

TABLE I
 URANIUM(V) ALKOXIDES $U(OR)_3$

Empirical formula	Method of prep. (yield, %)	B.p., °C. (mm.)	Analyses, U, %	
			Calcd.	Found
$U(OCH_3)_3$	A(23), C(60)	Sub. 190–210 (0.01) ^a	60.5	60.0
$U(OC_2H_7-n)_3$	B(33), C(73), E(97)	162–164 (0.001) ^b	44.63	44.71, 44.65
$U(OC_2H_7-iso)_3$	B(26), E(89)	Sub. 160° (0.01) ^c	44.63	44.19, 44.25
$U(OC_4H_9-n)_3$	A(41), C(38), E(95)	192–194 (0.001) ^d	39.44	39.36, 39.27
$U(OC_4H_9-iso)_3$	A(32), B(31), E(97)	192 (0.009) ^e	39.44	39.40, 39.09
$U(OC_4H_9-sec)_3$	A(33), B(21), E(91)	175–180 (0.008) ^f	39.44	39.61, 39.28
$U(OC_4H_9-t)_3$	E(95)	Solid, not sublimed ^g	39.44	40.10
$U(OCH_2CF_3)_3$	D(45)	130 (0.008) ^h	32.45	32.55, 32.33
$U(OCH_2CH=CH_2)_3$	B(24)	175–180 (0.015) ⁱ	45.5	44.6, 44.5
$U\{OCH_2CH_2N(C_2H_5)_2\}_3$		Liquid, not dist.	29.1	29.3, 28.6
$U(OCH_2CH_2SCH_2CF_3)_3$		Liquid, not dist.	23.00	22.84, 23.10

^a Red, crystalline solid. The m.p. was above 210° but unfortunately was not carefully determined. ^b Other distillation temperatures: 151–152° (0.0003), 173–175° (0.006). ^c Brown crystalline solid; m.p. 320° dec. Soluble in petroleum ether. ^d Other distillation temperatures: 205–207° (0.008). ^e Brown crystalline solid; m.p. 100–104°. ^f Brown crystalline solid; m.p. 85°. Other distillation temperatures: 180–185° (0.009). ^g Tan crystalline solid, unfortunately no melting point was determined. ^h Brown-green crystalline solid at room temperature, no melting point was determined. ⁱ Some decomposition took place during distillation.

75 ml. of dry 1-propanol was added, and the mixture was stirred for one hour. Following this the mixture was concentrated in a distilling flask, and the residue was distilled under greatly reduced pressure. This procedure is described in greater detail for the preparation of uranium(V) ethoxide.

Uranium(V) 2,2,2-Trifluoroethoxide (Method D).—To a solution of 33.6 g. (0.336 mole) of dry 2,2,2-trifluoroethanol² in 500 ml. of anhydrous ether was added 27 g. (0.065 mole) of freshly prepared, powdered uranium(V) chloride.³ With vigorous stirring dry ammonia gas was passed into the mixture for two hours. The mixture was filtered with careful exclusion of moisture, and the filtrate was concentrated in a distilling flask. The residue of uranium(V) 2,2,2-trifluoroethoxide was a green-brown crystalline solid. It melted when warmed and was purified by distillation under high vacuum.

Uranium(V) *n*-Butoxide (Method E).—To 74 g. (1 mole) of dry 1-butanol was added 83 g. (0.18 mole) of uranium(V) ethoxide. The solution was heated for a short time, and then the alcohols were distilled first at atmospheric pressure, finally under reduced pressure. The brown liquid residue of uranium(V) *n*-butoxide was distilled under high vacuum.

(2) H. Gilman and R. G. Jones, *THIS JOURNAL*, **70**, 1281 (1948).

(3) O. Ruff and A. Heinzelmann, *Ber.*, **42**, 492 (1909).

Uranium(V) Ethoxide from Uranium(V) Isobutoxide and Ethanol.—To 50 ml. of absolute ethanol was added 6.3 g. of solid uranium(V) isobutoxide. A brown solution was formed. This was heated for a short time, and then the alcohol was distilled, finally under reduced pressure. The residual brown liquid was distilled under high vacuum to give 4.4 g. (90% yield) of uranium(V) ethoxide, b.p. 127° (0.007 mm.).

