Some Observations on the Conductometric Method for Determining Solvolytic Rate Constants

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A number of observations and criteria on the use of the conductometric method for determining solvolytic rate constants are described and illustrated with several substrates. The solvents systems examined are 60% (v/v) aqueous dioxane, 60% (v/v) aqueous acetone, acetic acid, and buffered acetic acid. In general, our experiences show that this method gives smaller variances (factor of 2–3) in rate constants determined from duplicate kinetic runs than those obtained from the titrimetric method.

The present study was undertaken as part of our investigation into the solvolyses of derivatives of certain strained ring systems and substituted 2-azulylethanols. Since only limited amounts of these compounds were available due to time and costs of synthesis, a procedure was needed for determining their solvolysis rates with good accuracy and precision in a number of solvent systems with various leaving groups and using only a few milligrams of substrate. To this end, it was felt that the conductometric method with appropriate modifications would meet these requirements.

Background of the Conductometric Method and Attended Errors.[2]—Logically, the determination of reaction rates by changes in conductance of the reaction solution should be applicable to any unimolecular or bimolecular solution process where conducting (nonconducting) species are produced or consumed from nonconducting (conducting) substrates (S_N1 and pseudo-first-order solvolyses) or different conducting species are produced compared to those consumed (most S_N2 reactions). The fact that the rates can be followed by continuous monitoring of a single solution of substrate makes the conductometric technique potentially more desirable than the more standard titrimetric methods requiring aliquot sampling; the total volume of solution required per run should be potentially smaller in the former method. The precision of results from the conductometric method should also be better than those expected from titrimetric data in terms of the specifications and significant figures for data read-out on "research grade," commercially available conductance bridges.

Conductivity measurements have been used in determination of the acidity or basicity of weak acids or bases[3a] and the rates of ionic reactions occurring in ionizing solvents such as water.[3b] Many examples of saponification, diazotization, esterification, and molecular rearrangement have been investigated in this way. Despite the success of the conductometric method in such cases, it has found only limited use in following the rates of first-order and pseudo-first-order solvolyses.

In calculating reaction rate constants from conductivity measurements, the approximation is usually made that the change in conductance is a linear function of the concentration. The error this introduces depends on the solvent, the electrolyte, and the concentration range over which measurements are made.[4] An error of only 0.2% using this conductivity–concentration approximation was reported in the hydrolysis of methyl *p*-toluenesulfonate.[5] In determining the rates of solvolysis of some arylmethyl tosylates in various dioxane–water mixtures (60, 70, and 79.5%), it was shown that conductance was proportional to concentration below about 10^{-4} *M;* duplicate runs agreed within 3% of the mean value.[6] Similarly, a linear correlation was found for the conductance of aqueous acetone or aqueous ethanol solutions below 10^{-3} *N* hydrochloric acid; an error of ±0.2% was obtained for triplicate determinations of the rates of solvolysis of some alkyl chlroides from 0 to 35° in both media.[7] The conductance parameters for hydrochloric acid and *p*-bromobenzenesulfonic acid in various 2,2,2-trifluoroethanol–water mixtures were reported to follow the limiting conductance law in the concentration range below 2×10^{-3} *M* for solvents containing 3% or more water. The precision in the determination of rate constants in these solvents was ±0.1%.[8]

Although work in the above polar solvents containing strong electrolytes has given good precision in the rate data, the results involving less polar solvents and/or weaker electroytes have been less satisfactory. In dimethylformamide at 30° errors of only ±1% were observed in the pseudo-first-order kinetics of certain bimolecular elimination reactions without the use of concentration–conductance corrections.[9] However, rate constants for the solvolyses of several arylmethyl chlorides in moist formic acid at 25° were considered to be accurate to ±5% even using concentration–conductance calibration curves.[10] The results reported for the unbuffered acetolyses of some alkyl nosylates showed that the errors averaged about ±6% for the conductometric rate constants without concentration–conductance correction compared to the results from titrimetric data.[11] Another report of unbuffered acetolyses gave ±3% errors in the conductometric rate constants compared to the rate constants obtained from titrimetric studies, but averages of rate

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(1) NASA Research Fellow, 1967–1968.

(2) The references included in this section are not intended to be a comprehensive review of the literature on the conductometric method. Rather, they are given to illustrate uses of the technique.

(3) (a) G. Kortum, "Treatise on Electrochemistry," Elsevier, Amsterdam, 1965, p 265; (b) R. Livingston, "Technique of Organic Chemistry," Vol. 8, A. Weissberger, Ed., Interscience, New York, N. Y., 1951, p 65.

(4) B. L. Murr and V. J. Shiner, *J. Amer. Chem. Soc.*, **84**, 4672 (1962).

(5) R. E. Robertson, *Can. J. Chem.*, **33**, 1536 (1955).

(6) M. D. Bentley and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **92**, 3991 (1970).

(7) W. M. Schubert and R. G. Minton, *ibid.*, **82**, 6188 (1960).

(8) (a) V. J. Shiner, W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, *ibid.*, **91**, 4838 (1969); (b) V. J. Shiner, R. D. Fisher, and W. Dowd, *ibid.*, **91**, 7748 (1969).

(9) W. M. Jones, T. G. Squires, and M. Lynn, *ibid.*, **89**, 318 (1967).

(10) M. J. S. Dewar and R. J. Sampson, *J. Chem. Soc.*, 2789 (1956).

