KINETIC STUDIES ON THE SOLVOLYSIS OF CYCLOALKYLCARBINYL TOSYLATES

By

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A THESIS

Submitted in partial fulfillment of the requirements for the
degree of Master of Science in Chemistry in the
Department of Chemistry in the Graduate
School of the University of Alabama

UNIVERSITY, ALABAMA

1965

ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr. Robert H. Garner for his sincere and dedicated guidance during the course of this study.

The author is grateful to Dr. Robert D. Brown and to the Department of Chemistry for a teaching assistantship during the course of this study.

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CHAPTER I

INTRODUCTION

A solvolysis reaction may be considered as a nucleophilic substitution or elimination reaction in which the attacking nucleophile is the solvent. As a result of the work of Hughes, Ingold, and co-workers nucleophilic substitution reactions are generally discussed in terms of the two distinctly different mechanistic paths designated by the well-known symbols S_N1 and S_N2.[1,2] However, despite the usefulness of the Hughes and Ingold concepts, it has become progressively clearer that these reaction paths strictly apply only to extreme cases, and that most compounds solvolyze by some intermediate mechanism.

Many ideas have been presented recently as to the type of mechanisms involved in solvolysis reactions. Prominent among these postulations is the idea of a "push-pull"

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[1] J. E. Gleave, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 236 (1935).

[2] E. D. Hughes and C. K. Ingold, *Ibid.*, 244 (1935).

mechanism, which assigns both a nucleophilic, or "bond-making," and an electrophilic, or "bond-breaking," role to the solvent, and allows the relative importance of each role to vary widely from case to case.[3] As a result solvolysis reactions may be considered termolecular or even polymolecular.

Attempts have been made to correlate the rates of solvolysis of a compound to the mechanism of solvolysis and to the sensitivity of the compound toward the nucleophilicity and ionizing power of the solvent. Winstein, Grunwald, and co-workers[4,5,6] have attempted to correlate rates of solvolyses in terms of solvent ionizing power, Y, and nucleophilicity, N, by the following equation:

$$d \log k = \left(\frac{\partial \log k}{\partial Y} \right)_N dY + \left(\frac{\partial \log k}{\partial N} \right)_Y dN. \qquad (1)$$

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[3] C. G. Swain and W. P. Lansdorf, J. Am. Chem. Soc., 73, 2813 (1951).

[4] Ernest Grunwald and S. Winstein, Ibid., 70, 846 (1948).

[5] S. Winstein, Ernest Grunwald, and H. Walter Jones, Ibid., 73, 2700 (1951).

[6] S. Winstein and Henry Marshall, Ibid., 74, 1120 (1952).

In the case of solvents of approximately equal nucleophilicity, such as ethanol and water, the second term approaches zero, and in such cases equation 1 is reduced to

$$\left(\frac{\partial \log k}{\partial Y}\right)_N = m \qquad (2)$$

where m is the slope of the line formed by plotting log k versus Y. As thus defined m is a measure of the susceptibility of the substrate to the ionizing power of the solvent. In order to establish points of reference for quantitative comparisons, 80% aqueous ethanol was selected as a standard solvent with a Y value of 0.00, and reactions of *tert*-butyl chloride were assigned m values of 1.00. A simple interpretation of m values calculated from the Winstein-Grunwald correlation emphasizes the possible relative importance of the three contributing resonance structures, I, II, and III, in the transition state of the solvolysis reaction.[7] Structure III makes

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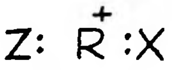
[7] Winstein, Grunwald, and Jones, *loc. cit.*

$Z\colon\ R-X$ I

$Z-R\ :X$ II



$Z\colon\ \overset{+}{R}\ :X$ III

relatively large contributions to systems which easily accommodate a positive charge. In such systems the value of $\left(\frac{\partial \log k}{\partial Y}\right)_N$ is large (hence, m is large), and the value of $\left(\frac{\partial \log k}{\partial N}\right)_Y$ is small. Winstein defines systems for which $\left(\frac{\partial \log k}{\partial N}\right)_Y = 0$ as "limiting;" that is, systems which react by a pure S_N1 mechanism. Conversely, reactions of systems for which $\left(\frac{\partial \log k}{\partial N}\right)_Y$ is very large would approach a pure S_N2 solvolysis. Any value between these extremes would suggest some sort of intermediate mechanism.

It should be noted, however, that this correlation has its limitations. Different m values for the same compound are obtained with solvent systems other than ethanol-water. Probably the fundamental difficulty is that different solvent systems cannot be assigned equal nucleophilicities with a high degree of certainty. An expedient which leads to better correlations, but reduces the utility of the Winstein-Grunwald correlation, is to assign each substrate a different m value for each type of solvent system.[8]

In an attempt to develop a correlation which would not show deviations in different solvent systems Swain, Mosely, and Bown proposed a four-parameter equation

$$\log k/k_o = c_1d_1 + c_2d_2 \qquad (3)$$

where k is the rate constant of the compound in any solvent, k_o is the corresponding rate constant in a standard solvent, 80% ethanol, c_1 and c_2 are the measures of the sensitivity of the substrate to nucleophilic character and ionizing power, respectively, of the solvent, and d_1 and d_2 are measures of the nucleophilic and electrophilic character, respectively, of the solvent. It would seem that since four variables are taken into account as compared to two in the Winstein equation, better agreement with experimental results would be obtained. The difficulty of this correlation lies in the selection of points of reference for the variables. Because of the convention of setting $c_1 = c_2 = 1.00$ for tert-butyl chloride, most of the c values have

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[8] Winstein, Fainberg, and Grunwald, Ibid., 79, 1597 (1957).

no significance. For example, this equation shows that methyl bromide is less sensitive to nucleophilicity of the solvent than _tert_-butyl chloride.[9]

Many primary carbinyl systems have been studied in solvolysis reactions. Winstein and co-workers studied the solvolysis rates of a series of primary _p_-toluenesulfonates including methyl, ethyl, isobutyl, and neopentyl.[10] They suggested that changes in reactivity as solvent composition changes from ethanol to acetic acid to formic acid provide a basis for differentiating the driving forces of the solvolysis reaction. In absolute ethanol the relative reactivities of the _p_-toluenesulfonates are 4000:1750:80:1 for the above sequence. For the same sequence of compounds the relative reactivities are 10:9:2.8:1 in acetic acid and 0.56:1.0:1.22:1.0 in formic acid. Winstein explained this increase in the relative reactivity of isobutyl tosylate in terms of the β-methyl and/or β-hydrogen substituents providing rate enhancement as the solvent conditions change toward those favoring the limiting (S_N1) type of solvolysis.

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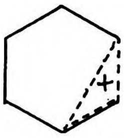
[9] Andrew Stritwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Company, Inc., New York, 1962, p. 65.

[10] Winstein, Grunwald, and Jones, _loc. cit_.

This same phenomenum is also noted in the case of neopentyl tosylate despite its large steric hindrance to back-side attack of the solvent. In this case assistance must be provided by β-methyl groups.

Bartlett and co-workers[11] have recently studied the solvolysis of cyclopentylcarbinyl p-nitrobenzenesulfonate and observed an accelerated solvolysis rate in acetic acid. The products of the acetolysis were largely cyclohexene and cyclohexyl acetate, which would result from rearrangement. The formation of these products indicates a large degree of anchimeric assistance by a β-carbon substituent. Bartlett discussed the possible role of an ion-pair intermediate involving the unsymmetrical bridged-ion represented by structure IV. It is interesting to note in this connection that the product ratio observed in this experiment is different from that resulting from the acetolysis of cyclohexyl p-nitrobenzenesulfonate. Thus it appears that the solvolysis



IV

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[11] Paul D. Bartlett, William D. Closson, and Thomas J. Cogdell, J. Am. Chem. Soc., 87, 1308 (1965).

of the cyclopentylcarbinyl compound does not proceed through a "free" cyclohexylcarbonium ion.

Le Ny[12] studied the products of the acetolysis of the p-bromobenzenesulfonates of isobutyl alcohol, cyclopentylcarbinol, and cyclohexylcarbinol. It was found that the isobutyl compound gave 32% of a primary acetate and 32% of the tertiary acetate. For the cyclopentyl compound the reaction gave 71% cyclohexene, 15% cyclohexyl acetate, and 9% of the cyclopentylcarbinyl acetate. For the cyclohexylcarbinyl compound 50% of the product was the cyclohexylcarbinyl acetate, and there was no trace of the cycloheptylacetate or cycloheptene. Le Ny concluded that the cyclopentylcarbinyl system went through a concerted mechanism involving a bridged-ion intermediate.

Since cyclopentylcarbinyl and cyclohexylcarbinyl derivatives appear to be capable of markedly different behavior in solvolysis reactions, it seemed reasonable to subject these systems to an investigation of their relative sensitivities to solvent properties. The experiments described in this thesis attempt to provide such data.

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[12] G. Le Ny, Compt. Rend., 250, 368 (1960).

CHAPTER II

EXPERIMENTAL

Preparation of Cyclopentylcarbinol.--Cyclopentylcarbinol was prepared according to the method described for the preparation of cyclohexylcarbinol by Gilman and Catlin.[1] A three-liter, three-necked, round-bottomed flask was charged with 67 g. (2.7 moles) of magnesium turnings and fitted with a stirrer, a 500 ml. dropping funnel, and a reflux condenser protected with a calcium chloride tube at the top. A mixture of 100 ml. of anhydrous ether, 15 ml. of bromocyclopentane (Eastman), and a small iodine crystal was added to the flask. This mixture was heated until refluxing occurred and continued for ten minutes, after which an additional 750 ml. of anhydrous ether was added. Stirring was then initiated, and an ice bath was placed beneath the flask to control the rate of reaction.

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[1] Henry Gilman and W. E. Catlin, "Organic Syntheses," Collective Volume I, Revised Edition, John Wiley and Sons, Inc., New York, N. Y., 1958, p. 188.

An additional 257 ml. of bromocyclopentane was added dropwise to the flask over a period of two hours. A total of 373 g. (2.5 moles) of bromocyclopentane was used. The mixture was allowed to stand for an additional ten minutes until all the bubbling had subsided.

The separatory funnel was replaced by a 12-mm. glass tube which extended to about one inch above the solution. This tube was connected to a 500-ml. round-bottomed flask containing 95 g. of paraformaldehyde (equivalent to 3.2 moles of formaldehyde) which had been dried in a desiccator over phosphorus pentoxide. This flask was fitted with an inlet tube for nitrogen gas and a thermometer. The stirring was resumed, and a slow stream of nitrogen gas was admitted in order to carry the depolymerized formaldehyde into the reaction system. The paraformaldehyde was slowly heated over a period of 2 1/2 hours to a maximum temperature of 125°. The tube was insulated to keep the formaldehyde from repolymerizing. Refluxing became vigorous, and an ice bath was again used to control the reaction rate.