Anal. Calcd. for $U(OC_2H_5)_3$: U, 51.4. Found: U, 50.1, 50.2.

Uranium(V) *t*-Butoxide.—To a solution of 3.4 g. (0.0074 mole) of uranium(V) ethoxide in 10 ml. of dry ether was added 4 ml. of dry *t*-butyl alcohol. A tan solid precipitated. The solvents were distilled, finally under reduced pressure leaving the crystalline *t*-butoxide; yield 4.2 g. (95%).

Anal. Calcd. for $U(OC_4H_9)_3$: U, 39.44. Found: U, 40.10.

The above solid was dissolved in 50 ml. of absolute ethanol and the excess solvent was distilled, finally under reduced pressure. The residual brown liquid was distilled under high vacuum; b.p. 132–135° (0.012 mm.).

Anal. Calcd. for $U(OC_2H_5)_3$: U, 51.4. Found: U, 50.6.

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[CONTRIBUTION FROM THE McPHERSON CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY AND KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

Anodic Reactions. II. The Mechanism of the Kolbe Electrosynthesis¹

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Studies of the mechanism of the Kolbe electrosynthesis lead to the conclusion that only the discharged ion theory appears tenable. This is based largely on an investigation of the kinetics of the electrode processes using variable frequency square wave A-C. This technique is designed to determine the molecularity of the slow step in the sequence of reactions occurring after the initial transfer of an electron to the electrode. Results of studies using square wave A-C indicate that: (a) the order of the reaction of acetic acid at the anode to produce ethane is the same in water and in glacial acetic acid; (b) the reaction in (a) is apparently first order in acetoxyl radicals; (c) the reaction of propionic acid at the anode to produce ethylene (not butane) is apparently second order in propionoxyl radicals. Additional evidence is presented to support these views.

Three theories concerning the mechanism of the Kolbe electrosynthesis³ in aqueous media have been advanced. These are the following: 1. The discharged ion theory proposed by Brown and

Walker⁴ in 1891. The important steps in this mechanism are the direct oxidation of the carboxylic anion and subsequent decomposition of the radicals formed. 2. The acyl peroxide theory proposed by Fichter⁵ in 1925. Fichter contends that the electrode process is not direct oxidation of the

(1) Presented before the Division of Organic Chemistry, 128th meeting of the American Chemical Society, Minneapolis, September, 1955.

(2) Hudson Foam Plastics Corp., Yonkers, New York.

(3) H. Kolbe, *Ann.*, **69**, 279 (1849).

(4) A. Brown and J. Walker, *ibid.*, **261**, 107 (1891).

(5) F. Fichter, *Trans. Am. Electrochem. Soc.*, **45**, 131 (1924).

organic acid but that a diacyl peroxide is the intermediate which gives rise to the products. 3. The hydrogen peroxide theory proposed by Glasstone and Hickling⁶ in 1934. According to this concept hydrogen peroxide or the hydroxyl radical initiates the fatty acid decomposition.

Considerable evidence⁷ has accumulated to support each mechanism but none has received universal acceptance.

An investigation of the kinetics of the reaction was initiated in an effort to decide which mechanism is most reasonable. Accordingly a technique was designed to determine the molecularity of the slow step in the sequence of reactions occurring after the initial electron transfer at the electrode. This, known as the variable frequency square wave technique, is discussed and applied to the Kolbe electrolysis. In addition, other evidence is presented to support the picture established by the kinetics studies.

Experimental

The Square Wave Generator.—This was a motor driven polarity reversing switch made from a war-surplus motor generator and a Cenco variable speed stirrer Model 18805. The commutator was divided into two equal segments separated by strips of bakelite for insulation. Four stationary brushes 90° apart made contact with the spinning commutator. Wire leads from two of the opposing brushes made contact with an Edison cell D-C source while the leads from the other brushes carried current to the electrolysis cell. Varying the speed of the motor stirrer changed the speed of the commutator and hence changed the frequency of the square wave current.