(11) P. D. Bartlett and G. D. Sargent, *J. Amer. Chem. Soc.*, **87**, 1297 (1965).

constants from replicated run (2–12) by the conductoetric method agreed with those determined by other methods.[12]

It is interesting that, when good precision in rate constants is required in solvolysis studies, such as in the determination of secondary deuterium isotope effects, the conductometric method is the one most successfully utilized.[4,13]

Discussion of the Experimental Technique.[14]—The conductivity cell used throughout this investigation was the M-D Mini-Cell[15] owing to its small (3 ml) working volume and cell constant of about 0.075 cm^{-1}. The cell was connected to a Beckman RC-18A conductivity bridge with external capacitance supplied by a Heath Model EUW-29 capacitance substitution box. A 2:1 sulfuric–nitric acid mixture was used to clean the cell;[16] the use of chromic acid causes contamination and should be avoided.[17] The shiny platinum electrodes in the cell gave a system with good stability at reasonably elevated temperatures and were readily cleanable when the solvent system was changed. Conditioning of the cell to the solvent under study was imperative for precise results.

The solvents used in this investigation were generally distilled twice in all-glass apparatus under nitrogen, and all manipulations involving these solvents were then carried out in a glove box in a nitrogen atmosphere. This was critical since simply transferring a solvent from one container to another in the laboratory atmosphere would drastically increase the observed conductance of that solvent; carbon dioxide is a probable culprit. The purity of the solvents was ascertained from their specific conductance values which are given in Table I. Water showed the largest deviation from the literature value, but this difference was not large enough to interfere with the measured conductance readings during a run in a mixed solvent containing water.

TABLE I

SOME PHYSICAL PROPERTIES OF SOLVENTS AT 25°[a]

Solvent	L (obsd), mhos/cm	L (lit.), mhos/cm
Water	6.1×10^{-7}	5.8×10^{-8}
Acetone	5.5×10^{-8}	5.5×10^{-8}
Dioxane	$<10^{-10}$	5.0×10^{-15}
Acetic acid	5.9×10^{-9} [b]	1.1×10^{-8}
Acetic anhydride[c]		4.8×10^{-7}

[a] B. E. Conway, "Electrochemical Data," Elsevier, Amsterdam, 1952, p 12. [b] Measurement taken at 24.0°. Professor S. G. Smith (private communication) has found a similar result of 6.39 × 10^{-9} mhos/cm at 25°. [c] This solvent was never measured by itself, but only in acetic acid solution.

The stability of the cells and solvent systems at elevated temperatures was determined to see what range of temperatures could be used. Table II lists the solvents and the temperatures investigated. Unbuffered acetic acid has presented many problems to workers[11,12,18] who have used this solvent in conductometric rate studies at elevated temperatures.[19]

TABLE II

STABILITY OF SOLVENT SYSTEMS AT ELEVATED TEMPERATURES

Solvent	Temp, °C	Reading, mhos/cm	% drift/hr[a]
60% (v/v) aqueous acetone[b]	25.00	4.146×10^{-5}	0.00
	50.00	5.515×10^{-5}	0.05
	70.00	6.620×10^{-5}	0.67
	90.00	7.502×10^{-5}	2.59
Unbuffered acetic acid	25.00	5.9×10^{-9}	0.00
	50.00	2.86×10^{-8}	0.71
Buffered acetic acid[c]	25.00	5.77×10^{-7}	0.00
	50.00	1.223×10^{-6}	0.00
	75.00	3.667×10^{-6}	0.00
	90.00	4.302×10^{-6}	0.00
	95.00	4.872×10^{-6}	0.02

[a] Per cent change in reading per hour. [b] Contained 1.198 × 10^{-3} *M* 3,5-dinitrobenzoic acid. [c] Contained 1.227 × 10^{-3} *M* potassium acetate.

The purity of the compounds to be studied was as important as the purity of the solvents. Since there was no convenient method of detecting trace amounts of conducting impurities in substrate samples, the standard methods of purification and analysis had to be employed. Solid derivatives were recrystallized repeatedly after reaching a constant melting point. This procedure generally ensured sufficient purity of the compound for it to be used in a kinetic determination.

The use of conductivity measurements in the determination of first-order rate constants requires that the conductivity precisely measure the concentration of starting material and/or product formed in the reaction at any time. Murr and Shiner[4] used an Onsager-type equation to represent the data on the conductance of hydrochloric acid in their ethanol–water mixtures. They found that the most time consuming aspect of this technique was the independent determination of the conductance parameters. This was avoided in the present study by simply constructing a correlation curve of specific conductance (L) *vs.* concentration (c) of the conjugate acid of the leaving group from about 1 × 10^{-5} to 1 × 10^{-3} *M*. One curve had to be constructed for each change in solvent, leaving group, and temperature. Figure 1 gives some representative plots for *p*-nitrobenzoic acid in 60% (v/v) aqueous acetone and 60% (v/v) aqueous dioxane. The data produced smooth curves indicating considerable ion pairing of the electrolyte.[20] Similar curved lines were found for *p*-toluenesulfonic acid in unbuffered acetic acid, and 3,5-dinitrobenzoic acid in 60% aqueous acetone. These correlation curves were used directly to determine the concentration of acid which corresponded to each specific conductance obtained during a kinetic run.

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[12] H. A. Hammond and A. Streitwieser, *Anal. Chem.*, **41**, 2032 (1969).

