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RESEARCH ON ELECTROCHEMICAL ENERGY CONVERSION SYSTEMS. (U)
JUL 76 A A ADAMS, R T FOLEY

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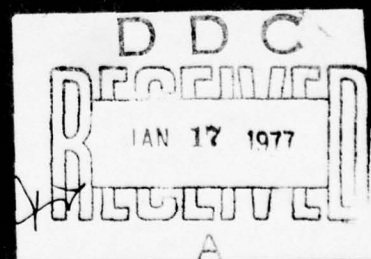
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The same reaction order had been established previously for low molecular weight alkanes in inorganic acids such as HF, H₂SO₄, and H₃PO₄. In the case of each alkane the electrochemical activity in the sulfonic acid was significantly greater than that in phosphoric acid under the same conditions.

The electrooxidation of each alkane was evaluated over the temperature range from 95°C to 135°C.

The experimental data collected during this reporting period confirm the previous finding that trifluoromethanesulfonic acid monohydrate represents an improved electrolyte for the hydrocarbon-air fuel cell.

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Research on Electrochemical Energy Conversion Systems

Final Technical Report

by

A. A. Adams and R. T. Foley

July 1976

to

U. S. Army Mobility Equipment Research
and Development Command

Fort Belvoir, Virginia

Prepared by

The American University

Washington, D. C.

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SUMMARY

The project on electrochemical energy conversion systems has involved two tasks: the determination of the electrochemical behavior of low molecular weight hydrocarbons and alcohols as well as other possible fuels in trifluoromethanesulfonic acid monohydrate and the examination of the electrochemical interaction of fuel cell reactants with platinum surfaces in trifluoromethanesulfonic acid monohydrate.

The order of reactivity for low molecular weight alkanes was determined to be $C_3H_8 > C_2H_6 > n-C_4H_{10} > CH_4$ in trifluoromethanesulfonic acid monohydrate. The same reaction order had been established previously for low molecular weight alkanes in inorganic acids such as HF, H_2SO_4 , and H_3PO_4 . In the case of each alkane the electrochemical activity in the sulfonic acid was significantly greater than that in phosphoric acid under the same conditions.

The electrooxidation of each alkane was evaluated over the temperature range from 85° to 135°C.

The experimental data collected during this reporting period confirm the previous finding that trifluoromethanesulfonic acid monohydrate represents an improved electrolyte for the hydrocarbon-air fuel cell.

FOREWORD

This research on electrochemical energy conversion systems has been sponsored by the U.S. Army Mobility Equipment Research and Development Command at Fort Belvoir, Virginia, under Contract No. DAAG 53-76-C-0001 with The American University. The work was authorized under DA Project/Task Area/Work Unit No. 1T161102A34A 03 100 EF.

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1.0 Introduction

This is the final technical report on Contract No. DAAG 53-76-C-0001 sponsored by the U.S. Army Mobility Equipment Research and Development Command at Fort Belvoir, Virginia. The project entitled "Research on Electrochemical Energy Conversion Systems" consists of two technical tasks both of which are directed toward the investigation of the properties of trifluoromethanesulfonic acid monohydrate as an electrolyte for the hydrocarbon-air fuel cell.

Task I: The determination of the electrochemical behavior of low molecular weight hydrocarbons and alcohols as well as other possible fuels in trifluoromethanesulfonic acid monohydrate.

Task II: An examination of the electrochemical interaction of fuel cell reactants with platinum surfaces in trifluoromethanesulfonic acid monohydrate:

The main effort during this reporting period was devoted to Task I.

2.0 Task I The Determination of the Electrochemical Behavior of
Low Molecular Weight Hydrocarbons and Alcohols in Aqueous
Trifluoromethanesulfonic Acid

2.1 Introductory

The previous study of trifluoromethanesulfonic acid monohydrate demonstrated the dramatic effect of the electrolyte on fuel cell performance (1). Hydrogen and propane electrooxidations were shown to support significantly higher current densities than those obtained in phosphoric acid and the reduction of air began from a higher open circuit potential. The net effect is a theoretical complete, energy producing cell substantially higher energy density than that available from the present state-of-the-art.

The rates of electrooxidation of the low molecular weight alkanes have been shown to follow the series $C_3H_8 > C_2H_6 > n-C_4H_{10} > CH_4$ in the common inorganic acid systems (2). It is of theoretical and practical interest to investigate this series of alkanes in $CF_3SO_3H \cdot H_2O$ to determine the relative electrooxidation characteristics. Further, from a technological standpoint, the detailed investigation of methane electrooxidation is of considerable importance due to the availability of methane as a high purity fuel.

2.2 Experimental

Electrochemical apparatus and techniques

The cell used for the experiments was a standard three-compartment cell. The cell used for the experiments on trifluoromethanesulfonic acid monohydrate shown in Figure 1 was of approximately 30 ml capacity. The working electrode in the central compartment of the cell consisted of a platinum wire mesh electrode of approximately 4.0 cm^2 real surface area spot-welded to a platinum wire lead. The counter electrode compartment was separated from the working compartment by a fritted glass disc. The counter electrode (left compartment, Figure 1) was platinized platinum mesh connected to a platinum wire lead.

The reference electrode system was separated from the working electrode compartment by inserting a fritted glass disc behind the Luggin capillary. The reference electrode is of the dynamic reference electrode design of Giner (3). This reference electrode system consists of two platinized platinum electrodes [A] and [B]. When a current density of 1 ma/cm^2 is impressed between electrode [A] and [B], H_2 is evolved from the cathode, [A], and O_2 is evolved from the anode, [B]. The cathode is kept 1 - 2 cm lower than the anode to prevent diffusion of O_2 from the anode to the cathode. Temperature control was achieved by maintaining the cell in an air oven.