The Circuit.—Figure 1 is a diagram of the square wave circuit. Current from the D-C source was regulated by a slide wire rheostat, measured by a Weston Model 489 D-C ammeter and fed into the square wave generator. From the generator it passed through a Weston Model 528 A-C ammeter and to the electrolysis cell. A Dumont oscillograph Model 208B was connected in parallel with the cell. This was used to measure the frequency of the square wave.

Measurement of Frequency.—Frequency measurements were made by adjusting the sweep frequency of the oscillograph until a stationary pattern of a single square wave was visible. The value was then read directly from the scale on the instrument. This scale is not exact but the same oscillograph was used in all measurements of frequency. It is estimated that the accuracy of the frequency measurements was within 2 cycles/sec.

Measurement of Rate of Gas Evolution.—Rates of gas evolution, required for calculating current efficiencies, were measured in gas burets containing a salt solution.

The Cell.—This was a 150-ml. Pyrex test-tube fitted with a rubber stopper containing the electrodes, a thermometer and gas exit tubes. The stopper was sealed to the cell with collodion. Twenty gage platinum wire pieces, each 1.52 cm.² in area, served as electrodes.

Temperature Control.—Cells were immersed in 2-l. Dewar flasks which were filled with ice-water, ice-salt-water or propanol and Dry Ice depending on the temperature desired.

Preparation of Electrodes.—The electrodes were placed in aqua regia for five minutes. Then, after washing thoroughly with water, they were washed with the solution to be electrolyzed and placed in the cell.

Gas Analysis.—The carbon dioxide, ethylene and ethane were determined by infrared absorption spectrometry.

Samples were collected in a Baird 1028-6 gas analysis cell of approximately 100-ml. capacity having sodium chloride windows and twin brass needle valves for entrance and exit of gases. Gases leaving the electrolysis cell were passed through a Dry Ice trap to remove water vapor and collected in the gas cell by displacement of air. A volume of gas at

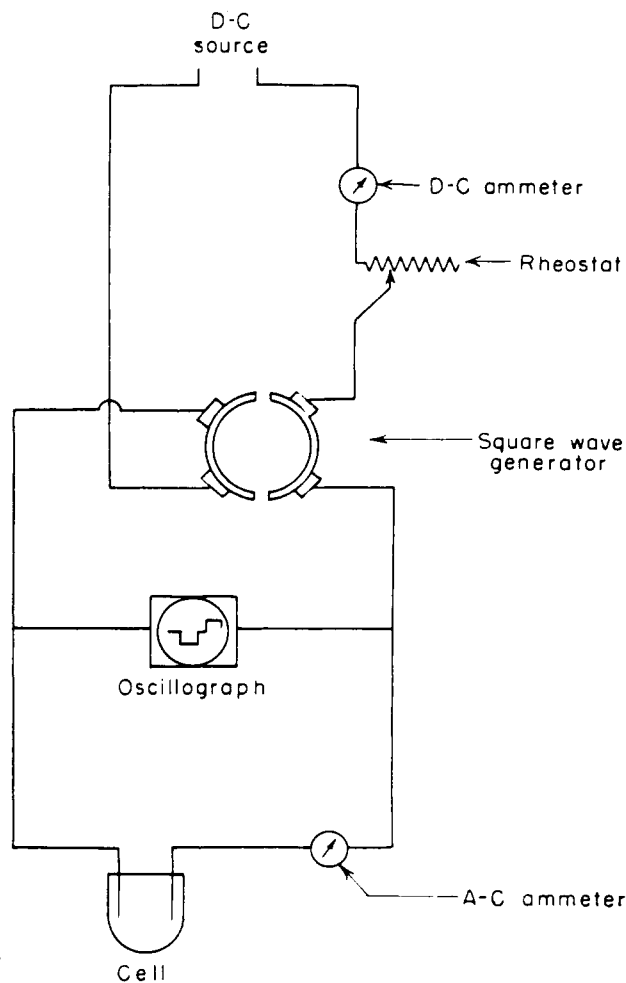


Fig. 1.—Generator circuit for square wave alternating current.

least twenty times the volume of the gas cell was allowed to pass before the needle valves were closed and the sample analyzed. After each analysis the cell was flushed with nitrogen before being used again.

