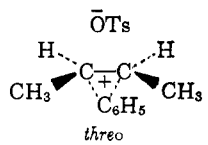
TABLE II

RATE CONSTANTS FOR THE ACETOLYSIS OF *threo*- AND *erythro*-3-PHENYL-2-BUTYL TOSYLATE AT 74.8°

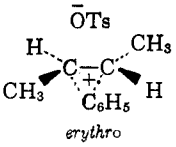
Tosylate	k_{-1}/k_3	$k_3/(k_{-1} + k_3)$	$k_1 \times 10^5$, sec.$^{-1}$	$k_2 \times 10^5$, sec.$^{-1}$
threo	10.3	0.09	27.4	2.2
erythro	4.4	0.19	20.7	1.4

tailed considerations of the mechanism of the solvolyses of the tosylates of 3-phenyl-2-butanol, 4-phenyl-3-hexanol, and 2,5-dimethyl-4-phenyl-2-hexanol, Cram, Nyquist, and Abd Elhafez[1c] made the then reasonable assumption that the ratio $k_3/(k_{-1} + k_3)$ was the same in the respective *threo* and *erythro* systems. The results (Table II) obtained in this study are at variance with this assumption.

The geometric structures of the pertinent phenonium ion tosylate ion pairs may be represented as



threo



erythro

Plainly eclipsing effects due to the methyls may be found in the *threo* but not in the *erythro* ion pair. Dissociation of the intimate ion pair into a solvent-separated ion pair or to a phenonium ion acetate ion pair should leave the geometry of the phenonium ion relatively unchanged and might be reasonably supposed to proceed with about the same rate for either isomer. However, collapse back to the starting tosylate should be favored in the more highly strained *threo* ion pair. Thus, the ratios of k_{-1}/k_3 can be rationalized with our determinations.

The second point arises from a consideration of the ratio $k_1(erythro)/k_1(threo)$. Based on the assumption of equal values of $k_3/(k_{-1} + k_3)$, Cram, Nyquist, and Abd Elhafez[1c] calculated the value of this ratio as 1.5 compared to our experimental value of 0.8. While the error in our experiments must be taken into account, it is evident that in actual fact the rate of phenonium ion formation for the *threo* isomer is at least as fast or perhaps even a little faster than the rate for the *erythro* isomer. This result implies that the energy differences between the ground state and transition state for the k_1 process are very nearly alike. Clearly the differences imposed by eclipsing effects of the methyls are negligible in these systems.[6]

Acknowledgment.—The conception of this problem developed during the course of discussions held several years ago between Dr. D. J. Cram, Dr. C. J. Collins, and W. B. S. Grateful acknowledgment to these gentlemen for their help and encouragement is hereby extended. This work was supported by a grant from the Robert A. Welch Foundation whose aid is also gratefully acknowledged.

(6) For further inferences about eclipsing effects of methyls in related ionic reactions see W. B. Smith and W. H. Watson, *J. Am. Chem. Soc.*, **84**, 3174 (1962).

[CONTRIBUTION FROM THE RESEARCH CENTER OF THE SPRAGUE ELECTRIC CO., NORTH ADAMS, MASS.]

The Electrochemical Oxidation of Acetic Acid in the Presence of Aromatic Hydrocarbons

BY SIDNEY D. ROSS, MANUEL FINKELSTEIN, AND RAYMOND C. PETERSEN

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The electrochemical oxidation of acetic acid in the presence of benzene, ethylbenzene, *t*-butylbenzene, mesitylene, naphthalene, and phenyl acetate has been studied. Rates of gas evolution and the compositions of the gases produced have been determined. The major nongaseous products have been identified and determined. These products include both acetoxyl and methyl derivatives with substitution occurring in both the ring and side chain. The many paths by which these products may have arisen are discussed, and particular attention is given to the possibility that many of the products arise from a prior discharge of the aromatic substrate at the anode to form a radical cation.

