]

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[1] Carbide and Carbon Fellow 1955–1956; du Pont Summer Research Fellow, 1956.

[2] Wisconsin Alumni Research Foundation Fellow, 1956–1957.

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