[13] For example, see V. J. Shiner and R. D. Fisher, *J. Amer. Chem. Soc.*, **93**, 2553 (1971), and J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **93**, 2551 (1971), and references therein.

[14] B. L. Murr (Ph.D. Thesis, Indiana University, 1961) outlined the precautions and procedures necessary to obtain a precision of ±0.03% in conductometric rate constants in solvolysis studies with certain alkyl chlorides in aqueous ethanol at or near room temperature. These guidelines were very beneficial to the present study.

[15] Available from R-M Research Products, Inc., Manhattan, Kan.

[16] F. C. Mathers, *Chemist-Analyst*, **54** [13], 10 (1965).

[17] E. P. Laug, *Ind. Eng. Chem., Anal. Ed.*, **6**, 111 (1934).

[18] P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *J. Amer. Chem. Soc.*, **87**, 1288 (1965).

[19] The point at which the stability of a solvent system should no longer be considered adequate depends on several factors including the rate of the reaction at that temperature and the magnitude in the spread of the points observed during the course of the reaction. Generally, a solvent system was not considered useful if the per cent drift per hour exceeded 1%.

[20] R. M. Fouss and F. Accascina, "Electrolytic Conductance," Interscience, New York, N. Y., 1959.

TABLE III

EFFECT OF THE USE OF CORRELATION CURVES ON RATE CONSTANTS[a]

Compd	Registry no.	With correlation		Without correlation		Error,[d] %
		10^4k,[b] sec^{-1}	Av 10^4k,[c] sec^{-1}	10^4k,[b] sec^{-1}	Av 10^4k,[c] sec^{-1}	
		60% (v/v) Aqueous Dioxane, 25.0°				
α-(p-Tolyl)-γ-methylallyl p-nitrobenzoate	36740-13-3	8.481 ± 0.012		9.757 ± 0.047		
			8.512 ± 0.032		9.795 ± 0.038	15
		8.544 ± 0.010		9.833 ± 0.058		
		60% (v/v) Aqueous Acetone, 25.0°				
α-(p-Tolyl)-γ-methylallyl p-nitrobenzoate		16.25 ± 0.02		18.86 ± 0.09		
			16.28 ± 0.04		18.93 ± 0.07	17
		16.32 ± 0.02		18.99 ± 0.08		
		60% (v/v) Aqueous Acetone, 50.0°				
α-Methyl-γ-(p-tolyl)allyl 3,5-dinitrobenzoate	36740-14-4	7.560 ± 0.009		9.294 ± 0.073		
			7.512 ± 0.047		9.135 ± 0.159	21
		7.465 ± 0.010		8.976 ± 0.090		
		Unbuffered Acetic Acid, 49.8°				
exo-Bicyclo[2.2.1]hept-2-yl tosylate	959-42-2	4.405 ± 0.020		5.677 ± 0.020		
			4.402 ± 0.003		5.596 ± 0.082	27
		4.399 ± 0.018		5.514 ± 0.019		
		Buffered Acetic Acid, 50.0°				
exo-Bicyclo[2.2.1]hept-2-yl tosylate		4.573 ± 0.009		4.559 ± 0.010		
			4.565 ± 0.008		4.552 ± 0.007	0
		4.558 ± 0.006		4.545 ± 0.004		

[a] Reference 22. [b] Errors are standard deviations. [c] Errors are maximum deviations from the average. [d] Difference in av 10^4k's divided by av 10^4k with correlation.

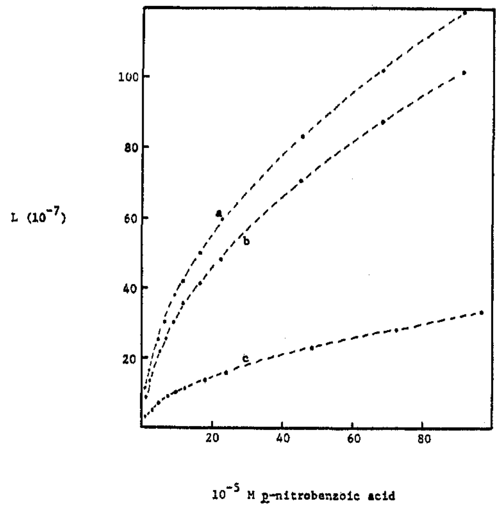

Figure 1.—Specific conductance of p-nitrobenzoic acid in (a) 60% (v/v) aqueous acetone at 35°, (b) 60% (v/v) aqueous acetone at 25.0°, and (c) 60% (v/v) aqueous dioxane at 25.0°.

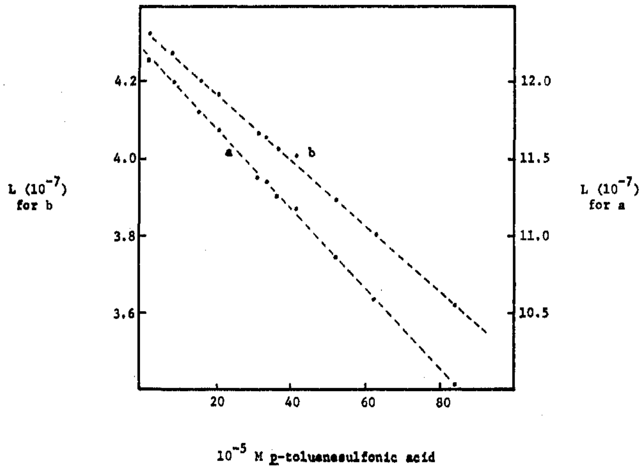

Figure 2.—Specific conductance of 6×10^3 M KOAc–HOAc with added p-toluenesulfonic acid at (a) 50.0° and (b) 25.0°.