The Baird Infrared Spectrophotometer Model B and the Perkin-Elmer model 12C infrared spectrometer were used to analyze the gases. The latter instrument was used for the kinetics studies.

Calibration curves using pure samples of carbon dioxide, ethane and ethylene were obtained for each of the instruments by regulating the pressure of the gas in the cell using a gas handling system. These curves give directly the relations between peak height and gas pressure. In all analyses two wave lengths were used for each compound, the one serving as a check on the other. For carbon dioxide the bands at 4.4 and 14.8 μ were used, for ethane those at 3.2 and 6.8 μ were used and for ethylene the 3.2 and 10.5 μ bands were used.

Peak heights were determined by the base line density method.

The per cent. of the component in the gaseous mixture was obtained by dividing the pressure of that component by the atmospheric pressure and multiplying by 100.

A check on the infrared analysis of carbon dioxide was made by absorption of the gas in potassium hydroxide.

Electrolyses

Aqueous 5.0 M HOAc, 0.5 M KOAc.—Acetic acid (150 g., 2.5 moles) and potassium acetate (23 g., 0.25 mole) were dissolved in enough water to make 500 ml. of solution.

A 100-ml. portion of this mixture was placed in an electrolysis cell having unused platinum electrodes of 1.52 cm.² in area and placed 2.54 cm. apart. Nitrogen was

(6) S. Glasstone and A. Hickling, *J. Chem. Soc.*, 1878 (1934).

(7) S. Glasstone and A. Hickling, "Electrolytic Oxidation and Reduction," Chapman and Hall, Ltd., London, 1935, pp. 312-317.

bubbled through the solution for two minutes and the square wave current turned on. The current was adjusted to 0.45 amp./cm.² and the temperature to 25°. Samples were taken every hour for four hours after the first 30 minutes. The rate of gas evolution was measured by allowing the gas to pass into gas burets after flowing through the gas analysis cell. The results of analyses for a variety of frequencies are given in Table I. The yields quoted are current efficiencies assuming each electron transferred to the anode should give rise to one-half molecule of ethane and one molecule of carbon dioxide.

Aqueous 7.5 M HOAc, 0.5 M KOAc.—Acetic acid (225 g., 3.75 moles) and potassium acetate (24.5 g., 0.25 mole) were dissolved in enough water to make 500 ml. of solution. This solution was treated exactly as outlined above except that a current density of 0.8 amp./cm.² was used (Table I).

Glacial Acetic Acid, 1.0 M KOAc.—Potassium acetate (9.8 g., 0.1 mole) was dissolved in enough acetic acid to make 100 ml. of solution. This was treated exactly as above except that a current density of 0.8 amp./cm.² was used (Table I).

Aqueous 5.0 M EtCO₂H, 0.5 M EtCO₂K.—Propionic acid (203.5 g., 2.25 moles) and potassium hydroxide (14 g., 0.25 mole) were dissolved in enough water to make 500 ml. of solution. This solution was treated as outlined above. (Table I). Current efficiencies in Table I assume each electron should give one-half molecule of ethylene and one-half molecule of carbon dioxide.