The potential-time sequence shown in Figure 2 was used to determine the "real" surface area of the electrode. The pretreatment

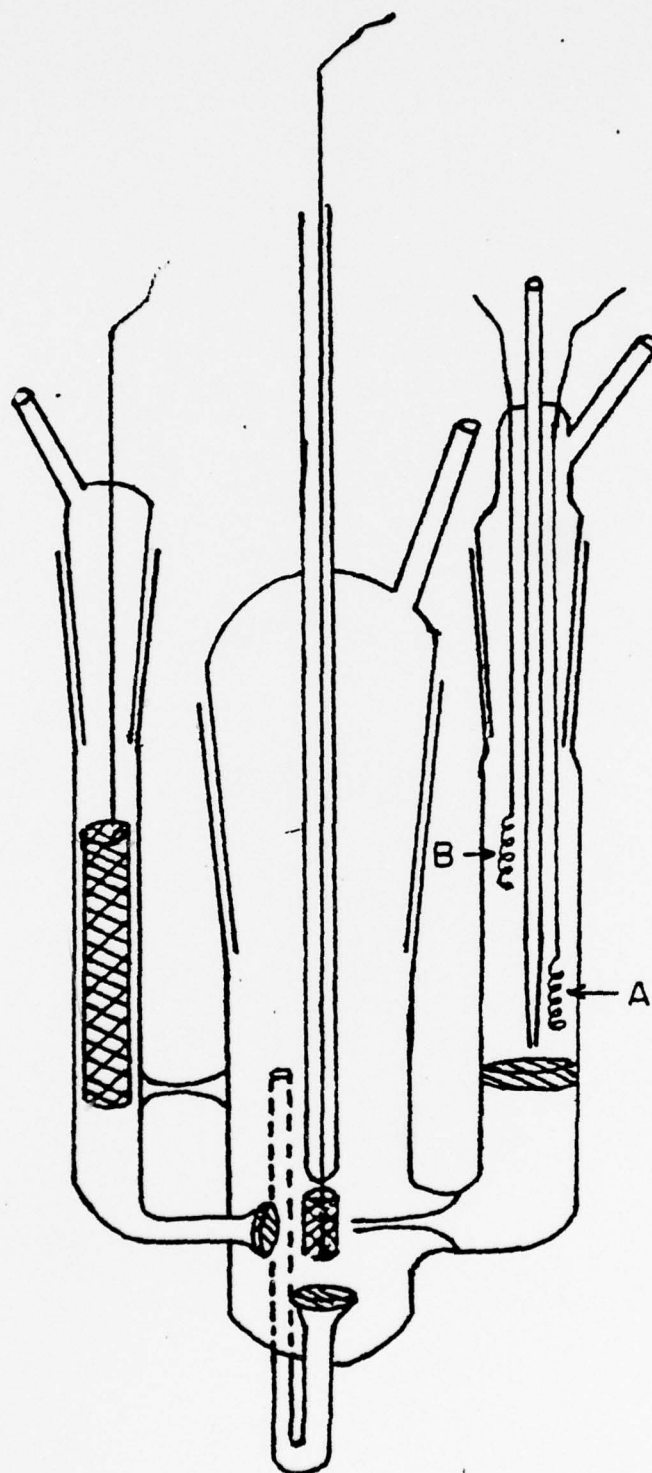


Figure 1. Electrochemical cell used for experiments with trifluoromethanesulfonic acid

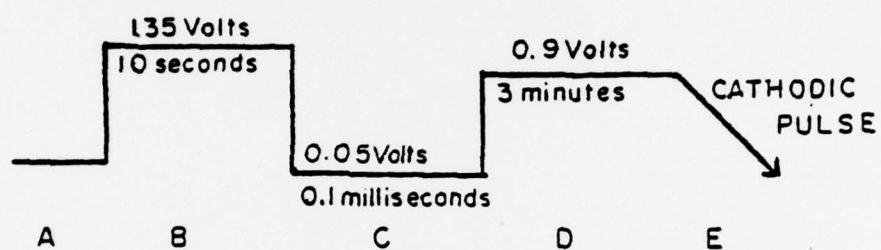


Figure 2. Potential-time sequence used to determine real surface area of electrodes.

steps are used to prepare a reproducible electrode surface for each measurement. During step B the electrode is brought to +1.35 volts which oxidizes oxidizable impurities on the electrode surface and forms a passive oxide layer on the platinum surface. The potential is stepped down to +0.05 volt, step C, where the oxide layer is reduced. The potential is then raised to 0.95 volt, step D, to desorb H atoms adsorbed at 0.05 volt. Step D was set at 0.95 volt after variations in measured surface areas were observed when potentials below 0.75 volt were used. Potentials above 0.75 volt gave reproducible values for the surface area. A cathodic galvanostatic pulse of 25 to 75 milliamps/cm² was applied, (step E), to measure the charge associated with the coverage of hydrogen. The maximum cathodic galvanostatic charge for depositing H atoms on a clean electrode prior to H₂ evolution, after correction for double layer effects, is 210 μ coulombs/cm². It is known that this value changes with temperature and electrolyte composition to some degree, however, within experimental limitations used here, the value of 210 μ coulombs/cm² may be used (4).

Current density vs. potential diagrams were constructed with measurements for helium, methane, ethane, and n-butane. Experiments with all gases were run at 95°, 115°, and 135°C. An automated electrochemical station, designed previously, was used to develop the current-potential diagrams (1). The schematic of the system is shown in Figure 3. The system consists of A, the programmable timing controller, B, the potential step device, C, the basic electrochemical system, D, the data acquisition system, and E, the computer to