The electrochemical oxidation of carboxylate anions, described by Kolbe in 1849,[1] has been a subject of continuous investigation since that time.[2] Although still subject to controversy, the most widely accepted theory concerning the mechanism of this reaction is the discharged ion theory, proposed by Brown and Walker in 1891[3] and given experimental support by Clusius, *et al.*[4]

When 5 *N* aqueous acetic acid is electrolyzed under optimum conditions of high current density and high anodic potential, the anodic products are almost entirely carbon dioxide and ethane, formed in a mole ratio of 2 to 1 and with a current efficiency approaching 100%.[5] In less concentrated solutions or at lower current densities or at lower anode potentials other anodic products—oxygen, methane, and methyl acetate—are also found.

In glacial acetic acid as solvent, the electrolysis of acetate ion is an even cleaner reaction, the over-all electrode reactions are almost exactly

$$2CH_3COO^- \longrightarrow 2CO_2 + C_2H_6 + 2e \quad (1)$$

$$2H^+ + 2e \longrightarrow H_2 \quad (2)$$

and the coulombic yield approaches 2 moles of CO_2, 1 mole of H_2, and 1 mole of C_2H_6 per 2 Faradays.[6] We find that when potassium acetate (5 g.) in glacial acetic acid (60 ml.) is electrolyzed at 20° at 0.4 amp. (1 cm.^{2} platinum electrodes at a separation of 0.6 cm.), the rate of total gas production is 100 ± 1% of that demanded by the above equations, with the ratio CO_2/

(1) H. Kolbe, *Ann. Chem.*, **69**, 257 (1849).

(2) For review articles see, B. C. L. Weedon, *Quart. Rev.* (London), **6**, 380 (1952); "Advances in Organic Chemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1960, p. 1.

(3) A. Brown and J. Walker, *Ann. Chem.*, **261**, 107 (1891).

(4) P. Hölemann and K. Clusius, *Z. physik. Chem.*, **35B**, 261 (1937); K. Clusius and W. Schanzer, *ibid.*, **192A**, 273 (1943).

(5) K. Sugino, T. Sekine, and N. Sato, *Electrochem. Tech.*, **1**, 112 (1963).

(6) C. L. Wilson and W. T. Lippincott, *J. Am. Chem. Soc.*, **78**, 4290 (1956).

C_2H_6 varying from 1.99–2.02. No more than trace amounts of methane are present in the gas mixture. Raising the temperature to 58° or reducing the current to 0.2 amp. does not detectably alter these results.

If a third substance, capable either of itself being discharged at an electrode or of reacting with primary species formed at an electrode to give, in either case, nongaseous products, is added to the above system, there will be a measurable decrease in the rate of total gas production. The measurement of the rate of total gas evolution in such a system can serve as a sensitive diagnostic tool for determining whether or not a given substrate participates in product-forming reactions at the electrodes, and the decrease in the rate of gas evolution can be an indication of the extent of that participation.

In exploratory experiments it was found that electrolysis of a solution of potassium acetate in glacial acetic acid containing added *n*-hexane generated gas at a rate which was experimentally indistinguishable from that observed in the absence of the hydrocarbon. The addition of alkyl-substituted benzenes, on the other hand, resulted in clearly measurable decreases in the gassing rate, and the addition of naphthalene almost completely suppressed the generation of gaseous products at the anode. It is our present purpose to report a study of the electrochemical oxidation of acetate ion in the presence of added aromatic compounds. Included are measurements of the rates of gas evolution and determinations of the gas compositions. In addition, the major nongaseous products have been identified and their quantities have been estimated.