TABLE I
EFFECT OF SQUARE WAVE FREQUENCY IN KOLBE ELECTRO-
SYNTHESIS AT 25°

Fre- quen- cy, cy- cles/ sec.	Current density, 0.45 amp./cm. ²				Current density, 0.8 amp./cm. ²			
	KOAc, 0.5 M HOAc, 5.0 M in H ₂ O	EtCO ₂ H, 0.5 M EtCO ₂ K, 5.0 M in H ₂ O	EtCO ₂ H, 0.5 M EtCO ₂ K, 5.0 M in H ₂ O	EtCO ₂ H, 0.5 M EtCO ₂ K, 5.0 M in H ₂ O	KOAc, 0.5 M HOAc, 1.0 M in HOAc	KOAc, 0.5 M HOAc, 7.5 M in H ₂ O	KOAc, 0.5 M HOAc, 7.5 M in H ₂ O	KOAc, 0.5 M HOAc, 7.5 M in H ₂ O
	C ₂ H ₆	CO ₂	C ₂ H ₄	CO ₂	C ₂ H ₆	CO ₂	C ₂ H ₆	CO ₂
2	86.6	91.3	68.3	84.3				
7	85.4	90.8	48.2	63.2	92.5	91.2		
15	85.0	90.0	40.0	55.4	92.0	90.4	88.4	92.6
25	84.3	89.4	36.3	51.6				
30	83.6	88.7	34.4	49.5	93.2	91.0	88.6	93.5
40	82.1	87.2	33.2	47.8			87.3	92.5
50	81.6	87.0	32.4	47.0	92.6	92.4	88.2	91.9
69	80.7	86.5	30.8	46.5	93.3	91.8		
80	79.2	84.8	30.2	46.5				

Discussion

Variable Frequency Square Wave Treatment.

Square wave alternating current is similar to direct current in that the potential at the electrode is constant when current is flowing. However, if the frequency of the square wave is greater than 2 cycles per second, the steady state which is set up at the electrode during ordinary D-C electrolysis is never attained.⁸ In the absence of the steady-state simple kinetic considerations apply. If the square wave frequency is varied over a reasonable range and the yield of products plotted as a function of the frequency, the shape of the resulting curve will indicate whether the rate-determining process is first or second order. These considerations apply only when the process is not diffusion controlled.

This can be made clearer by reference to Fig. 2. The three wave patterns in this figure represent three different frequencies. The length of the top bar represents the time that current is flowing at each electrode in each cycle. Radicals are being produced as long as the current is flowing, which means that twice as many radicals are produced in one cycle of (1) than in one cycle of (2), etc. How-

ever, by allowing the cycles to be repeated n times in the first case, $2n$ times in the second case, and $4n$ times in the third case, the total number of radicals produced is the same in each case. But, since the radicals in one cycle cannot last until the next cycle starts, all radicals must react during the cycle in which they are formed. This has important consequences if the reaction is second order, because at low frequencies a large number of radicals are formed per cycle, whereas at high frequencies only a few radicals are formed per cycle. Hence, since the radicals must pair up to react, the yield will be higher at low frequencies than at high frequencies.

If, however, the reaction is first order there should be only a slight dependency of yield on frequency. This dependence is due partly to the time necessary to charge the double layer during each cycle and to the relative number of radicals destroyed when the current reverses. The reason for the weak frequency dependence in the first-order case is that the total number of radicals produced in (1), (2) and (3) of Fig. 2 is the same and if the energy distribution among these radicals is Maxwellian their decomposition rate will not depend on the number produced per cycle but only upon the total number produced in a given time.

Mathematical analysis of this treatment is as follows. Consider the electrode reaction proceeding under D-C conditions but before the steady state has been set up. Assume that the radical R formed at the electrode can react to form the products by a series of consecutive reactions only one of which is slow. Finally, assume for simplicity that this slow step is either first or second order.

For the first-order path the equations are

$$d[R]/dt = I - k_1[R] \quad (1)$$

$$d[\text{Products}]/dt = k_1[R] \quad (2)$$

where $[R]$ is the concentration of radicals in mole/l./cm.² of electrode surface, I is the equivalents of electricity passed per sec. for each cm.² of electrode surface, k_1 is the specific rate constant for the first-order radical reaction, $[\text{Products}]$ is the concentration of products in mole/l./cm.² of electrode surface and t is time in sec.