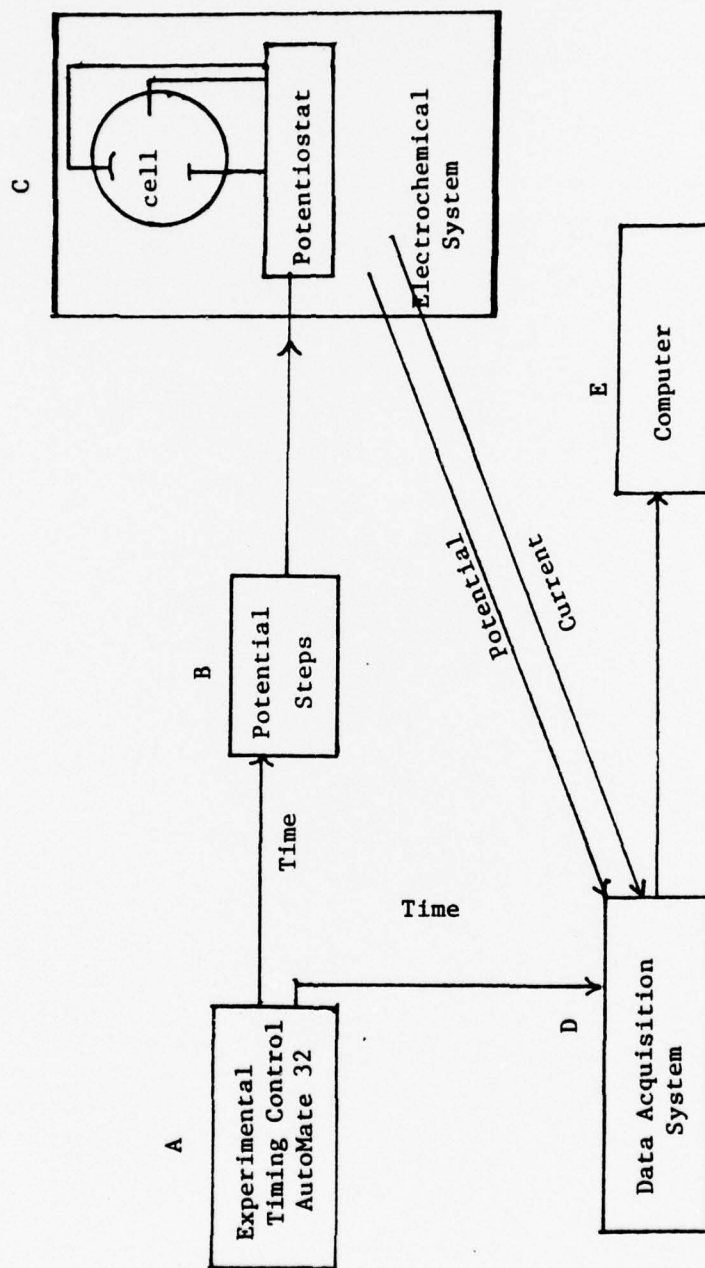


Figure 3. Schematic diagram of automated electrochemical station

process data.

The programmable timing controller, an AutoMate 32 (Reliance Electric Company, Cleveland, Ohio 44177), is a solid-state device having a stored program which controls outputs in a predetermined way in response to the action of the inputs. The major elements of the AutoMate 32 are shown in Figure 4. In addition to those shown, there is a manual programmer with its internal memory and processor which is used to program the Erasable Programmable Read Only Memory (EPROM). The major elements of the AutoMate 32 are A, the controller chassis, containing the power supply, processor and controller monitor; B, input cards; C, output cards; D, timer counter latch (TCL) cards; E, program memory module; F, communication interface and G, input and output blocks which connect with the input or output cards in the controller chassis. The analog timer elements (Model 325), mounted in the TCL card, are adjustable from 0.5 to 127.5 seconds per timer element. Times longer than 127.5 seconds are controlled by counter elements. Programming is done via a ladder diagram which symbolically represents the elements of the control circuit. The input devices and interlocking contacts are placed in the desired parallel or series combinations across the rung of the ladder with the last element on the rung being the output associated with the sequence.

The potential step device shown in Figure 3 has a variable base potential step and 2 times, 4 times, and 8 times this base step. These steps can be used individually, or in any combination, allowing 15 possible potential steps. These steps are programmed in any

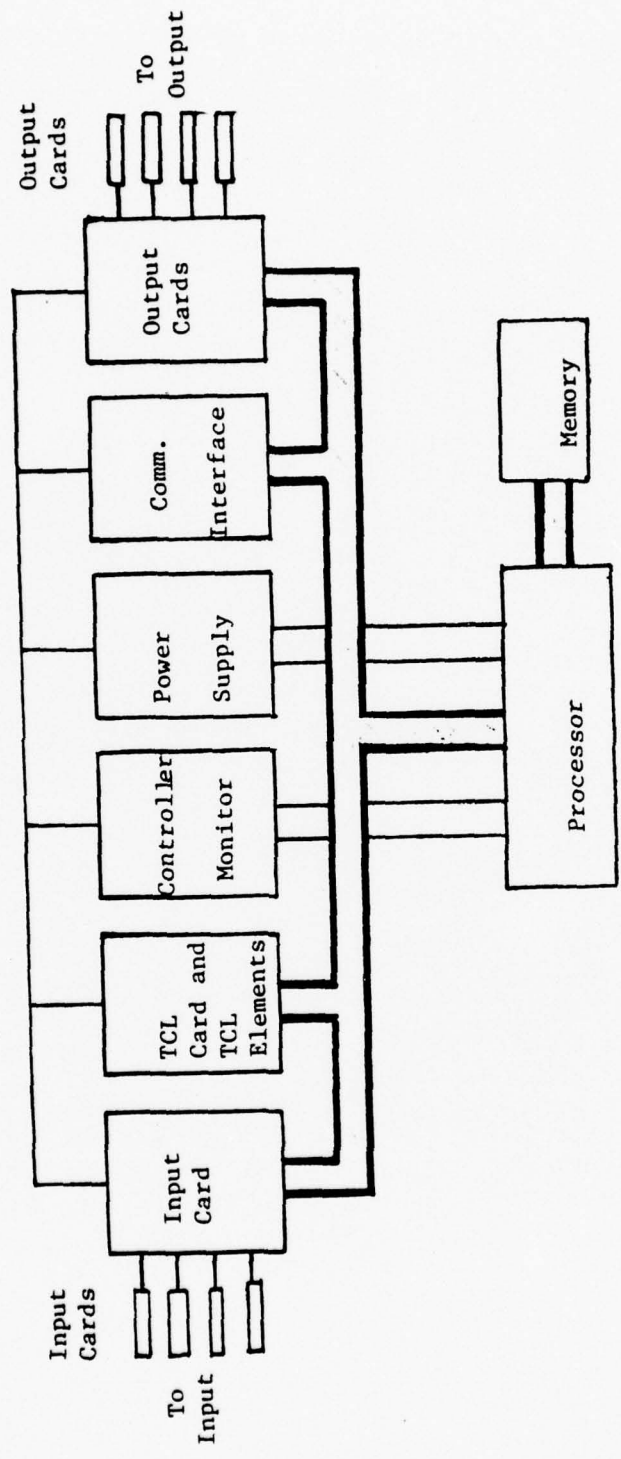


Figure 4. Major elements of Automate 32

sequence from the controller. If the base potential step is 10 mv a total of 150 mv may be algebraically added in 10 mv steps to the potential set in the potentiostat. If 50 mv is the base potential step, 750 mv may be added to the set potential. Initially the device has been used for development of current potential diagrams where time at each potential step is equal. However, it is possible to vary the time at any step or steps allowing great flexibility of the system.