Determination of the gas composition, in particular the CO_2/C_2H_6 ratio, is a useful guide to the nature of the liquid products formed in these reactions. A diminished rate of gassing, accompanied by the normal CO_2/C_2H_6 ratio of 2, points to acetoxylation of the substrate. On the other hand, the CO_2/C_2H_6 ratio will significantly exceed 2 when the predominant reaction is methylation of the substrate. In addition, the formation of appreciable quantities of either methane or methyl acetate will also result in a CO_2/C_2H_6 ratio greater than 2. The foregoing considerations will obtain even if the substitution on the substrate involves its discharge at the electrode to give a radical ion rather than a hydrogen abstraction step prior to formation of the final product. It should be noted that there are clear parallels between the use of rates of gas formation and analyses of gas composition in the present work and in the pioneering research of Szwarc on the decomposition of acetyl peroxide.[7] Both anodic methylations[8] and anodic acetoxylations[9] have been observed previously with aromatic substrates. The present investigation was motivated not by the synthetic promise of these reactions but by the hope of affording some fresh insight into the mechanisms and intermediate species involved in these complex electrode reactions.

(7) A. Rembaum and M. Szwarc, *J. Am. Chem. Soc.*, **76**, 5975 (1954); M. Levy, M. Steinberg, and M. Szwarc, *ibid.*, **76**, 5978 (1954); M. Levy and M. Szwarc, *ibid.*, **76**, 5981 (1954); W. J. Heilman, A. Rembaum, and M. Szwarc, *J. Chem. Soc.*, 1127 (1957).

(8) L. F. Fieser, R. C. Clapp, and W. H. Daudt, *J. Am. Chem. Soc.*, **64**, 2052 (1942); S. Goldschmidt and M. Minsinger, *Chem. Ber.*, **87**, 956 (1954).

(9) R. P. Linstead, B. R. Shephard, and B. C. L. Weedon, *J. Chem. Soc.*, 3624 (1952); T. Hayashi and C. L. Wilson, Abstracts, 126th National Meeting of the American Chemical Society, New York, N. Y., 1954, p. 78-O.

Experimental

Apparatus.—The reaction cell was a water-jacketed cylinder of slightly more than 60-ml. capacity, maintained at constant temperature with water circulated from a thermostat. The two platinum electrodes, each 1 cm.^{2} in area and at a separation of 0.6 cm., were inserted into the center of the cell through a ground glass joint at the top. The cell was connected to a gas collection apparatus the design and calibration of which has been described previously.[10] A small trap containing acetic acid was placed between the cell and the gas buret.

Gas Analyses.—Aliquots of the total gas, anodic and cathodic, were collected at regular intervals and analyzed with a Perkin–Elmer Model 154 Vapor Fractometer, using a Perkin–Elmer J column (silica gel packing).

Nongaseous Products.—At the end of the electrolysis the cell and trap contents were poured into 500 ml. of water. This mixture was extracted with three 200-ml. portions of ether; the combined ether extracts were magnetically stirred with a suspension of sodium bicarbonate in water. When no further effervescence occurred on addition of more sodium bicarbonate, the ether was separated, and the remaining suspension was extracted with ether. The combined ether extracts were dried over magnesium sulfate and concentrated through a Vigreux column. For analysis the residue was diluted to 50 ml. with ether.

The ether solutions were analyzed by v.p.c. using a Perkin–Elmer large diameter Golay column of 0.06 in. i.d. and 300 ft. length in which the stationary phase was Ucon polyglycol LB-550-X. The unknown solutions were compared with standards prepared from the identified components.

Materials.—ACS reagent grade benzene was distilled, and a middle cut was taken. Naphthalene was crystallized from methanol; m.p. 80–81°. Mesitylene was twice distilled at atmospheric pressure, only middle cuts being taken each time; b.p. 160–161°. *t*-Butylbenzene, twice distilled as above, had b.p. 162–164°. Eastman Kodak white label ethylbenzene was distilled at atmospheric pressure, and a middle cut, b.p. 134–135°, was used. Eastman Kodak white label phenyl acetate was used without purification. It was shown by v.p.c. that none of these substrate materials contained any of the products which were identified after electrolysis. The glacial acetic acid used was ACS reagent grade from the General Chemical Co. Analyzed, reagent grade potassium acetate was obtained from the J. T. Baker Chemical Co.