Integration of 1, substitution in 2 and subsequent integration of 2 neglecting square terms and higher gives

$$[\text{Products}] = It - \frac{I}{k_1} (1 - e^{-k_1 t}) \quad (3)$$

In the second-order case the equations are

$$d[R]/dt = I - k_2[R]^2 \quad (4)$$

$$d[\text{Products}]/dt = k_2[R]^2 \quad (5)$$

where the symbols have their previous significance except that k_2 is now the specific rate constant for the second-order radical reaction. Proceeding as before and again neglecting square terms and higher gives

$$[\text{Products}] = It/4 (1 - t\sqrt{Ik_2}) - (\sqrt{I/k_2}) \log_e 2 \quad (6)$$

Equations 3 and 6 apply to one cycle only of the square wave current. The quantity It represents the amount of current passed during one cycle and $[\text{Products}]/It$ will, therefore, be a measure of current efficiency.

Rewriting equations 3 and 6 to express current

(8) B. Ershler, *Disc. Faraday Soc.*, **1**, 269 (1947).

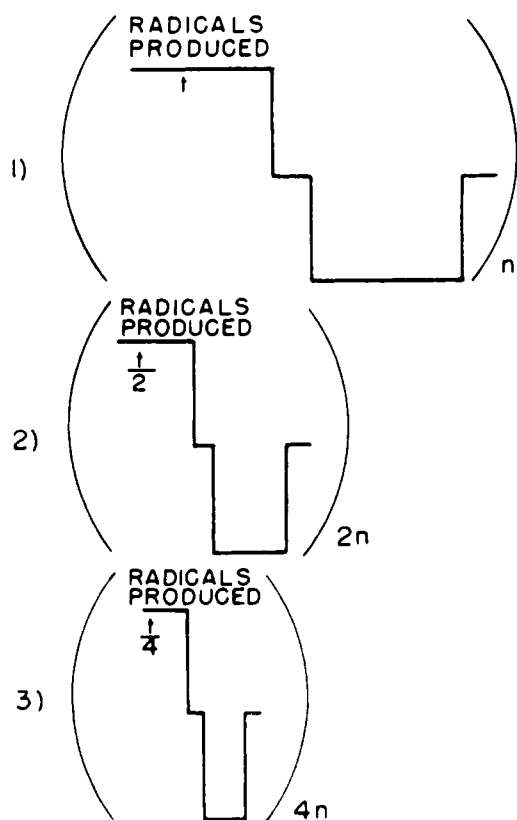


Fig. 2.—Wave patterns for variable frequency square wave treatment.

efficiency and substituting f for frequency, *i.e.*, the reciprocal of t , gives

$$\text{current efficiency (1st order)} = 1 - (f/k_1)(1 - e^{-k_1/f}) \quad (7)$$

$$\text{current efficiency (2nd order)} = \frac{1}{4f}(f - \sqrt{Ik_2}) - f(\log 2)/\sqrt{Ik_2} \quad (8)$$

It will be seen that if equation 7 is followed and the radicals disappear by a first-order reaction then current efficiency will be almost linear with respect to frequency but with a small negative slope ($-(1/k_1)(1 - e^{-k_1/f})$) whereas if equation 8 is followed and the radicals disappear by a second-order reaction then the relationship is more complex but characterized by a rapidly falling current efficiency at high values of frequency.

Application to the Kolbe Electrosynthesis.—The results of applying square wave current to the Kolbe reaction are recorded in Table I and Fig. 3. In all instances the current densities were sufficiently low so that diffusion was not rate determining. This was shown by the absence of dependence of products on speed of rotation of the anode.⁹ Three important conclusions can be deduced from the results. The first is that the order of the reaction of acetic acid is the same in water and in glacial acetic acid. Table I shows that the reaction is only slightly dependent and in a linear fashion on frequency in both solvents. This strongly suggests that the mechanism is the same in both solvents and presents strong evidence against the

(9) C. L. Wilson and H. V. Udupa, *J. Electrochem. Soc.*, **99**, 291 (1952).