The basic electrochemical unit is the potentiostat with function generator or galvanostat plugin and the electrochemical cell. This portion of the overall system can be used manually in the traditional manner or be tied to the controller for automated control.

The data acquisition system, Dymec DY-7061, (D in Figure 3) consists of a 25 channel input scanner (Model No. 2901B, Dymec Division, Hewlett Packard, Palo Alto, California), a digital clock (Model No. 3440A), a digital recorder (Model No. N39562A) and a paper tape punch (Model No. 5655). The data acquisition system scans up to 25 input signals, measures the dc voltage of each signal, and records the voltage measurements. This data system is adequate to record data for current-potential diagrams, but to cope with faster reactions, this portion of the electrochemical station will have to be updated. At this time, data are taken in eight channels, 2 for potential and 6 for current for a set period of time after equilibration time at a set potential (e.g., 30 seconds data recording after 5 minutes equilibration time.) For example, 18 current points and 6 potential points are recorded.

The computer (Xerox Sigma 2) processes the data, at present

stored on punch paper tape, to read potential and current density values. The current values over all channels scanned are averaged and divided by the real surface area of the electrode. The average potential values and current density values are output to the printer for future graphing of data. The graphing could be done via the computer by an addition to the computer program.

The entire system allows for automated control of the basic electrochemical system with data recorded and stored for future processing. This capability allows the basic system to be run overnight when no operator is available, or, particularly for current-potential diagrams, relieve the operator from the tedious task of taking data at prescribed intervals. Also, a greater number of current readings can be taken, allowing for greater precision in the current readings than is possible with a single reading by the operator.

Preparation of electrolytes

Trifluoromethanesulfonic acid monohydrate was prepared from trifluoromethanesulfonic acid (3M Corp., Lot 7 "Fluorochemical Acid FC-24") and water by the method of Gramstad and Haszeldine (5). Equimolar quantities of trifluoromethanesulfonic acid and water were added to a distillation flask. Fractional distillation was carried out with the fraction below 110°C collected and removed. The fraction above 110°C was collected as a white crystalline product with some viscous clear liquid. This fraction was distilled a second time with all material distilled below 150°C rejected and the fraction above 150°C retained for a third distillation. In the third distillation

only the fraction between 217-218°C (756.9 mm Hg) was retained as a white needle-like crystalline product, trifluoromethanesulfonic acid monohydrate. The $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ was found to have a melting point of 33.8°C which agrees well with the value of 34°C given by Gramstad and Haszeldine (5). No further purification was done before the trifluoromethanesulfonic acid monohydrate was added to the electrochemical cell.

Preparation and treatment of reactants

Helium, methane, ethane, and n-butane were used in different experiments. Helium (AIRCO) was passed over hot copper turnings to remove traces of oxygen before being passed into the cell. Methane (Matheson, high purity), ethane (Matheson, instrument grade), and n-butane (Air Products, instrument grade) were used without pretreatment. All gas lines were heated so that the gas entering the cell was close to the operating temperature of the cell.

2.3 Results and Discussion

The electrochemical behavior of helium, methane, ethane, and n-butane at a smooth platinum electrode in the $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ electrolyte was investigated at various temperatures in the range of normal fuel cell operation. The experiments with helium provided background, or base line, data for the electrolyte. The electrooxidation of methane, ethane, and n-butane were compared with those obtained previously with propane (1). The comparison of results with methane and propane are of significance due to the general availability of methane. The most common impurity in commercial methane is ethane, so the evaluation of ethane is of importance. These compounds also result from the incomplete cracking of hydrocarbon fuels. It has been reported previously that n-butane does not electrooxidize with as high current densities as does propane in the inorganic acids (2). The electrooxidation of n-butane was investigated to determine if this decrease in current levels also held in $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$.

Electrochemical behavior of methane in $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$

Figure 5 summarizes the data for the electrooxidation of methane at 95°C, 100°C, 115°C and 135°C. The current carrying capacity of the electrode clearly rises with the temperature as would be anticipated. The open circuit potential shifted to a slightly lower value with the change in temperature from 95° to 135°C; a total change of from 0.290 volt to 0.275 volt.

The current density at 0.5 volt at 135°C was $1.7 \mu\text{A}/\text{cm}^2$ as compared with $8.2 \mu\text{A}/\text{cm}^2$ for propane (1). Table I summarizes the open circuit