Figure 2 shows the data for specific conductance vs. concentration of a potassium acetate–acetic acid solution with added increments of p-tolenensulfonic acid. No correlation curves were needed between 1×10^{-5} and 5×10^{-3} M acid in 6×10^{-3} M buffer since conductance was directly proportional to concentration under these conditions.

Table III lists the rate constants calculated with and without the use of concentration–conductance correlation curves for five compounds in four different solvent systems. As can be seen, the only solvent system which gave acceptable results without the use of a correlation curve was buffered acetic acid.

Discussion of Kinetic Data Obtained by the Conductometric Method.—In Table IV the results of pairs of kinetic runs determined conductometrically and titrimetrically on the substrate, but at different concentrations, are compared. The conductometric runs were prepared with 1×10^{-3} M substrate and the titrimetric runs with 5×10^{-3} M substrate. The runs in aqueous acetone and aqueous dioxane averaged about 1.5% higher than their corresponding titrimetric values. The single comparison in unbuffered acetic acid is not considered reliable since the titrimetric work was a single determination obtained several years ago prior to the use of the automatic titrator (see Experimental Section). The first three comparisons in buffered acetic acid gave an average difference of 0.5% with the conductometric rates generally being higher. These results are in agreement with the fact that the conductometric method generally gives higher rates than those observed titrimetrically.[4,7] The average per cent error for all except the last comparison

TABLE IV

COMPARISON OF CONDUCTOMETRIC AND TITRIMETRIC METHODS[a]

Compd	Registry no.	Temp, °C	Conductometric		Titrimetric		Error,[d] %
			10^4k,[b] $\sec^{-1}$	Av 10^4k,[c] $\sec^{-1}$	10^4k,[b] $\sec^{-1}$	Av 10^4k,[c] $\sec^{-1}$	
			60% (v/v) Aqueous Dioxane				
α-(*p*-Tolyl)-γ-methylallyl *p*-nitrobenzoate		25.0	8.481 ± 0.012 8.544 ± 0.010	8.512 ± 0.032	8.538 ± 0.102 8.280 ± 0.111	8.409 ± 0.129[f]	1.2
			60% (v/v) Aqueous Acetone				
α-(*p*-Tolyl)-γ-methylallyl *p*-nitrobenzoate		25.0	16.25 ± 0.02 16.32 ± 0.02	16.28 ± 0.04	16.60 ± 0.26 15.87 ± 0.24	16.24 ± 0.37	0.3
α-Methyl-γ-(*p*-tolyl)allyl 3,5-dinitrobenzoate		50.0	7.560 ± 0.009 7.465 ± 0.010	7.512 ± 0.047	7.338 ± 0.182 7.420 ± 0.201	7.379 ± 0.041	3.1
			Unbuffered Acetic Acid				
exo-Bicyclo[2.2.1]hept-2-yl tosylate		49.8	4.405 ± 0.020 4.399 ± 0.018	4.402 ± 0.003	4.494 ± 0.050[e]		−2.1
			Buffered Acetic Acid				
exo-Bicyclo[2.2.1]hept-2-yl tosylate		25.0	0.2325 ± 0.0009 0.2336 ± 0.0010	0.2330 ± 0.0006	0.2325 ± 0.0027 0.2305 ± 0.0030	0.2315 ± 0.0010	0.6
2-(1-Azulyl)ethyl tosylate–TNB complex	36740-15-5	35.0	1.926 ± 0.001 1.960 ± 0.001	1.943 ± 0.017	1.950 ± 0.020 1.915 ± 0.010	1.932 ± 0.018	0.5
exo-Bicyclo[2.2.1]hept-2-yl tosylate		50.0	4.559 ± 0.010 4.545 ± 0.004	4.552 ± 0.007	4.571 ± 0.075 4.554 ± 0.043	4.562 ± 0.008	−0.2
2-(3-Nitro-1-azulyl)ethyl tosylate	26154-61-0	90.0	0.9519 ± 0.0024 0.9510 ± 0.0014	0.9515 ± 0.0005	1.029 ± 0.010 1.019 ± 0.010	1.024 ± 0.005	−7.6

[a] Reference 22. [b] Rate constants given with their standard deviations. [c] Average rate constants given with the maximum deviation from average. [d] Per cent error based on the conductometric value being correct. Sign of number is positive when conductometric value is higher. [e] C. E. Reineke, Ph.D. Thesis, Kansas State University, 1966; a value of 4.67×10^{-4} $\sec^{-1}$ was reported in ref 27. [f] Reference 21.

in Table IV was 1.1% indicating that this method gives results in close agreement with those obtained by the titrimetric method.