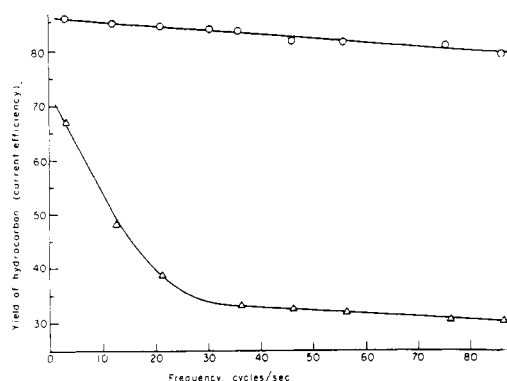


Fig. 3.—Effect of frequency on ethane and ethylene formation during square wave electrolysis of aqueous acetate and propionate. (Current density, 0.45 amp./cm.² temperature, 25°. O, ethane from 5.0 M HOAc, 0.5 M KOAc in H₂O; Δ, ethylene from 5.0 M HO₂CEt, 0.5 M KO₂CEt in H₂O.)

hydrogen peroxide theory since the electrode reaction in glacial acetic acid must, of necessity, be a direct reaction of the acid molecule.

The second conclusion is based on the only slight frequency dependence of the anodic decomposition of acetic acid (Fig. 3). This indicates a first-order decomposition of the radicals formed at the electrode and when combined with the conclusions stated above suggests that the slow step is decomposition of acetoxy radicals. Fichter's acyl peroxide theory requires that the reaction be second order in the radicals produced at the electrodes.

The third conclusion is obtained from the anodic oxidation of propionic acid to produce ethylene. This product can be obtained exclusively if the reaction is carried out at 25°. Ethylene production (Table I, Fig. 3) is strongly frequency dependent at low square wave frequencies which indicates a second-order reaction. This suggests a reaction involving two propionoxy radicals and simultaneously argues against formation of an acyl peroxide on the grounds that the peroxide would not be expected to yield ethylene exclusively even under the catalytic influence of the electrode.

The classic experiments of Holum and Clusius¹⁰ in which they showed that both β,β,β -trideuteropropionic acid and α,α -dideuteropropionic acid give 1,1-dideuteroethene at the anode suggests, in light of the kinetics studies, that when two propionoxy radicals react one extracts a β -hydrogen atom from the other. The biradical thus formed decomposes to give ethylene. This would also account for the low current efficiency in ethylene production.

Two additional pieces of evidence lend support to the conclusions stated above. The first is the fact that when anisole is added to an aqueous acetic acid solution and this mixture electrolyzed, O-acetoxyanisole is isolated in good yield.¹¹ This clearly shows that acyloxy radicals have finite lifetimes. The second piece of evidence is the fact that addition of hydrogen peroxide to an aqueous acetic acid mixture during D-C electrolysis results in a sharp decrease in the ethane yield from about

(10) P. Holum and K. Clusius, *Ber.*, **70**, 819 (1937).

(11) C. L. Wilson and T. Hayashi, Abstracts of Papers Presented at 120th Meeting of the American Chemical Society, New York, 1954.

88 to 55% while carbon dioxide remains unchanged at 95%. Hydrogen peroxide, therefore, is not a likely intermediate in this reaction as the Glassstone-Hickling theory predicts. The data in Table I illustrate some other interesting features relative to the Kolbe reaction and are worthy of comment. It will be recalled that the stoichiometry involved in the calculation of current efficiency assumes that the transfer of two electrons gives rise theoretically to one molecule of ethane and two molecules of carbon dioxide in the case of acetate and one molecule of ethylene but only *one* molecule of carbon dioxide in the case of propionate. The correctness of the assumption is borne out by the results. It is noteworthy that efficiency for both ethane and carbon dioxide are higher in acetic acid than water. This is because oxygen formation is greater in wa-

ter. On the other hand hydrocarbon efficiency is generally lower than carbon dioxide efficiency. This is pronounced with propionate at high frequencies. The reason must be further oxidation of the radical or the hydrocarbon to non-gaseous products. These considerations do not, however, affect the mechanistic arguments made earlier.