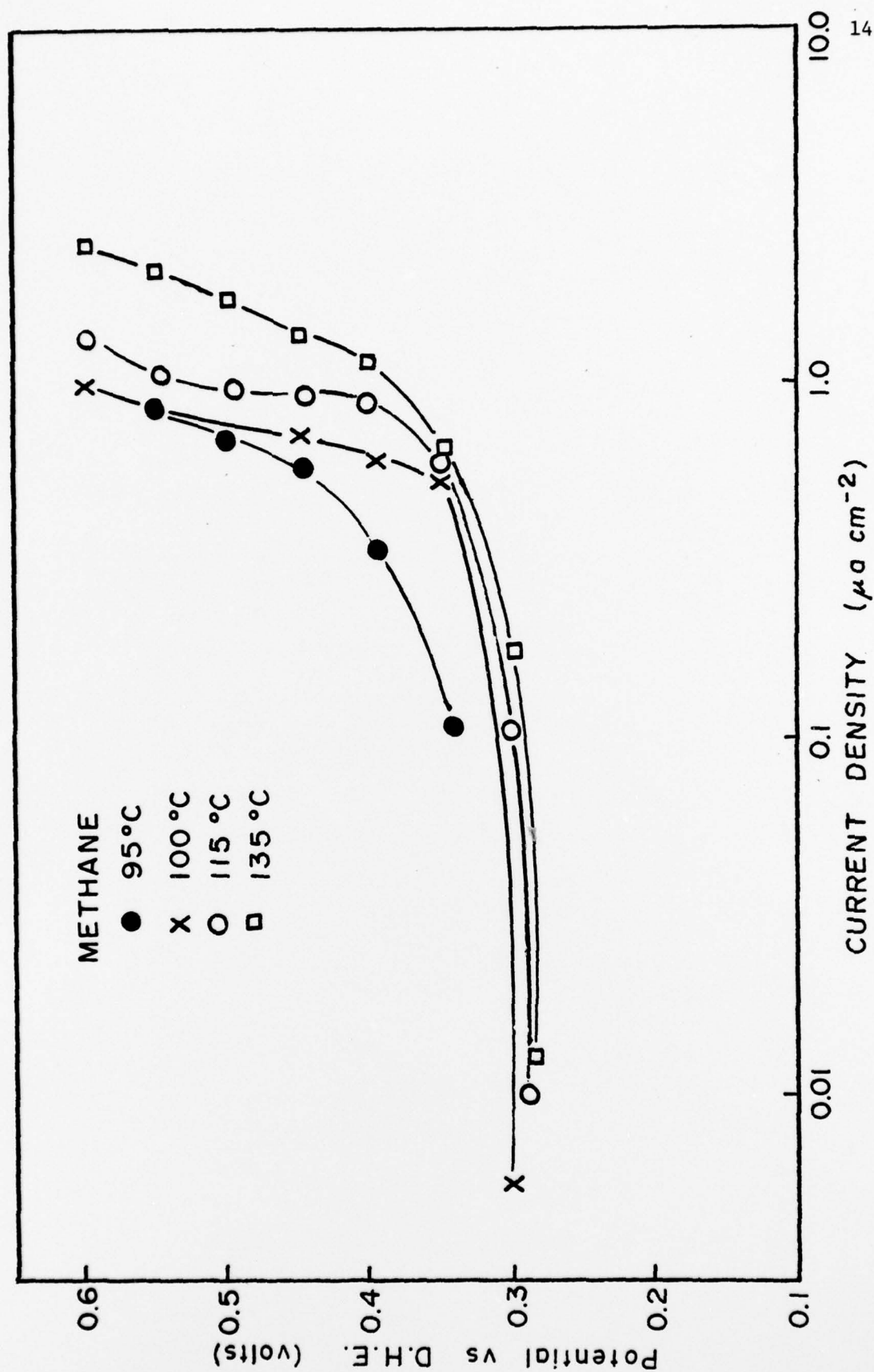


Figure 5. Electrooxidation of Methane in $CF_3SO_3H \cdot H_2O$

TABLE I
COMPARISON OF ELECTROCHEMICAL BEHAVIOR OF METHANE,
ETHANE, PROPANE AND n-BUTANE IN TRIFLUOROMETHANESULFONIC
ACID MONOHYDRATE ELECTROLYTE

		Open Circuit Potential	Current Density at 0.5 Volt
CH_4	95°	290 mv	0.71 $\mu\text{a}/\text{cm}^2$
	100°	285 mv	0.75 $\mu\text{a}/\text{cm}^2$
	115°	282 mv	0.98 $\mu\text{a}/\text{cm}^2$
	135°	272 mv	1.7 $\mu\text{a}/\text{cm}^2$
C_2H_6	85°	295 mv	0.74 $\mu\text{a}/\text{cm}^2$
	100°	290 mv	1.50 $\mu\text{a}/\text{cm}^2$
	115°	268 mv	2.20 $\mu\text{a}/\text{cm}^2$
	135°	265 mv	4.47 $\mu\text{a}/\text{cm}^2$
C_3H_8	95°	285 mv	2.80 $\mu\text{a}/\text{cm}^2$
	115°	280 mv	4.50 $\mu\text{a}/\text{cm}^2$
	135°	272 mv	8.20 $\mu\text{a}/\text{cm}^2$
n- C_4H_{10}	100°	292 mv	1.15 $\mu\text{a}/\text{cm}^2$
	115°	285 mv	1.55 $\mu\text{a}/\text{cm}^2$
	135°	278 mv	3.85 $\mu\text{a}/\text{cm}^2$

potential and current density values at 0.5 volt overvoltage for methane and for the other hydrocarbons evaluated.

Electrochemical behavior of ethane in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$

Figure 6 summarizes the results of the electrooxidation of C_2H_6 at 85°, 100°, 115°, and 135°C. Again, as would be anticipated, the current densities at each potential rise with increasing temperature. The shift of open circuit potential over a 50° temperature difference was about 30 millivolts. At all temperatures the rate of the electrooxidation of ethane was higher than that for methane. At 135°C, at 0.5 volt, the current density, $4.47 \mu\text{a}/\text{cm}^2$, can be compared with $8.2 \mu\text{a}/\text{cm}^2$ for propane in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$.

Electrochemical behavior of n-butane in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$

Figure 7 summarizes the results for n-butane at 100°, 115°, and 135°C in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$. Results with respect to temperature are analogous to methane and ethane. There is a shift in open circuit potential of 14 millivolts over a 35° temperature range for the reaction as is shown in Table I. The current density levels for the n-butane reaction are higher than those for methane but lower than those for propane and for ethane.