The major discrepancy in Table IV is the results for 2-(3-nitro-1-azulyl)ethyl tosylate whose difference in the conductometric and titrimetric rate constants is −7.6%. The difference in the results between the two methods is believed due to the smaller concentrations of substrate and buffer used in the conductometric determinations compared to those used in the titrimetric method and has been attributed to the presence of a special salt effect by potassium acetate.[23] This is similar though smaller in magnitude to the special salt effect by potassium acetate in the buffered acetolysis of 2-(*p*-anisyl)ethyl tosylate.[23] The data listed in Table V lists the buffered acetolysis data on 2-(*p*-anisyl)ethyl tosylate which we believe readily establishes this effect.[24]

Generally, the precision in obtaining rate constants increases when the spread in the observed bridge readings is increased during a kinetic run.[22] In Table VI are listed the spreads in conductance readings observed in kinetic runs using *exo*-bicyclo[2.2.1]hept-2-yl tosylate. The precision found in the runs in unbuffered acetic acid with this substrate is unusually good when compared to the precision obtained with other compounds under similar conditions.

In addition to the compounds listed in Tables III–V, we have determined the solvolysis rate constants for several other substrates (Table VII) by this conductometric technique to demonstrate the overall applicability of the method. Only three pairs of runs on two different compounds had a negative sign for the direction of the drift after 10 solvolytic half-lives. It is interesting to note that two of these compounds, 2-(5-methyl-1-azulyl)ethyl and 2-(4-methyl-1-azulyl)ethyl tosylates, were comparatively unstable and difficult to work with even as their *sym*-trinitrobenzene complexes.[25,26] The remainder of the compounds were relatively stable and easily handled. The average drift for all determinations in this study was 0.8%. The higher temperature runs with 3-(4-azulyl)propyl nosylate probably indicate that we are close to the temperature limit of buffered acetic acid in the absence of better temperature control since they showed the largest per cent drift. It should also be noted

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(21) R. A. Sneen, *J. Amer. Chem. Soc.*, **82**, 4261 (1960), reports $k = 7.40 \times 10^{-4}$ $\sec^{-1}$ in 60 vol. % aqueous dioxane for α-(*p*-tolyl)-γ-methylallyl *p*-nitrobenzoate.

(22) All kinetic data in Tables III–VII are given to four significant figures even though in several cases the latter figures are statistically meaningless due to the errors involved.

(23) R. N. McDonald and J. R. Curtis, *J. Amer. Chem. Soc.*, **93**, 2530 (1971).

(24) Most electrolytes have a temperature coefficient of conductivity of about 2.5%/°C at around room temperature which increased with increasing temperature. The temperature effect on equilibria involving free ions and ion pairs and higher aggregates is difficult to approximate in unstudied systems. While a temperature control of ±0.01° was adequate for runs involving 1×10^{-3} *M* substrate, kinetic runs with 5×10^{-3} *M* substrate will require better bath temperature control to minimize errors at elevated temperatures.

(25) H. E. Petty, Ph.D. Thesis, Kansas State University, 1971.

(26) N. L. Wolfe, Ph.D. Thesis, Kansas State University, 1972.

TABLE V

BUFFERED ACETOLYSIS RATE DATA OF 2-(*p*-ANISYL)ETHYL TOSYLATE[a,b]

Substrate (buffer), 10^{-3} *M*	Temp, °C	10^4k,[c] sec^{-1}	Av 10^4k,[d] sec^{-1}	Error,[e] %
		1.361 ± 0.030[f]		
5.00 (6.00)	95.00 ± 0.08		1.412 ± 0.052	
		1.464 ± 0.060[f]		
		1.123 ± 0.002		
1.02 (1.23)	95.00 ± 0.01		1.134 ± 0.012	−24.3
		1.146 ± 0.003		
		1.360 ± 0.004		
4.94 (5.93)	95.00 ± 0.01		1.319 ± 0.041	−7.1
		1.278 ± 0.004		

[a] Registry no. 5107-52-8. [b] Reference 22. [c] Rate constants given with their standard deviations. Conductometric determinations unless otherwise specified. [d] Average rate constants given with the maximum deviation from the average. [e] Per cent error based on the titrimetric value being correct. The sign of the per cent error is negative when titrimetric value is higher. [f] Titrimetric determination.

TABLE VI

COMPARATIVE CONDUCTANCE ACETOLYSIS RATE DATA FOR *exo*-BICYCLO[2.2.1]HEPT-2-YL TOSYLATE[a]

Substrate, 10^{-3} *M*	Buffer, 10^{-3} *M*	Temp, °C	10^8L,[b] mhos/cm	$10^8\Delta L$, mhos/cm	Av 10^4k,[c] sec^{-1}	Precision,[d] %
1.06		49.84 ± 0.01	8.21–16.27	8.06	4.402 ± 0.003	0.07
1.00	1.15	25.00 ± 0.01	42.76–35.23	7.53	0.2330 ± 0.0006	0.26
1.00	1.15	50.00 ± 0.01	119.5–100.8	18.7	4.552 ± 0.007	0.15
4.94	5.93	50.00 ± 0.01	307.5–250.8	56.7	4.618 ± 0.004	0.09

[a] Reference 22. [b] Specific conductance range of kinetic runs. [c] Average rate constants from duplicate runs given with the maximum deviation from the average. [d] The error in the average rate constants (in *c*) expressed as per cent.

that specific conductance increased rather than decreased (see Table VI) during the course of the reaction with this nosylate ester.

The four sets of runs made with *p*-fluoro- and *p*-methylbenzyl tosylates in unbuffered acetic acid were carried out since these compounds appeared to be particularly problematical acetolyses.[12] However, as can be seen in Table VII, the data for these compounds are excellent with the present technique.