Acknowledgments.—The authors wish to thank Drs. F. H. Verhoek, Boris Musulin and S. E. Lippincott for their helpful advice during the course of this investigation. They also wish to thank the du Pont Company for the Teaching Fellowship granted to W.T.L., and Mr. Kiefer Newman for designing and building the square wave generator.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

Isotope Effects in Carbonium Ion Reactions. II. The Decomposition of *p*-Toluenediazonium Ion¹

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A precise method for the measurement of diazonium salt decompositions is described. The rate of decomposition of *p*-trideuteriomethylbenzenediazonium ion in aqueous acid is shown to be about 1% faster than that of the undeuterated compound. The difference, which is significant, is understandable in terms of bond weakening by hyperconjugation and an aryl cation intermediate in diazonium salt decomposition.

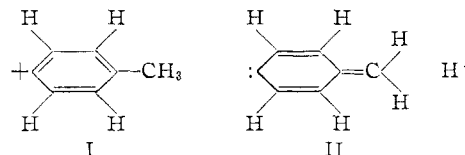
Introduction

The substitution of deuterium for hydrogen in certain positions results in a retardation of the rate of some ionization reactions.² The explanation of this retardation involved weakening of the carbon-hydrogen bonds in the transition state by the contribution of unbonded structures, due either to solvent attack,^{2a} or merely to hyperconjugation.^{2b,c}

It is expected that such a rate retardation by deuterium substitution will be observed in general when the bond to the deuterium atom (and the corresponding hydrogen in the undeuterated compound) is weaker in the transition state than it is in the initial state of the reacting molecule. An obvious extension is that a molecule containing a stronger carbon-hydrogen bond in the transition state than in the initial state should react more rapidly on substitution of deuterium for the hydrogen. However, a faster reaction for a deuterium compound has not been observed before.

A reaction with more extensive hyperconjugation in the initial state than in the transition state is the decomposition of *p*-toluenediazonium ion in aqueous acid. In this molecule the *p*-methyl group produces a retardation not ascribable to an inductive effect, since the *meta*-methyl group accelerates.³ The hyperconjugation in the diazonium

salt is presumably more important than that in the resulting *para*-methylphenyl cation, accounting for the marked difference between the effects of *meta* and *para* alkyl substitution.^{3b} In fact, the structures I and II do not combine for symmetry reasons, and the *para*-methyl group can stabilize



the phenyl cation only by an inductive effect.⁴ While the substitution of deuterium for hydrogen has influences other than that on the zero-point energy, it seemed, nevertheless, worthwhile to look at the sign and magnitude of the isotope effect in this reaction. Since only a very small effect can be expected, it was necessary to devise first a highly precise rate measurement usable with the small quantities of deuterated compound available.

Experimental

Materials.—*p*-Toluenediazonium fluoborate was made following the procedure of Lewis and Miller,^{3b} but the yield is not great enough to make this preparation suitable for the deuterated compound. The starting point in the synthesis of the deuterated compound was *p*-acetaminotriderotoluene (III), the synthesis of which will be described in detail in a subsequent publication. In essence the route involved the high temperature hydrolysis and decarboxylation of the sodium salt of dimethylphenylmalonate with deuterium oxide. The resulting triderotoluene was acetylated, then converted to the acetaminotriderotolu-

(1) Presented before the Division of Physical and Inorganic Chemistry, at the spring meeting of the A.C.S., Dallas, 1956.

(2) (a) V. J. Shiner, Jr., *THIS JOURNAL*, **75**, 5292 (1953); **76**, 1603 (1954); (b) C. E. Boozer and E. S. Lewis, *ibid.*, **74**, 6306 (1952); **76**, 794 (1954); **76**, 791 (1954); (c) E. S. Lewis and G. M. Coppinger, *ibid.*, **76**, 4495 (1954).

(3) (a) M. L. Crossley, R. H. Kienle and C. H. Benbrook, *ibid.*, **62**, 1400 (1940); (b) E. S. Lewis and E. B. Miller, *ibid.*, **75**, 429 (1953).

(4) We are indebted to Prof. M. G. Ettlinger for pointing out the orthogonality of the vacant orbital in I and the aromatic π -orbital.