Relationship between rate of electrooxidation and hydrocarbon number

The rate of adsorption of methane on a platinum electrode is known to be very slow and small in quantity. Ethane adsorption is more rapid and in larger quantities than methane, yielding higher current densities during the electrooxidation. Propane and n-butane adsorb in a way similar to ethane, with adsorption a function of

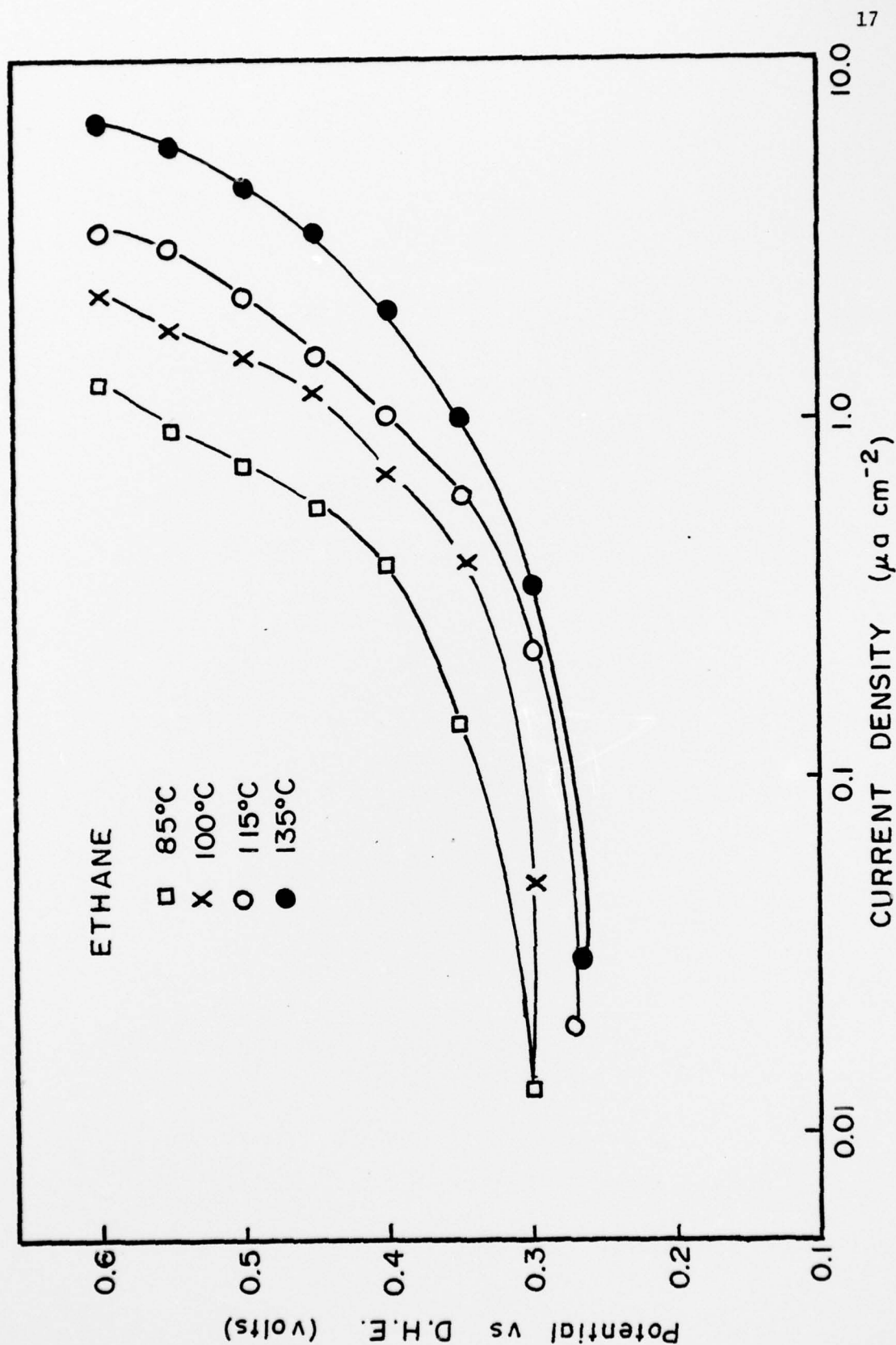


Figure 6. Electrooxidation of Ethane in $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$.