Materials Used in Preparing Standards.—The following acetates were prepared by treating the appropriate hydroxy compound with pyridine and acetic anhydride: *o*-*t*-butylphenyl acetate, b.p. 69° at 0.25 mm., $n^{23.5}D$ 1.4977[11]; *p*-*t*-butylphenyl acetate, b.p. 93° at 1.25 mm., $n^{23.5}D$ 1.4955[12]; *m*-*t*-butylphenyl acetate, m.p. 42–43° from alcohol; 4-*t*-butylcatechol diacetate, m.p. 79–81°[13]; *o*-ethylphenyl acetate, b.p. 49–50° at 0.15 mm., $n^{22}D$ 1.4972[14]; *m*-ethylphenyl acetate, b.p. 54–55° at 0.1 mm., $n^{23}D$ 1.4972[15]; *p*-ethylphenyl acetate, b.p. 45–47° at 0.05 mm., $n^{22}D$ 1.4986[16]; α-phenethyl acetate, b.p. 61–62° at 0.8 mm., $n^{24}D$ 1.4937[17]; acetoxymesitylene, b.p. 68° at 0.15 mm., $n^{22}D$ 1.4974[18]; 2,4,6-trimethylresorcinol diacetate, m.p. 58–60°.[19]

α-Naphthyl acetate, β-naphthyl acetate, hydroquinone diacetate, catechol diacetate, and resorcinol diacetate were prepared by adding acetic anhydride to a basic, aqueous solution of the hydroxy compounds as described by Chattaway.[20]

3,5-Dimethylbenzyl acetate[21] was prepared by treating 3,5-dimethylbenzyl bromide[22] with potassium acetate in acetic acid; b.p. 99–105° at 4 mm., $n^{23.5}D$ 1.5028.

3,5-Bis(acetoxymethyl)toluene[23] was prepared by treating the

(10) R. C. Petersen, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, **83**, 3819 (1961).

(11) C. S. Rondestvedt and H. S. Blanchard, *ibid.*, **77**, 1769 (1955).

(12) A. B. Sen and T. N. Kakaji, *J. Indian Chem. Soc.*, **29**, 950 (1952).

(13) F. Wessely, J. Kotlan, and F. Sinwel, *Monatsh.*, **83**, 902 (1952).

(14) C. M. Suter and R. D. Scheutz, *J. Org. Chem.*, **16**, 1117 (1951).

(15) J. Kenner and F. S. Statham, *J. Chem. Soc.*, 299 (1935).

(16) W. S. Emerson, J. W. Heyd, V. E. Lucas, W. B. Cook, G. R. Owens, and R. W. Shortridge, *J. Am. Chem. Soc.*, **68**, 1665 (1946).

(17) H. Olsson, *Z. physik. Chem.*, **133**, 233 (1928).

(18) K. von Auwers, H. Bundesmann, and F. Wieners, *Ann.*, **447**, 162 (1926).

(19) D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1 (1960).

(20) F. D. Chattaway, *ibid.*, 2495 (1931).

(21) P. Wispek, *Ber.*, **16**, 1577 (1883).

(22) L. H. Schwartzman and B. B. Corson, *J. Am. Chem. Soc.*, **78**, 322 (1956).

(23) J. Strating and H. J. Backer, *Rec. trav. chim.*, **62**, 57 (1943).

corresponding bromide[24] with potassium acetate in acetic acid.

5-Ethyl-*m*-xylene was obtained by treating the Grignard reagent from 3,5-dimethylbenzyl bromide with dimethyl sulfate.

The 2-, 3-, and 4-ethyltoluenes were obtained from the Aldrich Chemical Co. Isodurene was obtained from the Columbia Organic Chemicals Co.

A commercial mixture of α- and β-methylnaphthalene was separated, sufficiently for our analytical purpose, by a combination of crystallization and v.p.c.