After all the paraformaldehyde was depolymerized, cracked ice was added to the reaction mixture until all reaction ceased. Twice the theoretical amount (0.5 mole) of

30% sulfuric acid solution was added. The solution was steam distilled until the distillate contained no oily layer. The distillate was saturated with sodium chloride, and the alcohol-ether layer was removed. The water layer was then extracted with two 100-ml. portions of ether, which were added to the ether-alcohol mixture. The alcohol solution was dried with potassium carbonate, filtered, and the ether removed under reduced pressure using a rotary evaporator. Vacuum distillation of the residue yielded 178 g. (71.2%) of cyclopentylcarbinol, b.p. 81-83° (24 mm.), n_D^{25} = 1.4556; literature, b.p. 58-59 (14-15 mm.), n_D^{20} = 1.4579.[2]

Preparation of Cyclohexylcarbinyl Tosylate.--Cyclohexylcarbinyl tosylate was prepared according to a procedure similar to those of Winstein[3] and Tipson.[4] To 90 ml. of pyridine, which was dried and distilled over anhydrous barium oxide, 22.8 g. (0.2 mole) of cyclohexylcarbinol (Aldrich) was added. The solution was cooled in an ice

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[2] R. Ya. Levina and N. N. Mezentsova, Org. Khim., 7, 241 (1950); Chem. Abstr., 49, 3847^h (1955).

[3] S. Winstein, Ernest Grunwald, and L. L. Ingraham, J. Am. Chem. Soc., 70, 826 (1948).

[4] R. Stuart Tipson, J. Org. Chem., 9, 238 (1944).

bath to 5°, and then an equivalent amount (38 g.) of p-toluenesulfonyl chloride (Eastman) was added in one portion. The solution was stirred until all the p-toluenesulfonyl chloride dissolved. The temperature rose to 40° on dissolution of the p-toluenesulfonyl chloride. The solution was then cooled overnight at 0-5° in a refrigerator.

The reaction mixture, which contained crystals of pyridine hydrochloride, was then added to a beaker of ice containing 100 ml. of concentrated hydrochloric acid. An oil immediately separated and soon solidified at the bottom of the beaker. The crystalline solid was washed with cold water and dried in a desiccator containing calcium chloride. The reaction gave 51.6 g. (96.3%) of cyclohexylcarbinyl tosylate, m.p. 30-30.5°; literature, m.p. 30.5°.[5] An "infinity" titer indicated 98.0% purity. The infrared spectrum showed strong bands at 1362 $cm.^{-1}$, 1345 $cm.^{-1}$, 1182 $cm.^{-1}$, and 1170 $cm.^{-1}$, which are indicative of sulphonates. No absorption was observed in the region of O-H stretching.

<u>Preparation of Cyclopentylcarbinyl Tosylate</u>.--Cyclopentylcarbinyl tosylate was prepared in the same manner as previously

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[5] N. Mori, J. Chem. Soc. of Japan, 34, 1300 (1961).

described for the preparation of cyclohexylcarbinyl tosylate. This reaction was also run on a 0.2 mole basis using 20 g. of cyclopentylcarbinol, 38 g. of p-toluenesulfonyl chloride, and 90 ml. of pyridine. On addition of the reaction mixture to the ice-hydrochloric acid mixture an oil was obtained which could not be induced to crystallize. The oily product was washed several times with dilute hydrochloric acid solution until there was no pyridine odor. A methanol-water solution of the oil was treated with decolorizing carbon, warmed briefly, and filtered. This step was repeated several times. The product was then heated at 50-60° for eight hours under reduced pressure using a rotary evaporator. The product obtained was a light yellow oil weighing 20.6 g. (40.5%), n_D^{25} = 1.5176. An "infinity" titer indicated 100.8% purity. Anal. Found: C, 61.30%; H, 6.92%; S, 11.39%. Calculated for $C_{13}H_{18}O_3S$: C, 61.42%; H, 7.09%; S, 12.60%. The infrared spectrum showed strong bands at 1350-1360 $cm.^{-1}$ and at 1170 $cm.^{-1}$, which are indicative of sulphonates. No absorption was observed in the region of O-H stretching.

Preparation of Isobutyl Tosylate.--Isobutyl tosylate was prepared in the same manner as previously described for the preparation of cyclohexylcarbinyl tosylate. The reaction was run on a 0.3 mole basis using 57 g. of p-toluenesulfonyl chloride, 22.2 g. of isobutyl alcohol, and 100 ml. of pyridine. Although the product has a reported melting point of 13.5°[6], the oily product obtained in this experiment could not be made to crystallize and was purified in the same way as the cyclopentylcarbinyl tosylate. A light yellow oil was obtained weighing 37 g. (54.4% yield), n_D^{25} = 1.4988. An "infinity" titer indicated 103.2% purity. Anal. Found: C, 56.22%; H, 7.15%; S, 14.07%. Calculated for $C_{11}H_{16}O_3S$: C, 57.89%; H, 7.02%; S, 14.04%. The infrared spectrum showed strong bands at 1165 cm.$^{-1}$, 1350 cm.$^{-1}$, and 1390 cm.$^{-1}$, which are indicative of sulphonates. No absorption was observed in the region of O-H stretching.

Kinetic Investigations

Materials.--Absolute ethanol was prepared by the process described by Fieser in Experiments in Organic Chemistry.[7] A mixture of 5 g. of magnesium turnings, 60 ml. of commercial absolute ethanol, and 1 ml. of bromoethane was

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[6] S. Winstein and Henry Marshall, J. Am. Chem. Soc., 74, 1126 (1952).

[7] L. F. Fieser, "Experiments in Organic Chemistry," Third Edition, D. C. Heath and Company, Boston, Mass., 1955, p. 286.

refluxed in a moisture free apparatus until it appeared that most of the magnesium had reacted. An additional 900 ml. of commercial absolute ethanol was added, and the mixture was refluxed overnight. The ethanol was then distilled, and the first 15 ml. of distillate was discarded.

An 80 volume % aqueous ethanol solution was prepared by pipetting 100 ml. of distilled water into a 500-ml. volumetric flask and adding absolute ethanol in portions with mixing until the flask was filled to the mark.

Formic acid (100%) was prepared by the procedure of Winstein and Marshall.[8] Formic acid (Eastman, 97 + %) was purified in one-liter batches. The low boiling components were removed by distillation through a 3-foot spinning-band column until the head temperature reached 100.5°. After cooling, purified boric anhydride (Baker) was added. The amount of boric anhydride added was 4 g. per gram of water calculated on the basis of 3% water. After standing for three days, the solution was decanted and distilled from fresh boric anhydride under reduced pressure. The temperature of the distillation flask was held below 40°.

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[8] Winstein and Marshall, <u>loc. cit</u>.

Standard sodium hydroxide solutions were prepared by dilution of approximately 4 N sodium hydroxide made up using precautions to exclude carbonate. The solution was standardized with potassium acid phthalate which had been previously dried.

An approximately 0.01 N solution of sodium acetate was prepared by the method described by Winstein, et. al.[9] A calculated amount of sodium carbonate was dissolved in 1400 ml. of anhydrous acetic acid. The solution was then standardized by potentiometric titration with 0.1000 N perchloric acid in glacial acetic acid (Fisher).

Anhydrous acetic anhydride was prepared by the procedure described by Winstein, et. al.[10] Glacial acetic acid (Baker, 99.9%) was refluxed for four hours with enough pure acetic anhydride to react with the water, calculated on the basis of 0.1% water. The acetic acid was then distilled until approximately 25 ml. of solution was left in the flask.

Methods.--A. Solvolysis in Absolute Ethanol.--Ap-

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[9] Winstein, Grunwald, and Ingraham, loc. cit.

[10] S. Winstein, Carolyn Hanson, and Ernest Grunwald, Ibid., 70, 815 (1948).

proximately 0.02 M solutions of the tosylates were made up at room temperature in a 50-ml. volumetric flask using weighed portions of the tosylate. The solution was mixed thoroughly and then cooled in ice. Approximately 7-ml. portions of the solutions were then transferred to each of 7 ampoules prepared from 6-in. bacteriological tubes. The ampoules were cooled in ice and sealed.

Six of the ampoules were immersed in the constant temperature bath at $100.2^{\circ} \pm 0.2^{\circ}$. Time of immersion was counted as "zero time." The other ampoule was immediately opened, a 5-ml. aliquot taken, and titrated with standard sodium hydroxide solution to the phenolphthalein end-point. This titration was considered a blank. The other ampoules were taken out at suitable times, immersed in ice water, cooled for five minutes, allowed to warm to room temperature, and then a 5-ml. aliquot was titrated with standard sodium hydroxide solution to the phenolphthalein end-point. The solution was kept cold during the titration. The results are given in Tables I-III.

B.--Solvolysis in 80 Volume % Aqueous Ethanol.--For solvolysis in 80% ethanol the same procedure was used as described for the solvolysis in absolute ethanol. One minor difference was that the solution was not kept cold before being placed in the ampoules because of the limited solubilities of the tosylates in 80 volume % ethanol. The results are given in Tables IV-VI.

C.--Solvolysis in 100% Formic Acid.--Solutions approximately 0.02 M were made up at room temperature in a 100-ml. volumetric flask using weighed portions of the tosylate. Instead of the ampoule technique, an open system was employed since it is reported by Winstein and Marshall that ampoules occasionally burst due to decomposition of the formic acid.[11] The contents of the volumetric flask were then transferred to a round-bottomed flask fitted with a condenser and immersed in the constant temperature bath. Approximately 10-ml samples were withdrawn at appropriate times through the condenser opening using a capillary tube connected to a glass bulb fitted with a suction bulb. The samples were immediately cooled in ice water for 5 minutes. The solution was allowed to come to room temperature, and a 5-ml. aliquot was taken and delivered into a beaker containing 50 ml. of anhydrous acetic acid. The solution was titrated potentiometrically with

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[11] Winstein and Marshall, loc. cit.

0.00992 N sodium acetate in anhydrous acetic acid as described below. The first sample titrated was considered a blank, and the time of its removal from the bath was considered "zero time."

For the potentiometric titration a Beckman pH meter, Model H-2, with standard glass and calomel electrodes was employed. The beaker was wrapped with copper foil connected to ground. The electrodes were then immersed in the stirred solution to be titrated, and the millivolt reading was adjusted with the standardization knob on the pH meter to an arbitrary setting of 700 mv. on the 800 mv. scale. The millivolt readings were plotted against the volume of the standard sodium acetate solution. The concentration of the p-toluenesulfonic acid in the solution was calculated from the volume of titrant at the first inflection point as determined by the second differential method.[12] The results are given in Tables VII-XI.