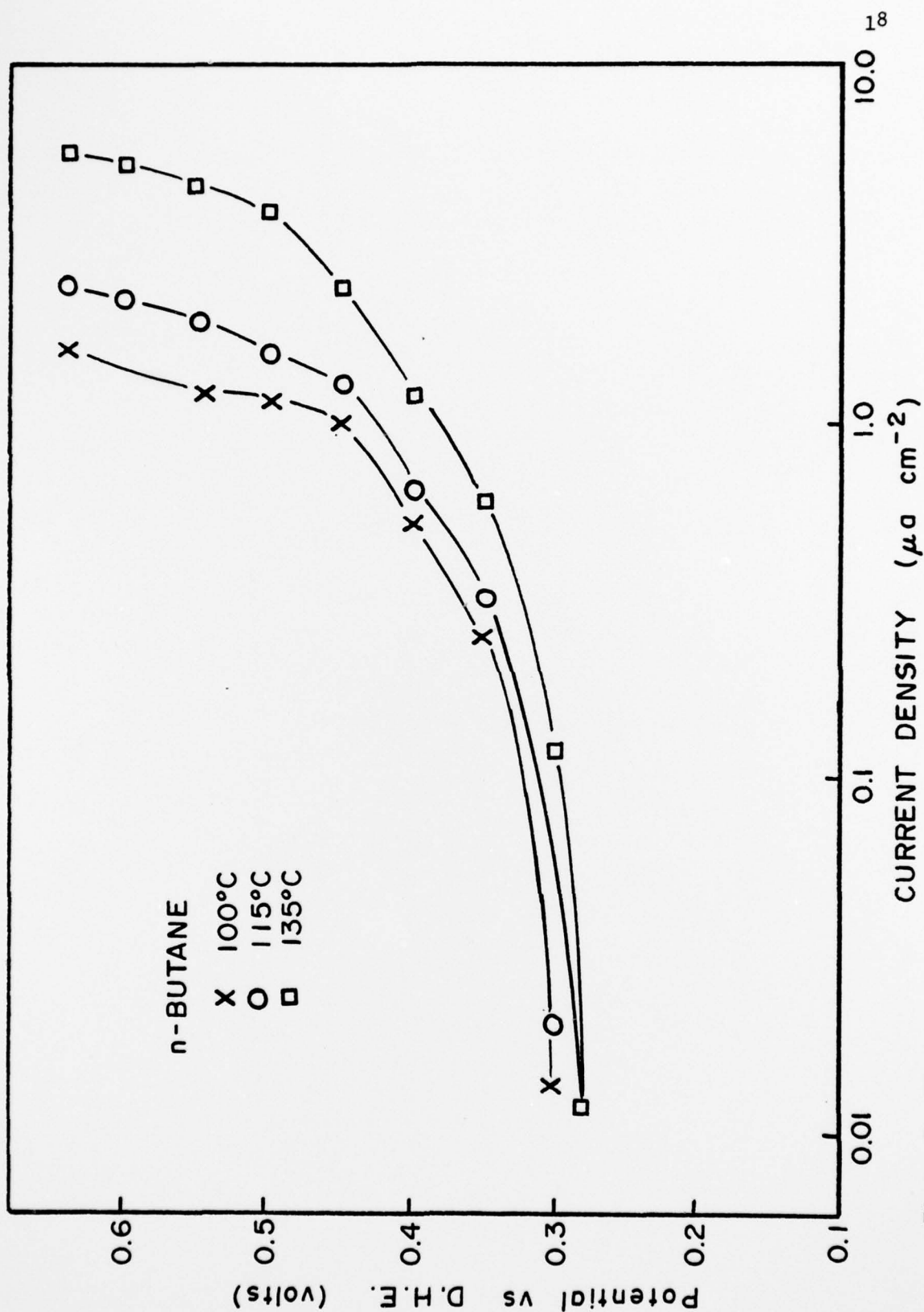


Figure 7. Electrooxidation of n-Butane in $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$.

temperature.

The materials found on the electrode surface have been termed: Type I (O-type), Type II (CH- α), and Type III (CH- β) (6). Type I is oxidized near 0.7 volt, but is not cathodically desorbable. Type II is oxidized at higher potentials and is cathodically desorbable. Type III is slowly oxidized at high potentials and is not reducible. As the carbon number of the alkane goes up, more of the difficultly oxidizable intermediates are formed, resulting in the observed $C_3H_8 > C_2H_6 > n-C_4H_{10} > CH_4$ series in the common inorganic acids such as HF, H_2SO_4 , $HClO_4$ and H_3PO_4 . It was of interest to determine if the alkane reaction was similar on a comparative base in $CF_3SO_3H \cdot H_2O$.

Figure 8 compares the carbon number of the alkane with the relative current density of the alkane with respect to the current density of propane at 0.5 volt at 135°C. As is evident, propane does support the highest current density in $CF_3SO_3H \cdot H_2O$ for the lower molecular weight hydrocarbons. Referring to Table I and previous results (1), the performance of the electrooxidation would be of the order, $C_3H_8 > C_2H_6 > n-C_4H_{10} > CH_4$. Though the activity of ethane, butane, and methane are quite low the results are still of interest. A similar activity series was observed for the inorganic acid electrolytes previously so the results are of interest mechanistically.

The temperature dependence for the electrooxidation of the four hydrocarbons is given in Fig. 9. The calculated activation energies are given in Table II. These values are about certain to only within ± 2 kcal considering the short temperature range but they do indicate extremely low values for the reactions.

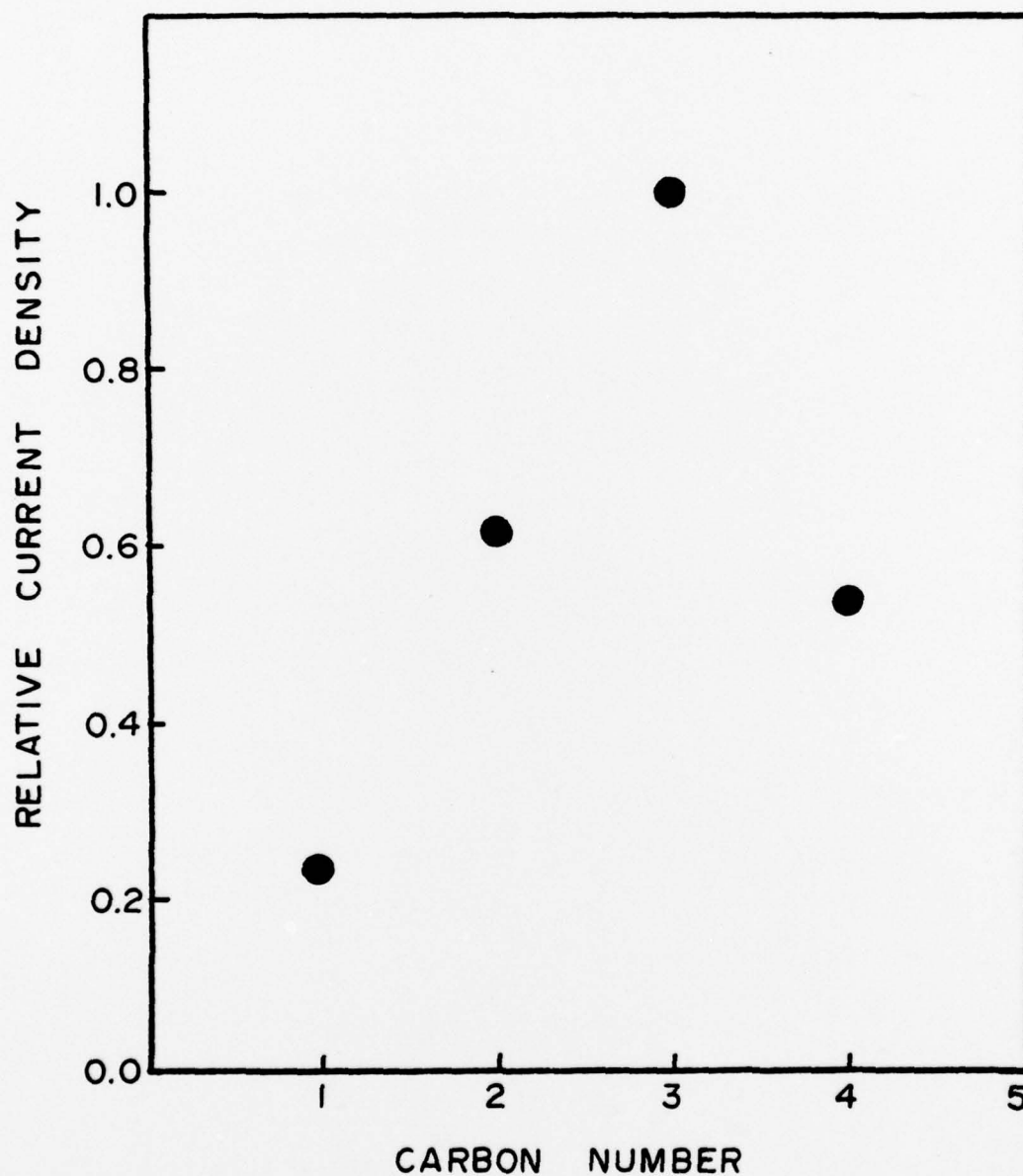


Figure 8. Relationship Between Electrooxidation Rate and Hydrocarbon Number.