In summary, we have found that the conductometric method for the determination of solvolytic reaction rate constants yields more readily duplicable values by a factor of better than 2 than are obtained, on the average, by titrimetric methods with a smaller sample size of substrate required and a reduced problem with substrate solubility if the solvent and sample are pure. As the kineticist's experience increases with this technique so should the precision of the kinetic data.

In all of the work here described, rough, "thumbnail" rate constants were determined for "new" substrates in a selected solvent system by titrimetric determinations on one or two sealed ampoules to establish reasonable solvolytic temperatures. Solvent systems and leaving groups could then be varied to achieve the desired kinetic result.

Experimental Section

Substrate Preparation.—The following section gives the known substrates prepared by literature procedures from the corresponding alcohols: α-(*p*-tolyl)-γ-methylallyl OPNB, mp 42–44° (lit.[21] mp 44.5–46.5°); *exo*-bicyclo[2.2.1]hept-2-yl OTs, mp 54–55° (lit.[27] mp 53.7–54.6°); *p*-methylbenzyl OTs, mp 47–48° (lit.[28] mp 57.9–58.5°);[29] *p*-fluorobenzyl OTs, mp 42–42.5° (lit.[30] mp 48.5–52.5°);[29] and 2-(*p*-anisyl)ethyl OTs, mp 38.5–39.0° (lit.[31] mp 35.5–36.6°). The nmr spectra of these esters were in agreement with their assigned structures.

α-Methyl-γ-(*p*-tolyl)allyl 3,5-Dinitrobenzoate.—To a stirred, cooled solution of 300 mg (1.83 mmol) of α-methyl-γ-(*p*-tolyl)-allyl alcohol[21] in 3 ml of pyridine was added 428 mg (1.85 mmol) of 3,5-dinitrobenzoyl chloride (recrystallized from benzene) in small portions. After stirring for an additional 1.5 hr, the mixture was poured into ice–water, extracted with ether which was washed with saturated sodium bicarbonate solution and water, and then dried ($MgSO_4$). Evaporation of the solvent gave a yellow oil which crystallized from ether–hexane. Recrystallization from this solvent mixture gave 528 mg (80%) of the desired product as a white, waxy solid: mp 77.5–78.5°; ir (Nujol) 5.80 μ (C=O); nmr ($CDCl_3$, internal TMS) τ 0.78 (s, ODNB H's, 3), 2.71 (m, Ar H's, 4), 3.39 (m, vinyl H's, 2), 4.02 (m, methine, 1), 7.66 (s, tolyl CH_3, 3), and 8.38 (d, CH_3, 3).

Anal. Calcd for $C_{18}H_{16}N_2O_6$: C, 60.67; H, 4.53. Found: C, 60.70; H, 4.71.

***exo*- and *endo*-Bicyclo[2.2.0]hex-2-yl 3,5-Dinitrobenzoates.**—Using the above procedure, 50 mg (0.51 mmol) of a mixture of *exo*- and *endo*-bicyclo[2.2.0]hexan-2-ol (64:36) and 324 mg (1.53 mmol) of 3,5-dinitrobenzoyl chloride in 1 ml of dry pyridine yielded 111 mg (75%) of fine white needles of product after recrystallization from ether–pentane: mp 89–92°; ir (Nujol) 5.81 μ (C=O); nmr ($CDCl_3$, internal TMS) τ 0.87 (s, ODNB H's, 3), 4.49 (m, C_2 H's, 1), and 6.30–8.53 (m, 8).

Anal. Calcd for $C_{13}H_{12}N_2O_6$: C, 53.43; H, 4.14. Found: C, 53.31; H, 4.20.

Although we were unable to determine the exact composition of this mixture of derivatives due to the similarities of the C_2 H's chemical shifts of the exo and endo isomers, this is of little consequence kinetically since $k_{endo}/k_{exo} > 10^7$.[32] The rate constant was calculated using the infinity "titer" and was linear through 2 half-lives.

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[27] P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Amer. Chem. Soc.*, **87**, 375 (1965).

[28] J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3443 (1953).

[29] As was previously pointed out by Streitwieser, *et al.*,[30] melting points of these benzylic tosylates are difficult to reproduce and are not a good criterion of purity.

[30] A. Streitwieser, H. A. Hammond, R. H. Jagow, R. M. Williams, R. G. Jesaitis, C. J. Chang, and R. Wolf, *J. Amer. Chem. Soc.*, **92**, 5141 (1970).

[31] S. Winstein, C. R. Lindgren, H. Marshall, and L. L. Ingraham, *ibid.*, **75**, 147 (1953).

[32] R. N. McDonald and G. E. Davis, *ibid.*, **94**, 5078 (1972).