Apparatus.--A constant temperature bath containing polyethylene glycol was equipped with a stirrer, a 750-watt base heater, a thermometer, and a heater controlled by a

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[12] J. J. Lingane, "Electroanalytical Chemistry," 2nd Ed., Interscience Publishers, Inc., New York, 1958, p. 93.

bimetallic thermoregulator. The thermometer was calibrated against a set of thermometers for which Bureau of Standards calibration tables were available.

TABLE I

FIRST-ORDER KINETIC DATA FOR THE SOLVOLYSIS OF CYCLOHEXYLCARBINYL TOSYLATE IN ABSOLUTE ETHANOL AT 100.2°.

Time (minutes)	$a \times 10^5$ mole	Sodium Hydroxide (ml.) 0.0112 N	$x \times 10^5$ mole	$k \times 10^4$ (min^{-1})
60	9.83	0.658	0.49	8.14
120	9.83	1.022	0.89	7.95
180	9.83	1.400	1.32	8.25
241	9.83	1.756	1.72	7.91
300	9.83	2.077	2.08	7.98
360	9.83	2.386	2.42	7.93
Average				8.03

a - The initial number of moles of cyclohexylcarbinyl tosylate in a 5-ml. aliquot.

x - The number of moles of tosylate which has reacted at any time.

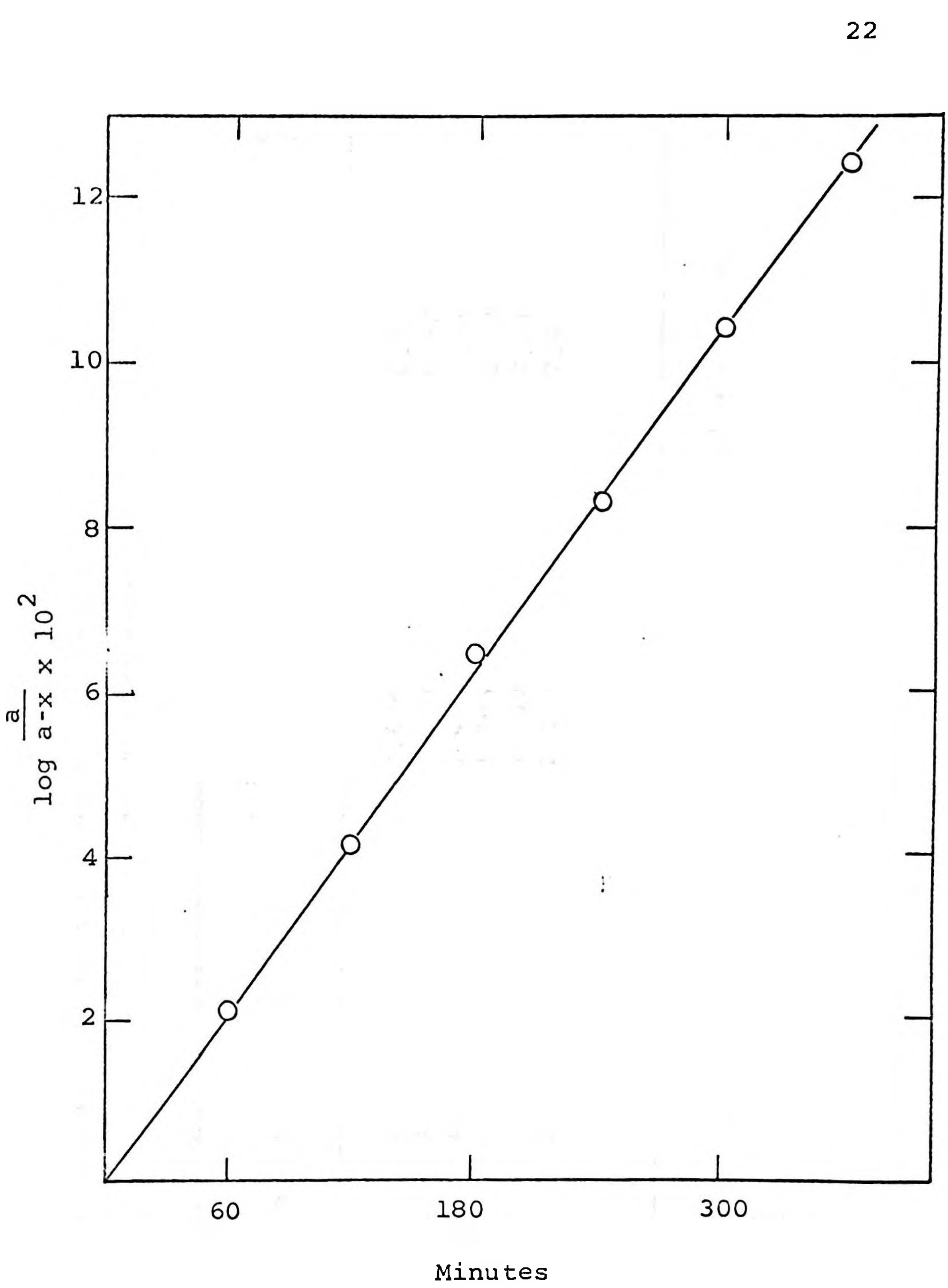

Figure 1. Solvolysis of Cyclohexylcarbinyl Tosylate in Absolute Ethanol at 100.2°.

TABLE II

FIRST-ORDER KINETIC DATA FOR THE SOLVOLYSIS OF ISOBUTYL TOSYLATE IN ABSOLUTE ETHANOL AT 100.2°.

Time (minutes)	$a \times 10^5$ mole	Sodium Hydroxide (ml.) 0.0112 N	$x \times 10^5$ mole	$k \times 10^4$ (min^{-1})
60	10.00	0.696	0.50	8.14
120	10.00	1.070	0.92	7.95
180	10.00	1.440	1.33	7.77
240	10.00	1.785	1.72	7.95
300	10.00	2.150	2.13	7.98
360	10.00	2.420	2.43	7.74
Average				7.92

a - The initial number of moles of isobutyl tosylate in a 5-ml. aliquot.

x - The number of moles of tosylate which has reacted at any time.

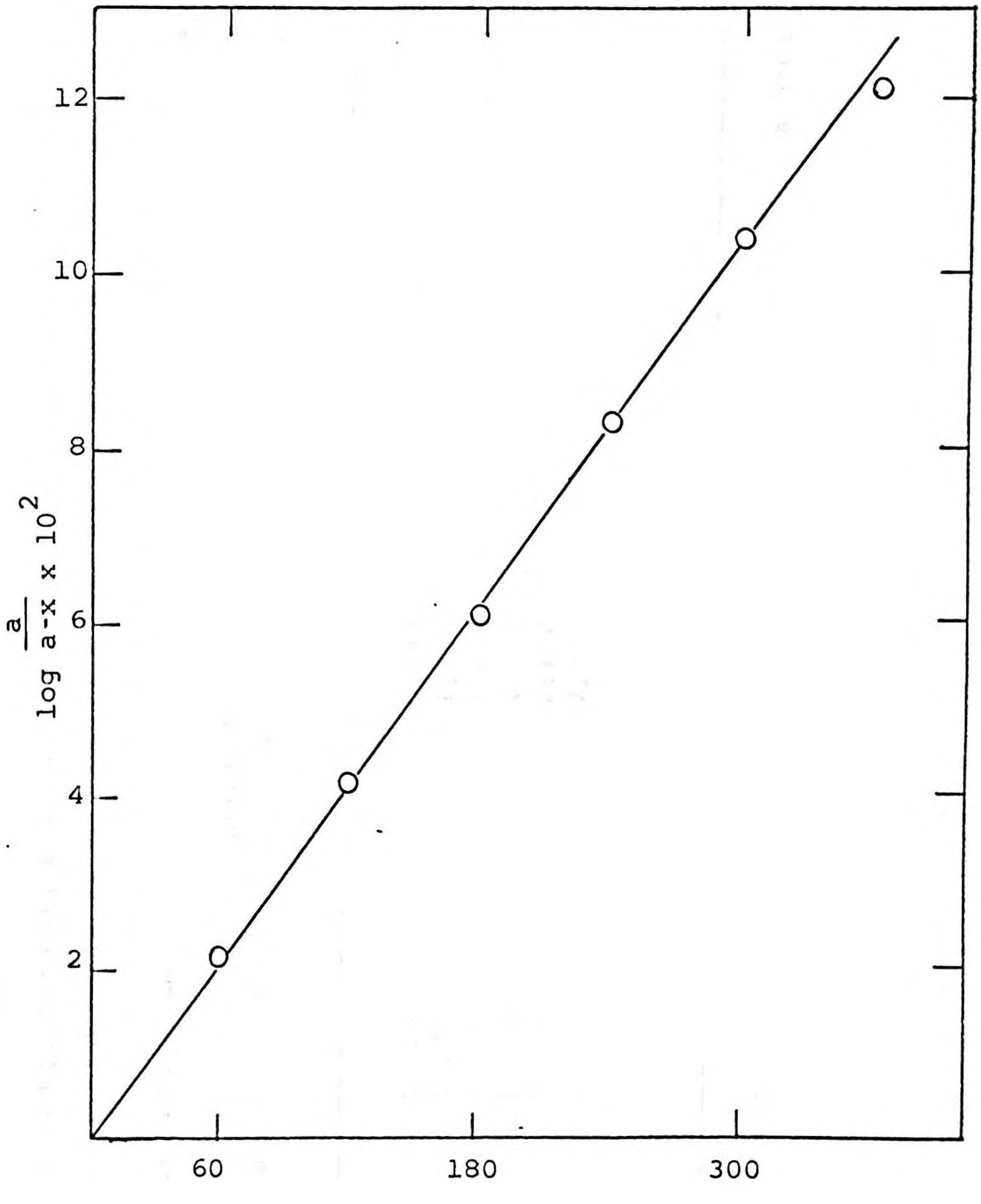

Figure 2. Solvolysis of Isobutyl Tosylate in Absolute Ethanol at 100.2°.

TABLE III

FIRST-ORDER KINETIC DATA FOR THE SOLVOLYSIS OF CYCLOPENTYLCARBINYL TOSYLATE IN ABSOLUTE ETHANOL AT 100.2°.

Time (minutes)	a x 10^5 mole	Sodium Hydroxide (ml.) 0.0112 N	x x 10^5 mole	k x 10^4 (min.$^{-1}$)
60	10.05	0.645	0.47	8.14
120	10.05	1.013	0.88	7.95
180	10.05	1.405	1.33	7.77
240	10.05	1.791	1.75	7.95
300	10.05	2.162	2.17	8.21
360	10.05	2.580	2.64	8.57
Average				8.10

a - The initial number of moles of cyclopentylcarbinyl tosylate in a 5-ml. aliquot.

x - The number of moles of tosylate which has reacted at any time.