Results

The effect of added aromatic substrates on the rate of anodic gas formation is shown in Table I. In each experiment a solution of 0.075 mole of the substrate and 0.0503 mole of potassium acetate made up to a volume of 60 ml. with glacial acetic acid was electrolyzed at 0.40 amp. Aliquots of the total gas formed were collected near the start of the electrolysis, just before terminating the reaction and at as many as 10 intervening points. Analyses of the gas mixtures indicated that within experimental error the decrease in the rate of gas formation was, in every case, caused by a decrease in the amount of gas formed at the anode, since for every 2 Faradays of charge passed almost exactly 1 mole of hydrogen was formed at the cathode. The values in column 3 of Table I were obtained by assuming that the theoretical amount of hydrogen was being produced at the cathode and that the decrease in the rate of gas formation was occurring entirely at the anode. The indicated spread in the values is that observed over the entire course of the reaction. In two cases, with phenyl acetate and with *t*-butylbenzene, there is a definite upward trend in the values as the reaction proceeds. In the other cases the variations appear to be random.

TABLE I

THE EFFECT OF ADDED SUBSTRATES ON GAS EVOLUTION DURING THE ELECTROLYSIS OF POTASSIUM ACETATE IN ACETIC ACID

Substrate	Electrolysis time, hr.	% of theoretical Kolbe anode gas	Volume ratio CO_2/ethane
Benzene	38.07	100.2 ± 1.2	2.02 ± 0.01
Phenyl acetate	14.63	84.1 ± 2.9	2.23 ± .07
Ethylbenzene	37.97	88.1 ± 0.4	2.08 ± .02
t-Butylbenzene	15.50	86.8 ± 2.0	2.09 ± .01
t-Butylbenzene	35.40	85.6 ± 1.8	2.08 ± .03
Mesitylene	28.00	84.4 ± 1.1	2.14 ± .02
Mesitylene	27.93	83.2 ± 1.6	2.20 ± .04

If the molar ratio of CO_2 to ethane were exactly 2, the theoretical volume ratio would be 2.000. The actual volume ratios, shown in column 4 of Table I, though slightly higher, are all very close to this value.

The addition of naphthalene (0.0375 mole of naphthalene to 0.0507 mole of potassium acetate made up to 60 ml. with glacial acetic acid) gave the very different results shown in Table II. Gas formation at the anode is almost completely suppressed initially but increases continuously with time. The volume ratio CO_2/ethane is at all times significantly larger than 2 and increases as the reaction proceeds.

TABLE II

THE EFFECT OF ADDED NAPHTHALENE ON GAS EVOLUTION DURING THE ELECTROLYSIS OF POTASSIUM ACETATE IN ACETIC ACID

Elapsed time, hr.	% of theoretical Kolbe anode gas	Volume ratio CO_2/ethane
0.50	6.1	3.62
1.97	12.2	6.87
3.02	14.6	7.07

The major nongaseous products formed in these reactions are listed in Tables III–VII. The experiment with naphthalene contained 0.0375 mole of the addend. In the other cases 0.075 mole of the substrate was added. The electrolysis times are those shown in Table I. In the experiment with benzene added, less than 50% of the benzene was accounted for, probably because of its high vapor pressure. In each of the remaining cases, the fate of more than 70% of the substrate has been determined. Nevertheless, the vapor phase chromatograms indicated the presence of additional

TABLE III

NONGASEOUS PRODUCTS FROM BENZENE AND FROM PHENYL ACETATE

	From benzene, mole	From phenyl acetate, mole
Benzene	0.0307	
Phenyl acetate	.00182	0.0679
Catechol diacetate	.00016	.00148
Hydroquinone diacetate	.00006	.00119
% of substrate accounted for	43.6	94.2

TABLE IV

NONGASEOUS PRODUCTS FROM ETHYLBENZENE

	Mole
Ethylbenzene	0.0439
α-Acetoxy-	.00480
o-Acetoxy-	.00288
m-Acetoxy-	.00072
p-Acetoxy-	.00240
Cumene	.00221
2-Ethyltoluene	.00019
3- and/or 4-ethyltoluene	.00028
% of substrate accounted for	76.5