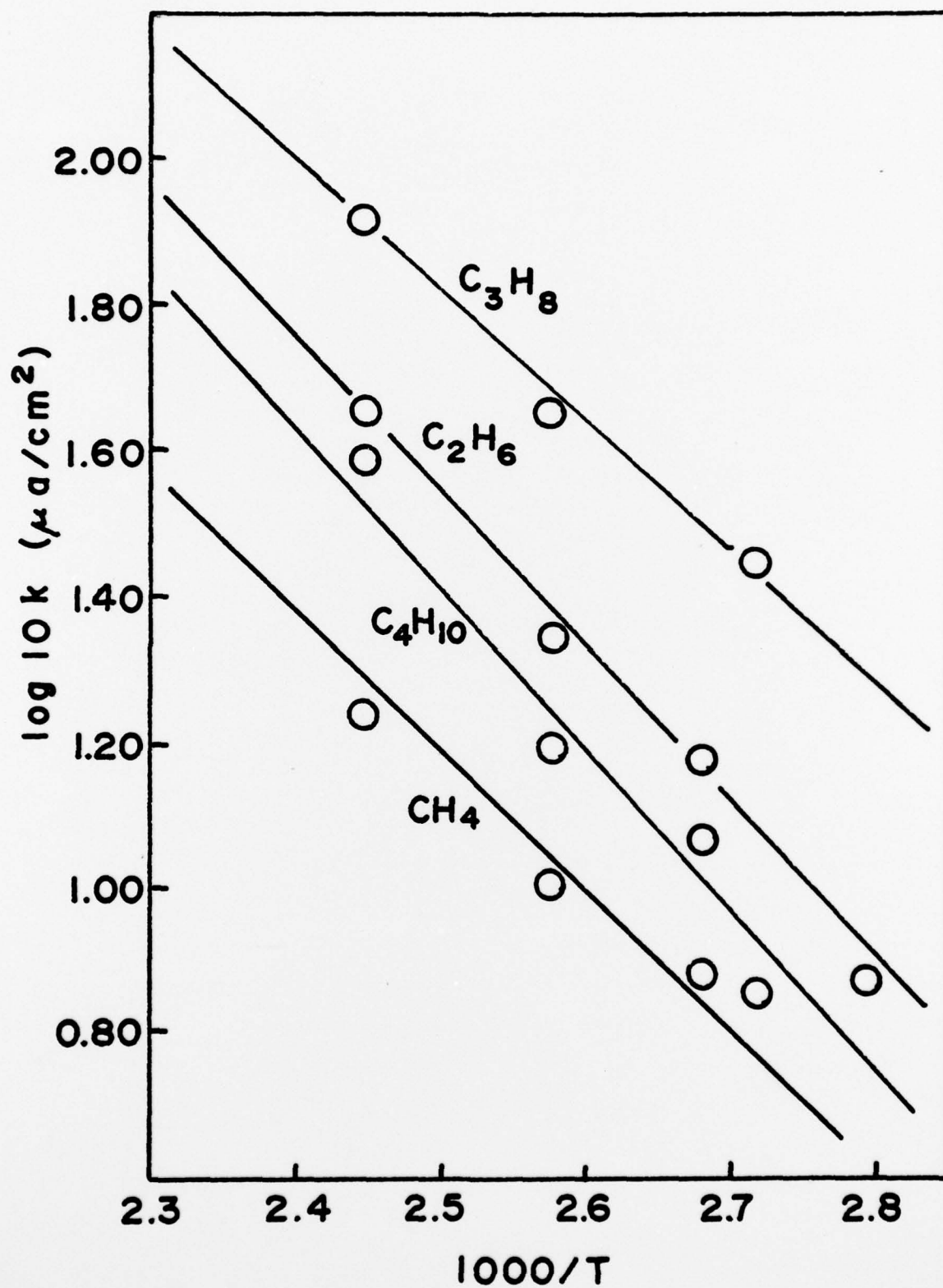


Figure 9. Temperature dependence for the electrooxidation of methane, ethane, propane, and butane.

TABLE II

ACTIVATION ENERGIES FOR ELECTROOXIDATION OF HYDROCARBONS

Methane	8.9 k cal mole ⁻¹
Ethane	9.8 k cal mole ⁻¹
Propane	8.3 k cal mole ⁻¹
n-Butane	10.1 k cal mole ⁻¹

2.4 Conclusions

These experiments indicate that the electrooxidation rates of the C_1 to C_4 alkanes follow the same relative sequence in trifluoromethanesulfonic acid monohydrate as previously observed in aqueous solutions of HF, $HClO_4$, H_2SO_4 , and H_3PO_4 . Propane has the highest oxidation rate but the other lower carbon compounds have sufficiently high rates to make them of interest as potential fuel cell reactants.

These results are net rates for an overall reaction that must involve many steps, so very little can be deduced relative to the mechanism of oxidation. These results, however, when coupled with some of the previous results, suggest that in the direct oxidation of these hydrocarbons, less "undesirable" material, such as polymeric species, are produced in the sulfonic acid.

In perspective, there appear to be certain statements that can be made. It is generally considered that the most active (electrochemically) of the hydrocarbons are those in the C_1 to C_4 range. The results reported here confirm the finding with respect to the general utility of trifluoromethanesulfonic acid monohydrate as an improved electrolyte for the hydrocarbon-air fuel cell.

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