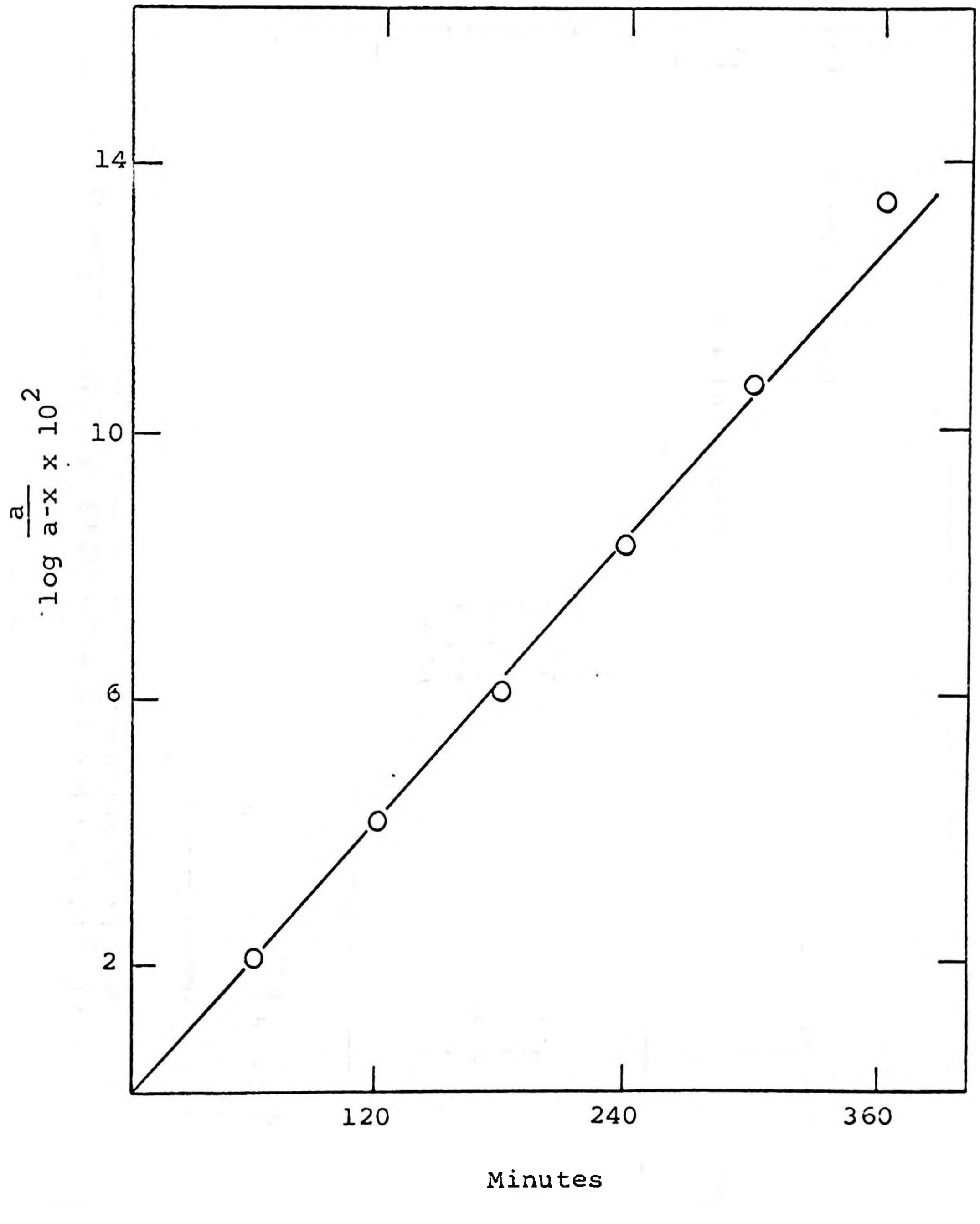

Figure 3. Solvolysis of Cyclopentylcarbinyl Tosylate in Absolute Ethanol at 100.2°.

TABLE IV

FIRST-ORDER KINETIC DATA FOR THE SOLVOLYSIS OF CYCLOHEXYLCARBINYL TOSYLATE IN 80 VOLUME % AQUEOUS ETHANOL AT 100.2°.

Time (minutes)	a x 10^5 mole	Sodium Hydroxide (ml.) 0.0112 N	x x 10^5 mole	k x 10^3 ($min.^{-1}$)
30	9.80	0.945	0.85	2.87
60	9.80	1.535	1.51	2.76
90	9.80	2.160	2.21	2.84
120	9.80	2.740	2.86	2.86
150	9.80	3.270	3.45	2.89
Average				2.84

a - The initial number of moles of cyclohexylcarbinyl tosylate in a 5-ml. aliquot.

x - The number of moles of tosylate in the 5-ml. aliquot which has reacted at any time.

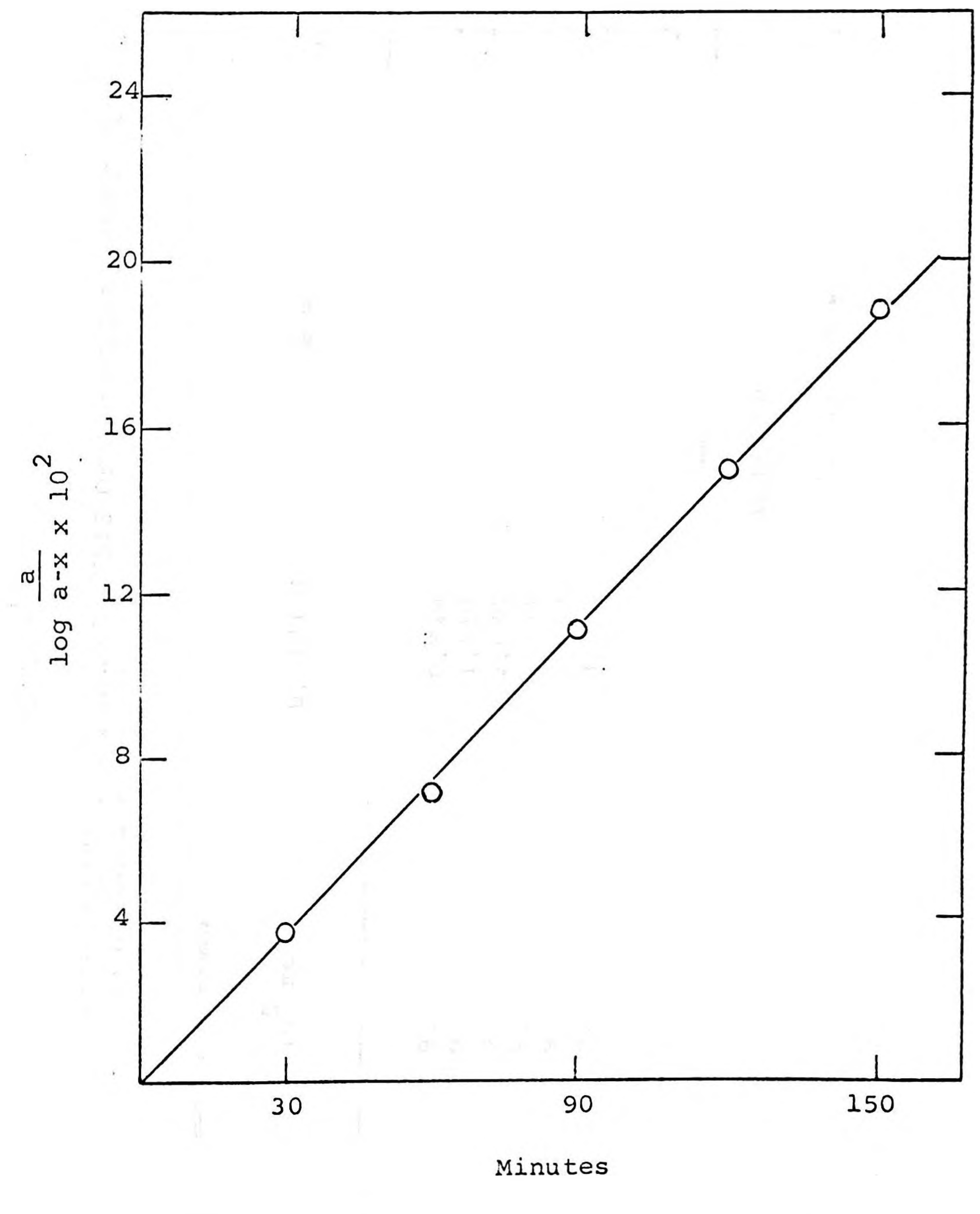

Figure 4. Solvolysis of Cyclohexylcarbinyl Tosylate in 80 Volume % Aqueous Ethanol at 100.2°.

TABLE V

FIRST-ORDER KINETIC DATA FOR THE SOLVOLYSIS OF ISOBUTYL TOSYLATE IN 80 VOLUME % AQUEOUS ETHANOL AT 100.2°.

Time (minutes)	$a \times 10^5$ mole	Sodium Hydroxide (ml.) 0.0123 N	$x \times 10^5$ mole	$k \times 10^3$ (min.$^{-1}$)
30	9.92	0.849	0.80	2.87
60	9.92	1.510	1.62	3.04
90	9.92	2.080	2.32	2.99
120	9.92	2.593	2.95	2.97
150	9.92	3.070	3.54	2.96
180	9.92	3.550	4.13	3.02
Average				2.98

a - The initial number of moles of isobutyl tosylate in a 5-ml. aliquot.

x - The number of moles of tosylate in the 5-ml. aliquot which has reacted at any time.