TABLE VII

OTHER COMPOUNDS SOLVOLYZED BY THE CONDUCTOMETRIC METHOD[a]

Compd	Registry no.	Temp, °C (±0.01°)	10^4k,[b] sec^{-1}	Av 10^4k,[c] sec^{-1}	Precision,[d] %	Drift,[e] %
		60% Aqueous Acetone				
endo-Bicyclo[2.2.0]hex-2-yl 3,5-dinitrobenzoate	36736-32-0	50.00	2.539 ± 0.015			
				2.524 ± 0.015	0.59	1.46
			2.509 ± 0.007			
		70.00	19.42 ± 0.08			
				19.52 ± 0.10	0.51	1.00
			19.62 ± 0.01			
		Unbuffered Acetic Acid				
p-Methylbenzyl tosylate	4606-98-8	49.84	24.80 ± 0.04			
			24.65 ± 0.04	24.70 ± 0.10[f]	0.40	1.57
			24.61 ± 0.06			
			24.74 ± 0.02			
p-Fluorobenzyl tosylate	3859-77-6	49.84	1.257 ± 0.008			
			1.260 ± 0.011	1.256 ± 0.006[g]	0.48	1.82
			1.258 ± 0.012			
			1.250 ± 0.012			
		Buffered Acetic Acid				
Mixture of 2-(5- and 2-(7-methyl-1-azulyl)ethyl tosylate–TNB complex	36740-18-8 (5-) 36826-33-2 (7-)	25.00	1.986 ± 0.005			
				2.020 ± 0.035	1.73	−1.35
			2.055 ± 0.005			
2-(4-Methyl-1-azulyl)ethyl tosylate–TNB complex	36740-19-9	25.00	1.100 ± 0.004			
				1.113 ± 0.013	0.92	−1.45
			1.126 ± 0.006			
		45.00	10.96 ± 0.01			
				10.94 ± 0.02	0.18	−0.20
			10.93 ± 0.01			
2-(6-Methyl-3-nitro-1-azulyl)ethyl tosylate	36740-20-2	70.00	0.2519 ± 0.0003			
				0.2512 ± 0.0007	0.28	0.60
			0.2505 ± 0.0004			
		90.00	1.888 ± 0.002			
				1.886 ± 0.002	0.11	0.35
			1.884 ± 0.004			
3-(4-Azulyl)propyl nosylate	36740-21-3	100.00	1.757 ± 0.007			
				1.725 ± 0.032	1.86	2.75
			1.693 ± 0.008			
		120.00	12.35 ± 0.06			
				12.54 ± 0.19	1.52	2.30
			12.73 ± 0.08			

[a] Reference 22. [b] Rate constants given with their standard deviations. [c] Average rate constants given with the maximum deviation from the average. [d] The error in the average rate constants expressed as per cent. [e] Observed drift expressed as a per cent of the infinity conductance. The sign is positive if the value proceeded in the same direction the points were changing during the run. [f] $k = 2.54 \times 10^{-3}$ sec^{-1}; ref 12. [g] $k = 1.23 \times 10^{-4}$ sec^{-1}; ref 12.

ω-(1-Azulyl)alkyl Tosylates.—The syntheses of these tosylates were carried out by standard procedures from the corresponding ω-(1-azulyl)alkanols[23,33] and will be reported in detail elsewhere. Each of these tosylate esters gave a satisfactory elemental analysis and the expected, characteristic nmr spectrum.

The inseparable mixture of 2-(5- and 2-(7-methyl-1-azulyl)-ethyl OTs was prepared by tosylation of the mixture of the corresponding ethanols obtained by β-hydroxyethylation of 5-methylazulene.[33] No deviation from linearity of the solvolysis rate was observed through 2 solvolytic half-lives which is the result expected from very similar methyl group effects at these two ring positions.

Titrimetric Method.—The rates for such solvolytic reactions were followed by potentiometric titrations of aliquots removed from sealed ampoules using a Metrohm E436D automatic titrator. In general, 12–15 points were determined through 2 solvolytic half-lives with two to three infinity ($10t_{1/2}$) points. Rate constants were calculated by a computer program RATSOL2 written in PL/I language for the IBM 360/50 computer by Professor K. Conrow, which gives essentially identical results as those from the LSKIN1 program,[34] and utilized experimental infinity titers.

Conductometric Method.—All of the rate measurements made using this method utilized a Beckman RC-18A conductivity bridge operating at 3000 Hz using shielded cables to connect the bridge to the M-D Mini-Cell;[15] added capacitance, when needed for low conducting solutions, was provided by a Heath EUW-29 capacitance substitution box. Bath control was ±0.01° using a bath oil.

All solvent handling, solution preparations, and cell loading were carried out in a nitrogen atmosphere glove box (dry conditions for nonaqueous solvents). The cell was rinsed five to eight times with the solvent to be used in the kinetic run and then two to three times with 2-ml portions of the substrate solution, filled, and sealed. (Filling and emptying of the cell were accomplished using a 12-in. flexible Teflon needle attached to a 5-ml all-glass syringe.) The cell was removed from the glove box, attached to the arm of the stirring apparatus, and lowered into the bath, and the stirrer was started. After allowing a few minutes for temperature equilibration, the first conductance reading was recorded as time zero. All further readings were made by setting the bridge at a value further along in the direction that the readings were changing and recording the time when the bridge was balanced with the conductance of the solution in the cell. In general, these bridge values were chosen to give 90–100 equally spaced points over the first 2 solvolytic half-lives. After this time, stirring was discontinued. To obtain the infinity point, stirring was begun 5 min before this point was to be taken.

To determine the amount of drift which occurred during a kinetic run, the cell was left in the constant temperature bath for a further convenient number of half-lives (2–4) and the conduc-

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(33) R. N. McDonald and H. E. Petty, *J. Org. Chem.*, **37**, 2957 (1972).