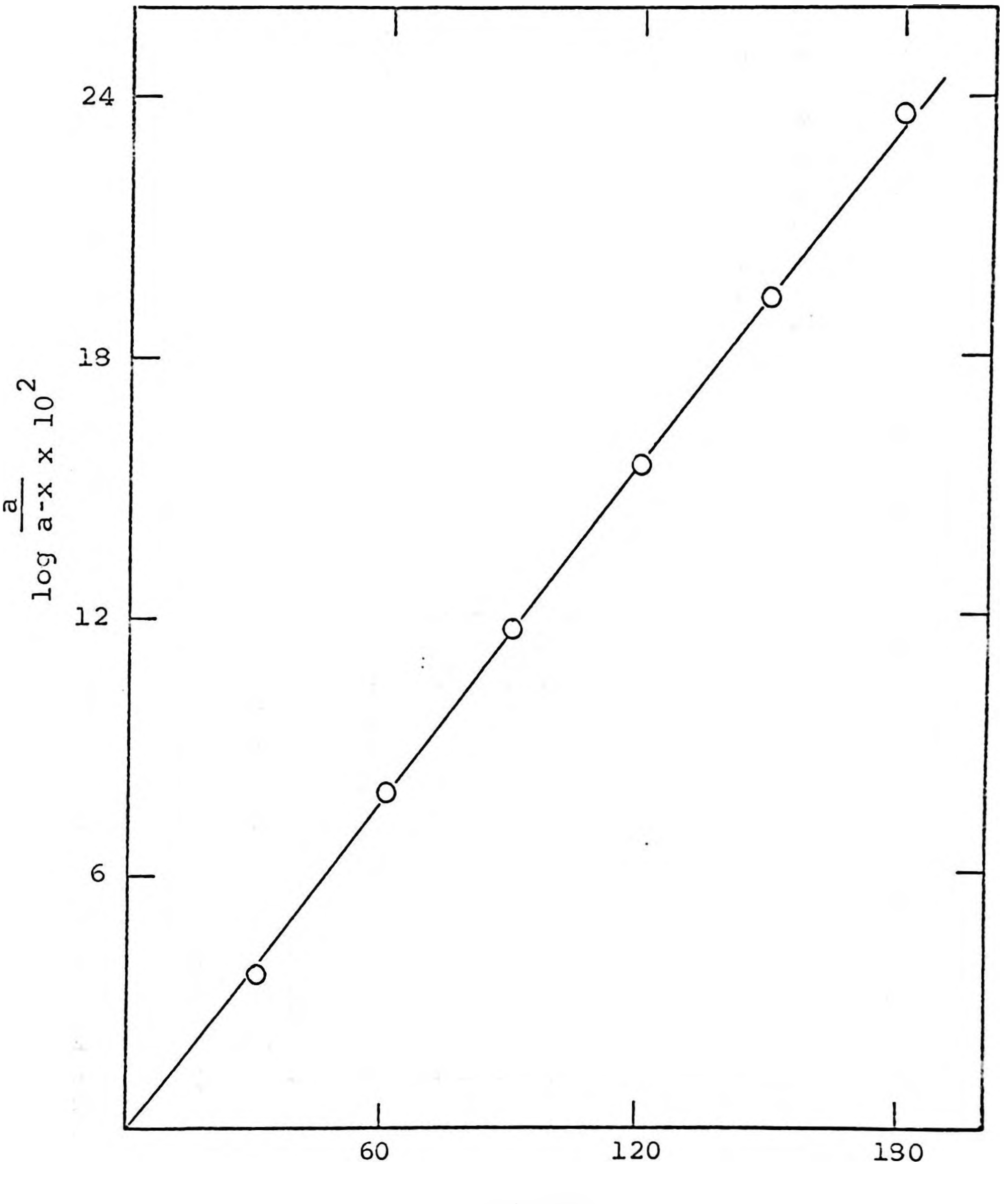

Figure 5. Solvolysis of Isobutyl Tosylate in 80 Volume % Aqueous Ethanol at 100.2°.

TABLE VI

FIRST-ORDER KINETIC DATA FOR THE SOLVOLYSIS OF CYCLOPENTYLCARBINYL TOSYLATE IN 80 VOLUME % AQUEOUS ETHANOL AT 100.2°.

Time (minutes)	a x 10^5 mole	Sodium Hydroxide (ml.) 0.0123 N	x x 10^5 mole	k x 10^3 (min.$^{-1}$)
30	10.41	1.135	1.26	4.37
60	10.41	2.115	2.47	4.49
90	10.41	2.920	3.45	4.50
120	10.41	3.724	4.62	4.89
140	10.41	4.130	4.94	4.59
160	10.41	4.418	5.30	4.46
Average				4.55

a - The initial number of moles of cyclopentylcarbinyl tosylate in a 5-ml. aliquot.

x - The number of moles of tosylate in the 5-ml. aliquot which has reacted at any time.

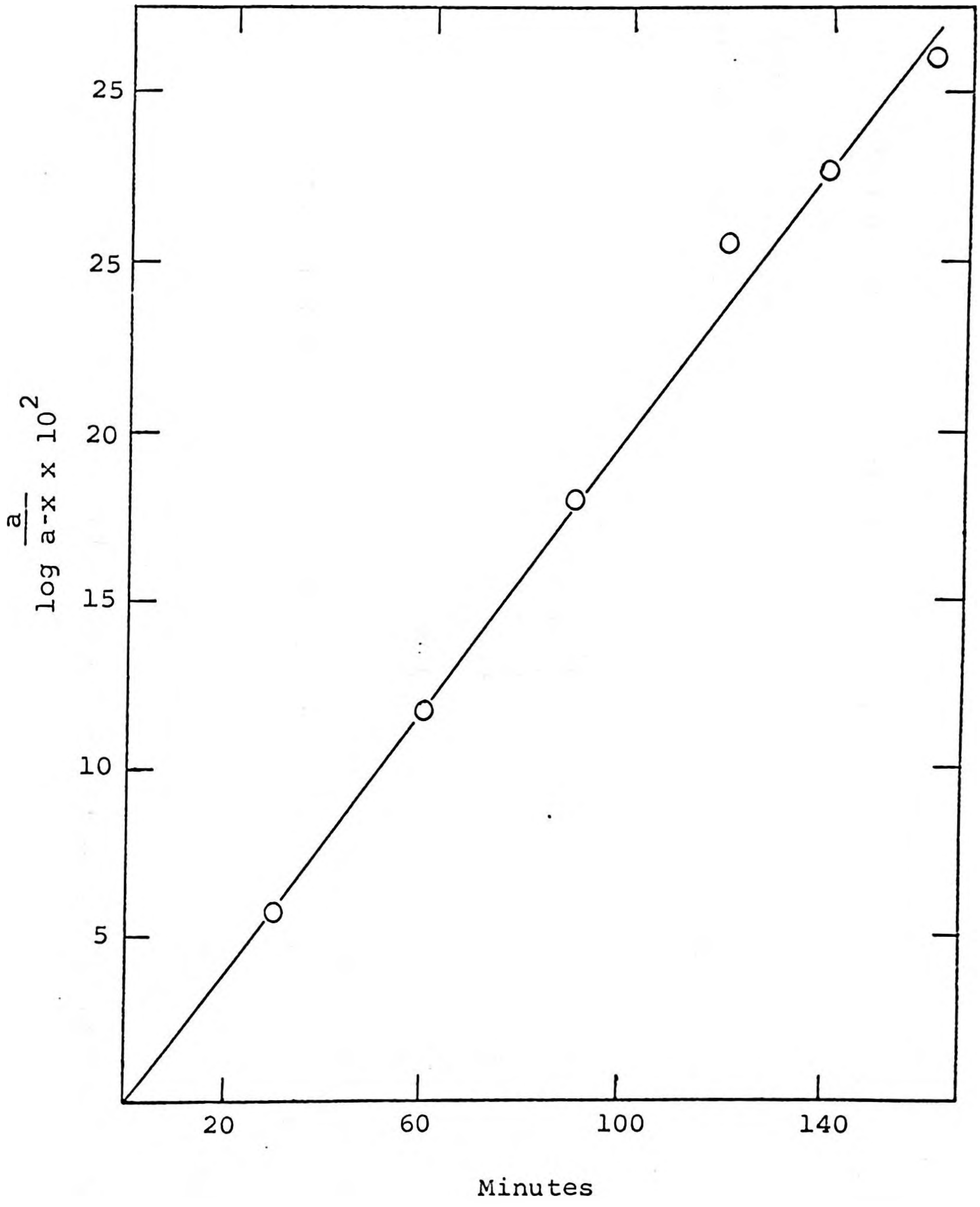

Figure 6. Solvolysis of Cyclopentylcarbinyl Tosylate in 80 Volume % Aqueous Ethanol at 100.2°.

TABLE VII

FIRST-ORDER KINETIC DATA FOR THE SOLVOLYSIS OF CYCLOHEXYLCARBINYL TOSYLATE IN 100% FORMIC ACID AT 100.2°.

Time (minutes)	$a \times 10^5$ mole	Sodium Acetate (ml.) 0.00992 N	$x \times 10^5$ mole	$k \times 10^2$ (min.$^{-1}$)
16	8.47	3.40	1.80	1.50
37	8.47	5.12	3.51	1.45
57	8.47	6.40	4.78	1.46
77	8.47	7.35	5.72	1.46
102	8.47	8.25	6.61	1.49
124	8.47	8.98	7.34	1.63
Average				1.50

a - The initial number of moles of cyclohexylcarbinyl tosylate in a 5-ml. aliquot.

x - The number of moles of tosylate in the 5-ml. aliquot which has reacted at any time.

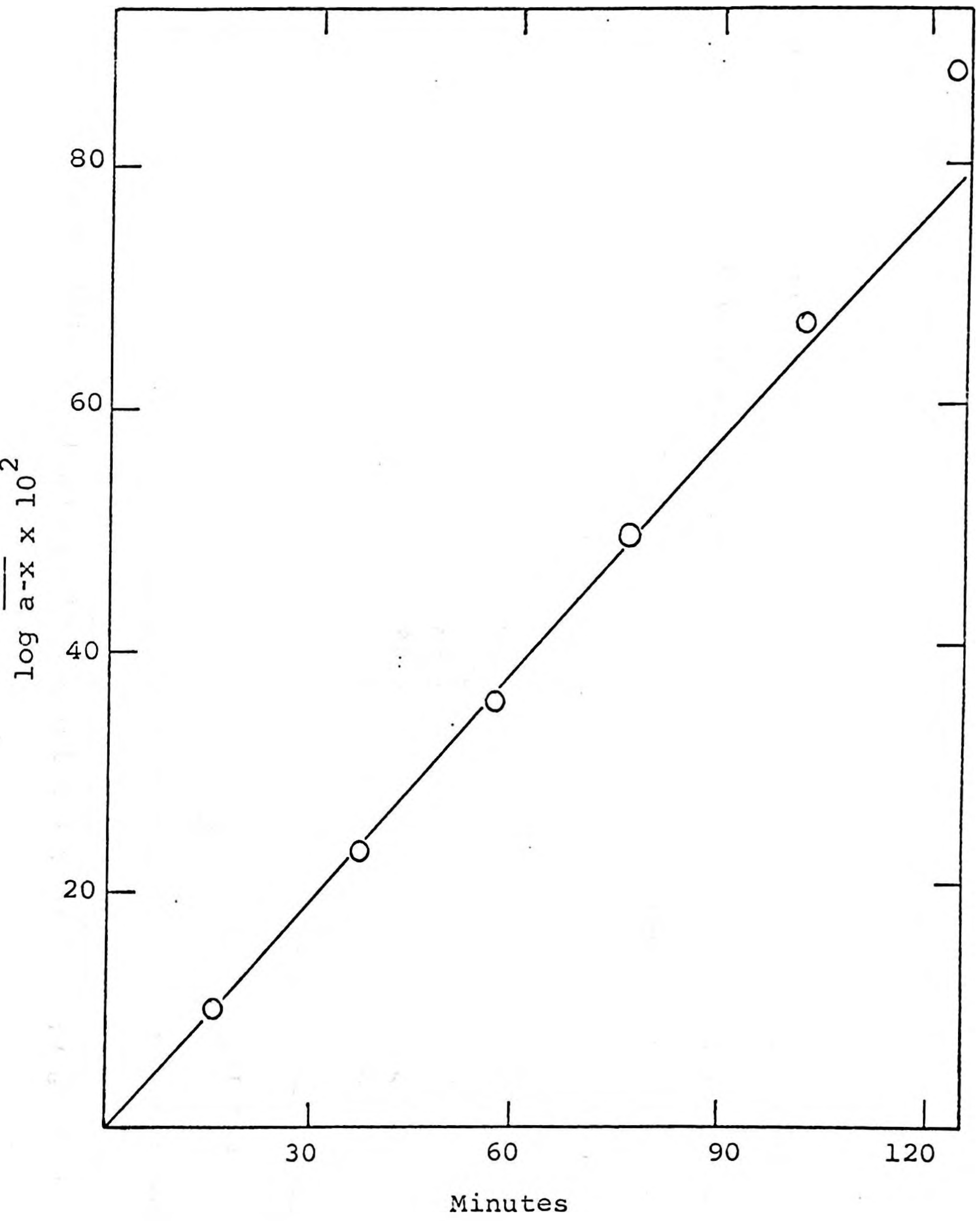

Figure 7. Solvolysis of Cyclohexylcarbinyl Tosylate in 100% Formic Acid at 100.2°.

TABLE VIII

FIRST-ORDER KINETIC DATA FOR THE SOLVOLYSIS OF ISOBUTYL TOSYLATE IN 100% FORMIC ACID AT 100.2°.

Time (minutes)	$a \times 10^5$ mole	Sodium Acetate (ml.) 0.00992 N	$x \times 10^5$ mole	$k \times 10^2$ (min.$^{-1}$)
19	9.38	3.85	2.78	1.84
39	9.38	5.84	4.75	1.82
56	9.38	7.20	6.10	1.88
73	9.38	8.19	7.07	1.92
92	9.38	8.96	7.85	1.97
110	9.38	9.40	8.28	1.95
Average				1.90

a - The initial number of moles of isobutyl tosylate in a 5-ml. aliquot.

x - The number of moles of tosylate in the 5-ml. aliquot which has reacted at any time.

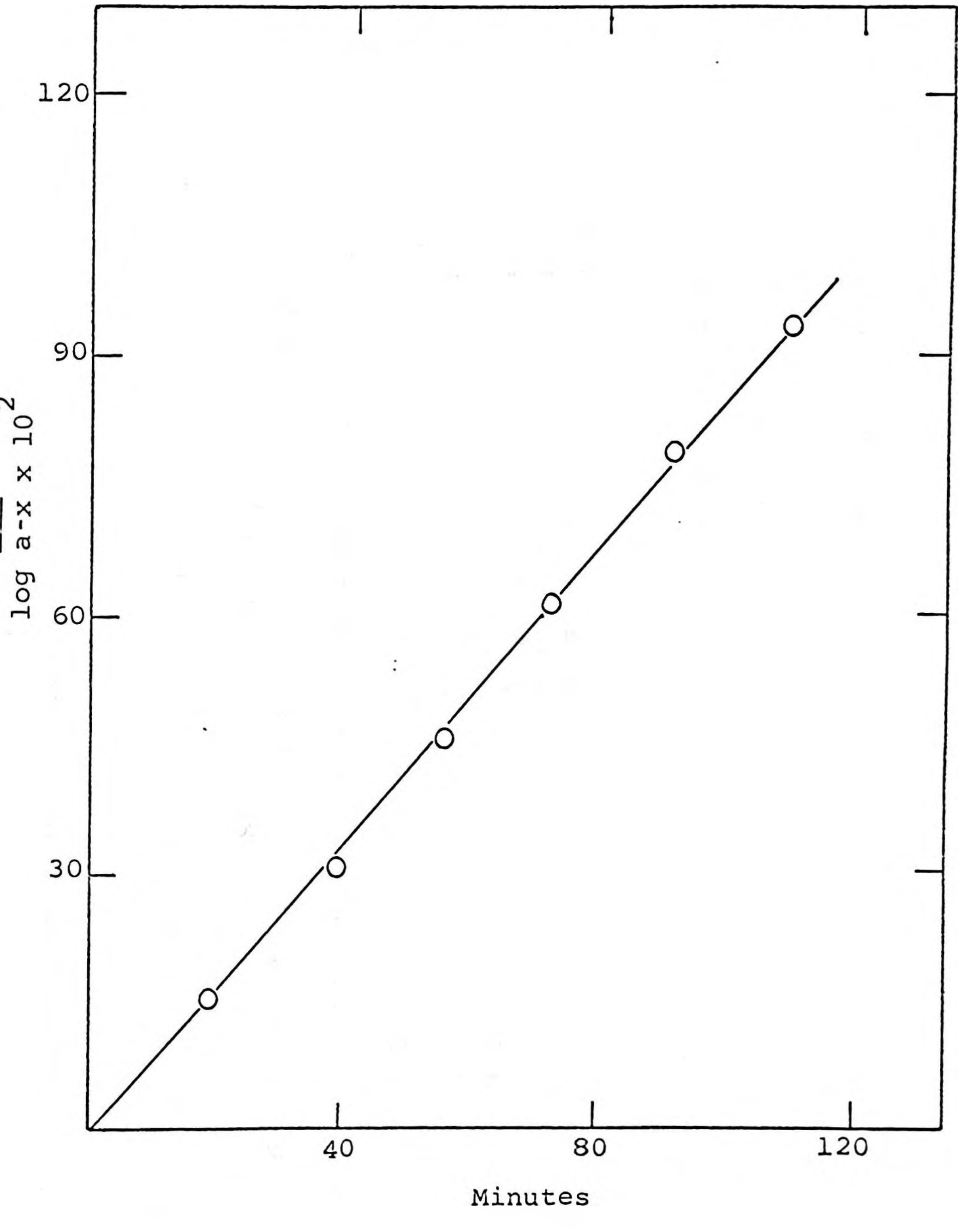

Figure 8. Solvolysis of Isobutyl Tosylate in 100% Formic Acid at 100.2°.

TABLE IX

FIRST-ORDER KINETIC DATA FOR THE SOLVOLYSIS OF CYCLOPENTYLCARBINYL TOSYLATE IN 100% FORMIC ACID AT 66.2°.

Time (minutes)	a x 10^5 mole	Sodium Acetate (ml.) 0.00992 N	x x 10^5 mole	k x 10^3 (min.$^{-1}$)
10	9.57	1.52	0.62	6.77
29	9.57	2.71	1.80	7.14
47	9.57	3.52	2.60	6.71
68	9.57	4.55	3.62	7.01
91	9.57	5.44	4.51	7.01
116	9.57	6.36	5.42	7.23
Average				6.98

a - The initial number of moles of cyclopentylcarbinyl tosylate in a 5-ml. aliquot.

x - The number of moles of tosylate in the 5-ml. aliquot which has reacted at any time.

TABLE X

FIRST-ORDER KINETIC DATA FOR THE SOLVOLYSIS OF CYCLOPENTYLCARBINYL TOSYLATE IN 100% FORMIC ACID AT 73.0°.

Time (minutes)	a x 10^5 mole	Sodium Acetate (ml.) 0.00992 N	x x 10^5 mole	k x 10^2 (min.$^{-1}$)
10	9.71	1.78	1.10	1.22
23	9.71	3.36	2.66	1.40
37	9.71	4.60	3.89	1.39
49	9.71	5.64	4.92	1.45
64	9.71	6.50	5.78	1.41
78	9.71	7.28	6.55	1.44
Average				1.39

a - The initial number of moles of cyclopentylcarbinyl tosylate in a 5-ml. aliquot.

x - The number of moles of tosylate in the 5-ml. aliquot which has reacted at any time.

TABLE XI

FIRST-ORDER KINETIC DATA FOR THE SOLVOLYSIS OF CYCLOPENTYLCARBINYL TOSYLATE IN 100% FORMIC ACID AT 81.9^{o}.

Time (minutes)	a x 10^{5} mole	Sodium Acetate (ml.) 0.00992 N	x x 10^{5} mole	k x 10^{2} (min.$^{-1}$)
13	8.85	4.68	3.33	3.61
27	8.85	7.22	5.85	4.01
40	8.85	8.00	6.63	3.46
53	8.85	9.00	7.62	3.72
65	8.85	9.40	8.01	3.61
Average				3.68

a - The initial number of moles of cyclopentylcarbinyl tosylate in a 5-ml. aliquot.

b - The number of moles of tosylate in the 5-ml. aliquot which has reacted at any time.