(34) D. F. DeTar and C. E. DeTar in "Computer Programs for Chemistry," Vol. I, D. F. DeTar, Ed., W. A. Benjamin, New York, N. Y., 1968.

tance reading recorded. By noting the direction of any drift and its magnitude, and assuming the drift to be constant throughout the run, the corrected infinity point was calculated. Rate constants were then calculated using the RATSOL2 computer program (see above). In several runs, we have plotted the concentrations of substrate from the computer output and found excellent first-order behavior over the 2 half-lifes examined.

Using the above procedure with the M-D Mini-Cell,[15] 30 ml of 10^{-3} *M* substrate solution is adequate to produce *duplicate* rate constants at *two* temperature and potentiometrically determined infinity titer checks at *both* temperatures.

Registry No.—Acetone, 67-64-1; acetic acid, 64-19-7; *p*-nitrobenzoic acid, 62-23-7; potassium acetate, 127-08-2; *exo*-bicyclo[2.2.0]hex-2-yl 3,5-dinitrobenzoate, 36740-22-4.

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Preparation of 3-(Hydroxymethyl)-4,4-dimethylpentanoic Acid γ-Lactone

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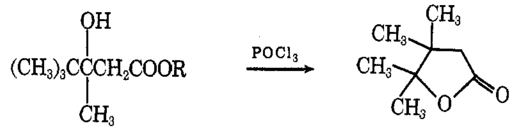
3-(Hydroxymethyl)-4,4-dimethylpentanoic acid γ-lactone can be prepared in 62% overall yield in four steps from ethyl 3-hydroxy-3,4,4-trimethylpentanoate. The latter was dehydrated to give a mixture of α,β- and β,γ-unsaturated esters which upon bromination with NBS yielded ethyl (*Z*)-3-(bromomethyl)-4,4-dimethyl-2-pentenoate. Thermal cyclization of the bromo ester produced 3-*tert*-butyl-2-buten-1,4-olide, which was hydrogenated to give the γ-lactone.

While preparing a number of conformationally biased compounds, 3-(hydroxymethyl)-4,4-dimethylpentanoic acid γ-lactone (**7**) was required as part of a synthetic scheme. It has been shown on several occasions[2a–c] that the material obtained from the dehydration of ethyl 3-hydroxy-3,4,4-trimethylpentanoate (**1c**) gives



1a, R = H
b, R = CH_3
c, R = C_2H_5

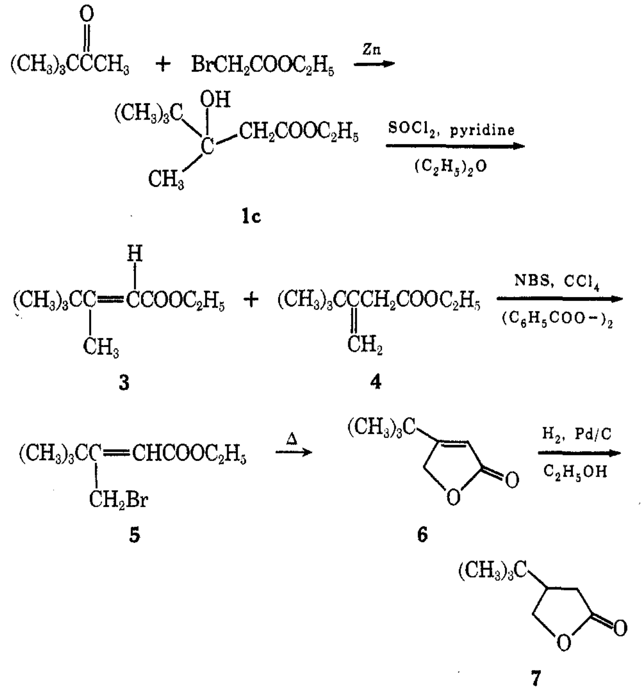
2

4-hydroxy-3,3,4-trimethylpentanoic acid γ-lactone (**2**) rather than **7** as originally thought.[2d] We have synthesized **7** in 62% yield from **1c** and now summarize our work.

The lactone **7** was prepared by the route shown in Scheme I. Using the procedure of Newman[2] and Heilman,[3] the hydroxy ester **1c** was dehydrated in good yield to give the two unsaturated esters **3** and **4** in equal amounts. After separation by preparative glc, ir, mass spectrum, and nmr analysis readily identified the compounds as **3** and **4**. This result agrees with the structural revision offered by Newman and Patrick[4] for the products which were obtained from the dehydration of **1b**.

The mixture of unsaturated esters **3** and **4** obtained by the dehydration of **1c** gave only **5** upon free-radical bromination using NBS. Compounds similar to **5** have been converted into 2-buten-1,4-olides by treating them with concentrated HCl under reflux.[5] Our preliminary studies indicated that the allylic bromide **5** could be converted into the unsaturated lactone **6** simply by heating for a few minutes at 220°. In addition, 80% of the theoretical amount of bromoethane was isolated, but the volatile distillate from the pyrolysis reaction (see Experimental Section) fumed when exposed to the air, undoubtedly because of the HBr present. Ethene was not looked for in this reaction but presumably was also formed.

Scheme I



The bromo ester **5** was assigned the *Z* configuration. The structural assignment is by no means definitive, since it is possible that the conditions of the thermal reaction or the HBr produced could cause isomerization from (*E*)-**5** to (*Z*)-**5** before ring closure.

The thermal reaction then provided an excellent route to **5** and subsequently to **6**. The lactone **7** was finally obtained by low-pressure hydrogenation of **6**.

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[1] NSF Undergraduate Research Participant.

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