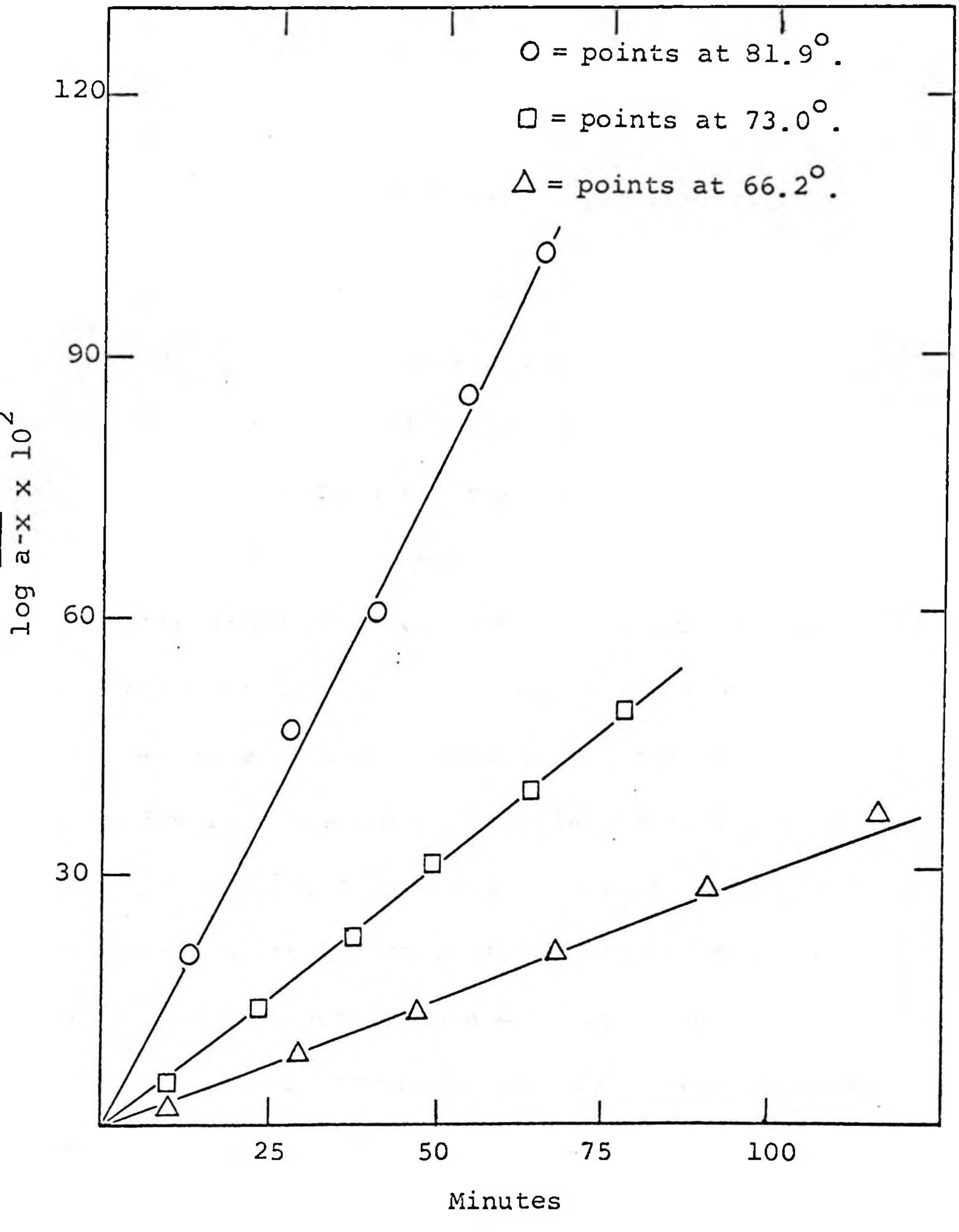

Figure 9. Solvolysis of Cyclopentylcarbinyl Tosylate in 100% Formic Acid at 66.2°, 73.0°, and 81.9°.

CHAPTER III

DISCUSSION OF RESULTS

Regardless of mechanism all the solvolysis reactions studied in these experiments would be expected to follow pseudo-first-order kinetics since the solutions were of such dilute concentration (approximately 0.02 M) that the concentration of solvent remained essentially constant throughout the reaction. A first-order constant was calculated for each point using the expression $k = \frac{2.303}{t} \log a/(a - x)$, where a is the initial concentration of the tosylate and x is the amount of tosylate that has reacted at any time, t. Since the points were sufficiently linear for each reaction, the average of the values of the constant for each point served as a working value.

In the case of the formolysis of cyclopentylcarbinyl tosylate at 100.2°, approximately 89% of the tosylate had solvolyzed after 15 minutes reaction time, thus making it impossible to take sufficient points for the determination of a meaningful rate constant. However, an estimated value of the rate constant at this temperature was obtained by determining the rate constants at three lower temperatures, plotting the logarithms of the rate constants vs. 1/T, and extrapolating to a 1/T value corresponding to 100.2°. The result is shown in Figure 10.

A summary of the kinetic data obtained in these experiments is given in Table XII. The only other data reported on solvolyses of these tosylates in similar solvents at this temperature is Mori's reported value of $k = 8.42 \times 10^{-4}$ min.$^{-1}$ for the solvolysis of cyclohexylcarbinyl tosylate in 98.5% ethanol.[1] Considering the slight difference in solvent composition the value of 8.03×10^{-4} min.$^{-1}$ obtained in this experiment appears to be in good agreement.

The relative ionizing powers of the solvents employed in these experiments are formic acid $>$ 80% ethanol-water $>$ absolute ethanol.[2] Absolute and 80% aqueous ethanol are considered to be approximately equal in nucleophilicity,

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[1] N. Mori, <u>Chem. Soc. Japan</u>, 33, 1300 (1962).

[2] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, (1963), p. 298.

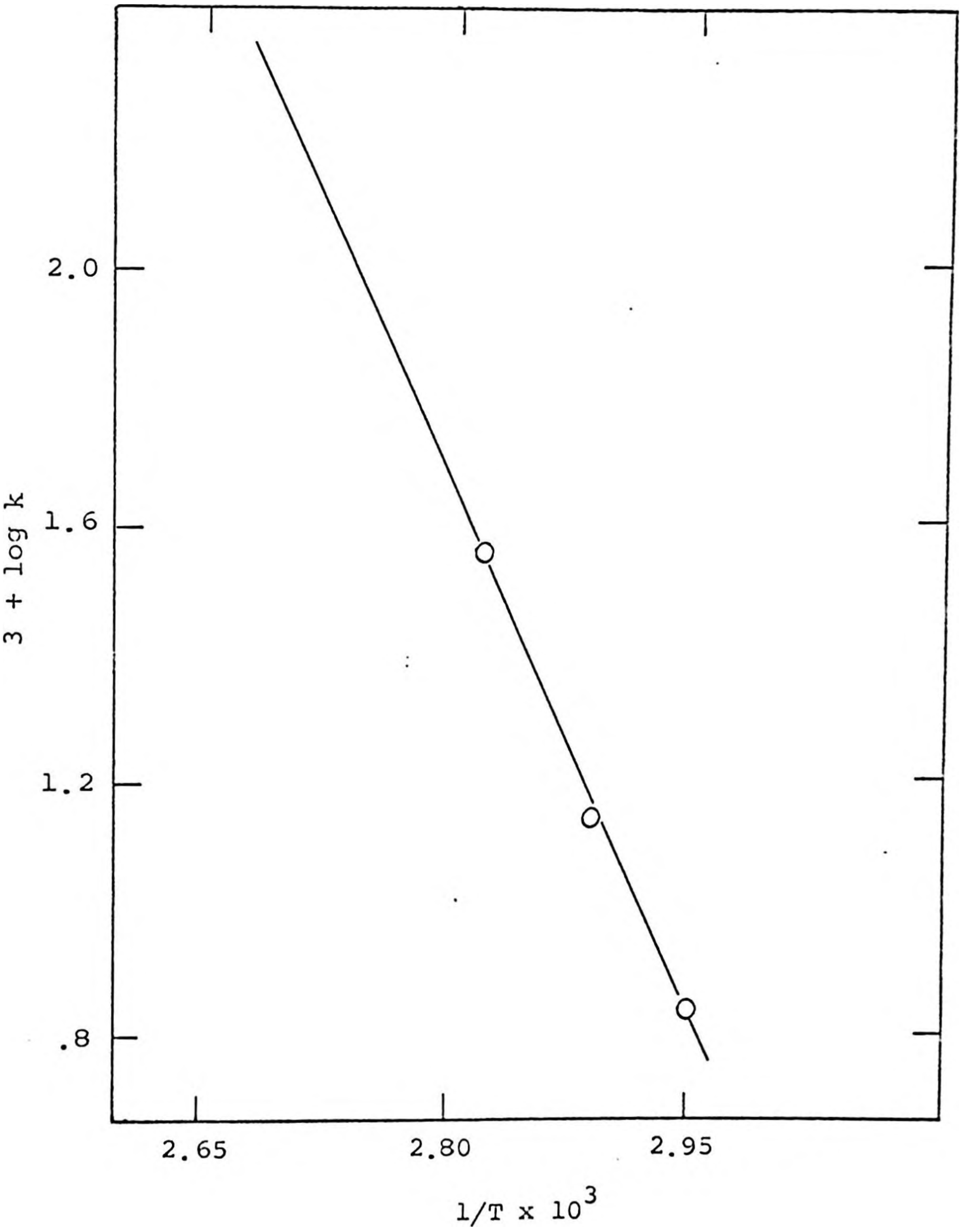

Figure 10. Plot for the Determination of k of Cyclopentylcarbinyl Tosylate at 100.2°.

TABLE XII

SUMMARY OF RATE CONSTANTS AT 100.2°.

Compounds	Solvents Absolute Ethanol k (min.$^{-1}$)	 80% Aqueous Ethanol k (min.$^{-1}$)	 Formic Acid (100%) k (min.$^{-1}$)
Cyclohexylcarbinyl Tosylate	8.03×10^{-4}	2.84×10^{-3}	1.50×10^{-2}
Cyclopentylcarbinyl Tosylate	8.10×10^{-4}	4.55×10^{-3}	*2.12×10^{-1}
Isobutyl Tosylate	7.92×10^{-4}	2.98×10^{-3}	1.90×10^{-2}

*Extrapolated value.

whereas formic acid is considerably less nucleophilic than the ethanolic solvents.

The results shown in Table XII reveal only small differences in the rate constants of solvolyses in absolute ethanol for the three compounds studied. Of the reactions studied those solvolyses in absolute ethanol would be expected to proceed by mechanisms most closely similar to the classical S_N2 reaction extreme; that is, mechanisms in which the transition state of the rate determining step receives a large degree of nucleophilic participation by the solvent and requires a minimum of charge stabilization. To a first approximation based on steric considerations, the three primary tosylates studied would appear to have equal propensities toward such a reaction since each contains two β-alkyl substituents. This position is roughly supported by the data of Williams which showed that whereas the reactivity of cyclohexylcarbinyl bromide toward iodide ion in acetone was somewhat greater than that of cyclopentylcarbinyl bromide, the difference could be attributed to an entropy effect.[3] In the present case the reactivity of

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[3] G. C. Williams, Thesis, University of Alabama, University, Alabama, 1957.

cyclopentylcarbinyl tosylate in absolute ethanol is slightly, and perhaps insignificantly, greater than that of cyclohexylcarbinyl tosylate, so apparently the entropy effect observed by Williams has been eclipsed by other factors as the reaction mechanism moves away from the S_N2 extreme.

As shown in Table XII, for any particular tosylate the reaction rates increase with increasing ionizing power of the solvent. However, the magnitude of the rate enhancement by increasing solvent ionizing power is much greater in solvolyses of cyclopentylcarbinyl tosylate than either isobutyl tosylate or cyclohexylcarbinyl tosylate.

These solvent effects may be most clearly seen by the comparisons of ratios of rate constants in various solvents shown in Table XIII. Thus we see that the ratios $k_{\text{80\% ethanol}}/k_{\text{absolute ethanol}}$ for cyclopentylcarbinyl tosylate, isobutyl tosylate, and cyclohexylcarbinyl tosylate are respectively 5.62, 3.76, and 3.54, and the ratios $k_{\text{HCOOH}}/k_{\text{absolute ethanol}}$ for the same compounds are respectively 262, 24.0, and 18.7.

The same point is emphasized by the additional comparisons shown in Table XIII. The divergence of reactivities of cyclopentylcarbinyl and isobutyl tosylates as solvent

TABLE XIII

SUMMARY OF RATIOS OF RATE CONSTANTS

Compound	$\frac{k\ 80\%\ \text{Ethanol}}{k\ \text{Absolute Ethanol}}$	$\frac{k\ \text{Formic Acid}}{k\ 80\%\ \text{Ethanol}}$	$\frac{k\ \text{Formic Acid}}{k\ \text{Absolute Ethanol}}$
A	3.54	5.28	18.7
B	5.62	46.6	262
C	3.76	6.38	24.0

Solvent	$\frac{k_B}{k_A}$	$\frac{k_B}{k_C}$	$\frac{k_A}{k_C}$
Absolute Ethanol	1.01	1.02	1.01
80% Ethanol	1.60	1.53	0.953
Formic Acid	14.1	11.2	0.789

A-Cyclohexylcarbinyl Tosylate
B-Cyclopentylcarbinyl Tosylate
C-Isobutyl Tosylate

ionizing power increases is quite pronounced; the ratios $k_{cyclopentylcarbinyl}/k_{isobutyl}$ in absolute ethanol, 80% aqueous ethanol, and formic acid are 1.02, 1.53, and 11.2, respectively. On the other hand, the reactivity of cyclohexylcarbinyl tosylate, as compared to isobutyl tosylate, diverges only slightly and in a negative direction as solvent ionizing power increases; the ratios $k_{cyclohexylcarbinyl}/k_{isobutyl}$ are 1.01, 0.95, and 0.79 in the same solvent sequence. The changes in the reactivities of cyclopentylcarbinyl and cyclohexylcarbinyl derivatives relative to the corresponding isobutyl compounds as solvent conditions change from those favoring S_N2 to S_N1 reactions may be summarized graphically as illustrated in Figure 11. However, a weakness of such a presentation is that the solvent condition coordinate is determined by multiple factors, including solvent ionizing power and nucleophilicity, and therefore it has no quantitative scale.

Application of the Winstein-Grunwald equation ($\log k = \log k_o + mY$) to the data for solvolyses in ethanolic solvents reveals m values of 0.27 and 0.28 for cyclohexylcarbinyl and isobutyl tosylates, respectively, while the m value for cyclopentylcarbinyl tosylate is somewhat larger,

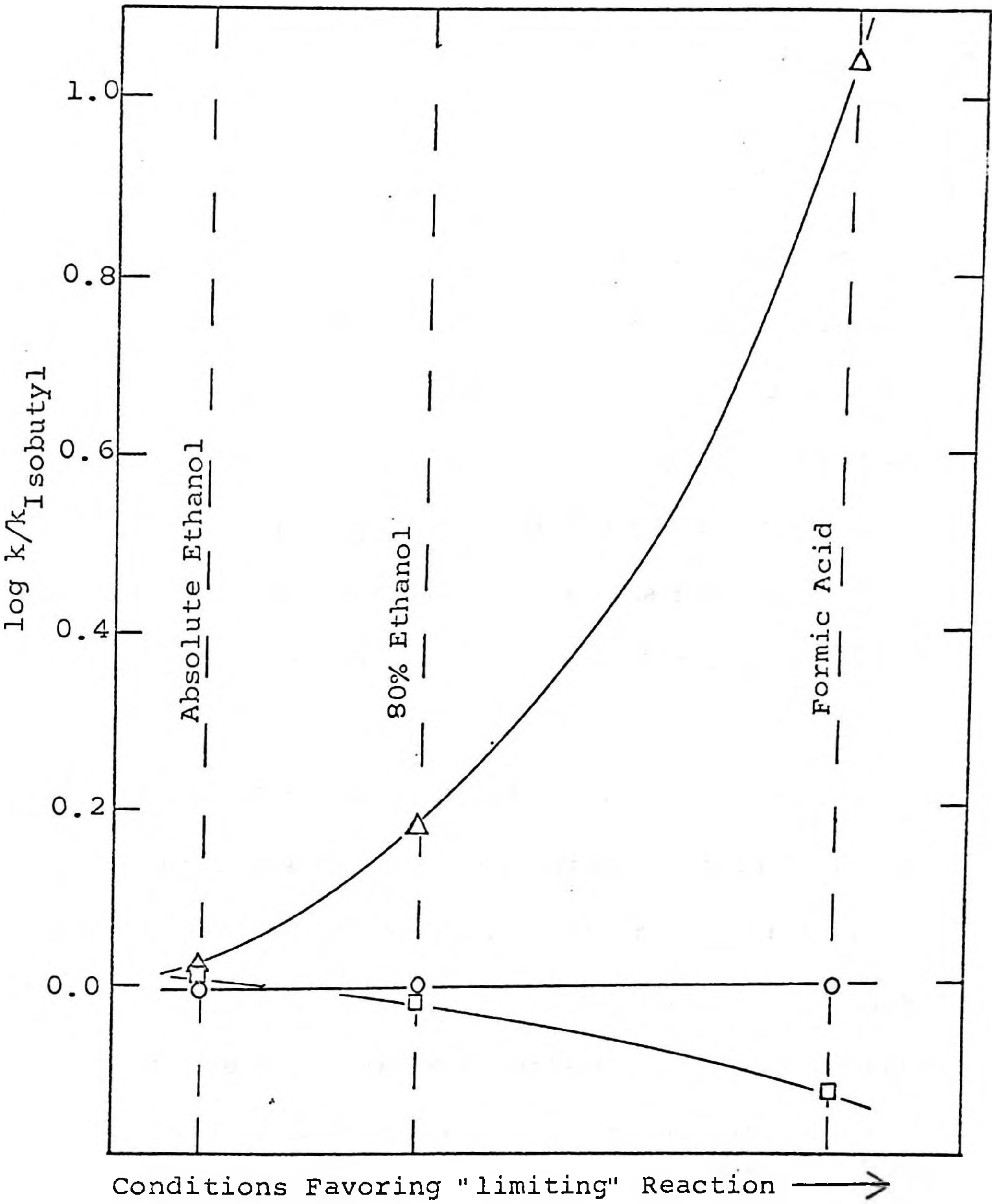

Figure 11. Reactivities of Cyclohexylcarbinyl Tosylate, □, and Cyclopentylcarbinyl Tosylate, △, Relative to Isobutyl Tosylate, ○, in Various Solvent Systems.

0.35. It is interesting to note that the m values for isobutyl and cyclohexylcarbinyl tosylates are quite close to the value of 0.26 reported for ethyl tosylate,[4] a compound whose solvolysis would be expected to proceed by a mechanism requiring only a small degree of charge development in the transition state. On the other hand, the m value for cyclopentylcarbinyl tosylate is fairly close to that reported for benzyl tosylate, 0.39,[5] a primary tosylate which would be expected to solvolyze by a mechanism involving a transition state receiving considerable charge stabilization.

In view of the pronounced tendency of cyclopentylcarbinyl derivatives to undergo rearrangement as compared to either the corresponding cyclohexylcarbinyl or isobutyl compounds, the most attractive interpretation of the data obtained in these experiments focuses attention on relative abilities of a neighboring alkyl group to assist in the solvolysis reaction as the ionizing power of the medium increases. As has been previously mentioned, intramolecular

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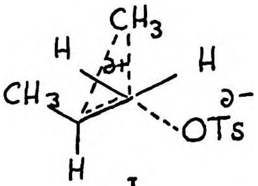
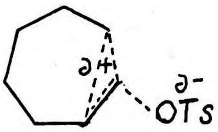
[4] S. Winstein and H. Marshall, <u>J. Am. Chem. Soc</u>., <u>74</u>, 1120 (1952).

[5] <u>Ibid</u>.

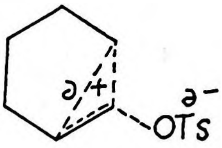
assistance by neighboring β-alkyl substituents has been shown to operate in the solvolyses of primary tosylates, including isobutyl tosylate.[6] Apparently such assistance to solvolysis is operating in the present cases but in strikingly different degrees. Thus, in all cases studied the transition state could be said to possess some bridged-ion character as shown in Structures I, II, III.



I



II



III

Such structures become important only when the solvent ionizing power permits the development of appreciable charge at the site of substitution. Moreover, when such solvent conditions exist, the contributions of structure III are considerably more important to the solvolysis of cyclopentylcarbinyl derivatives than structure I is to the corresponding reactions of isobutyl derivatives, and structure I plays a slightly more important role in reactions of isobutyl derivatives than structure II does in the reactions of corresponding cyclohexylcarbinyl compounds. In

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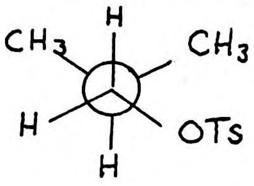
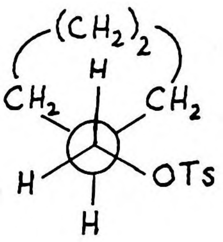
[6] Ibid.

fact, the transition state represented by structure III probably degenerates into an unsymmetrical bridged-ion-pair which more closely resembles a cyclohexyl cation than a cyclopentylcarbinyl cation, and thus the products obtained from reactions in which structure III is important would be expected to be largely rearranged.

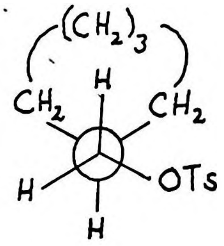
It should be noted in structures IV, V, and VI that



IV



V



VI

the most stable conformation of all three compounds studied has a bond to a β-substituent located in a position from which it can provide "backside" assistance leading to formation of bridged ions. A suggestion for the reason that structure III might be of greater relative importance than structure II is that there would be some relief of the interactions between the partially opposed bonds to ring substituents on the cyclopentane ring when structure III is formed. Since bonds to ring substituents are completely staggered in a cyclohexane ring, there would be no such relief of oppositions in the formation of structure II. In fact, since cycloheptane is slightly less stable than cyclohexane, the formation of II might bring about some small increase in steric interactions, resulting in a relatively less important role for structure II and structure I.

A less attractive explanation for the data obtained in these experiments is that the formation of a relatively free carbonium ion (S_N1 reaction) provides greater relief of oppositions of the carbinyl carbon with β-hydrogens in the case of cyclopentylcarbinyl systems than cyclohexylcarbinyl or isobutyl derivatives. However, such an effect would be very small and provides a basis for little or no correlation with observed relative tendencies for rearrangement.

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