TABLE V

NONGASEOUS PRODUCTS FROM *t*-BUTYLBENZENE

	Mole	
	After 15.5 hr.	After 35.4 hr.
t-Butylbenzene	0.0612	0.0531
o-*t*-Butylphenyl acetate	.0019	.0025
m-*t*-Butylphenyl acetate	.0017	.0024
p-*t*-Butylphenyl acetate	.0033	.0039
4-*t*-Butylcatechol diacetate	.0004	.0011
% of substrate accounted for	91.6	84.0

TABLE VI

NONGASEOUS PRODUCTS FROM MESITYLENE

	Mole
Mesitylene	0.0425
2,4,6-Trimethylphenyl acetate	.00947
3,5-Dimethylbenzyl acetate	.00376
5-Ethyl-*m*-xylene	.0022
Isodurene	.00078
% of substrate accounted for	78.2

TABLE VII

NONGASEOUS PRODUCTS FROM NAPHTHALENE

	Mole
Naphthalene	0.02181
α-Naphthyl acetate	.00331
β-Naphthyl acetate	.00064
α-Methylnaphthalene	.00083
β-Methylnaphthalene	.00006
% of substrate accounted for	71.1

(24) W. Ried and F. J. Königstein, *Chem. Ber.*, **92**, 2532 (1959).

products in lesser quantities which we have neither identified nor determined.

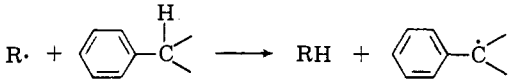
Both acetoxylation and methylation are observed, but the former appears to be the preferred reaction mode and predominates. Where there is a choice between the ring and a side chain containing an α-hydrogen, substitution frequently occurs at both sites, and at either locus the over-all reaction may be an acetoxylation or a methylation.

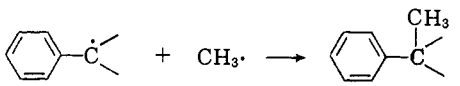
Discussion

The salient features of the present results, taken *in toto*, are the variety of products formed from the added substrate, the preponderance of acetoxylation products over methylation products, and the apparent randomness in the direction of ring substitution. These taken together create a strong temptation to attribute all of the products to the intervention of free-radical intermediates and to assign sufficient stability to the acetoxyl radical, in the presence of the electrode and/or the applied field, to permit its participation in product-forming reactions.

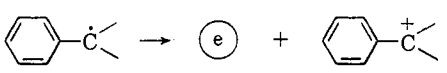
It is our present purpose to show that neither of these possible conclusions is fully justified. Perhaps the most direct way in which to achieve this is to catalog the paths by which the observed products may have arisen. In what follows, the primary electrode reaction involving acetate ion will be taken as a one-electron transfer to give an acetoxyl radical, which may or may not decarboxylate spontaneously to give methyl radical. Consideration will also be given to the possibility that the substrate is adsorbed on the electrode and discharged to give a radical ion.[25]

Only one path leading to side-chain methylation is probable. As shown below, where R· is methyl or acetoxyl, this involves a hydrogen atom abstraction and combination of the benzyl radical formed with a methyl radical.


(3)

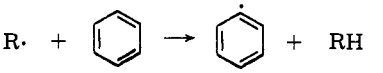

(4)

Combination of the benzyl radical, generated by (3), with an acetoxyl radical results in side chain acetoxylation. An alternate route to this same end result might involve an anodic, one-electron transfer from the benzyl radical to give a carbonium ion, which could then react with either acetate ion or acetic acid. This possibility cannot be dismissed as improbable since there is evidence for the anodic generation of carbonium ions from carboxylate anions.[26]


(5)

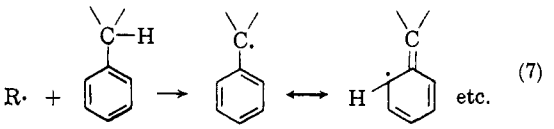
The formation of ring-substitution products offers a far broader spectrum of reaction possibilities. These may be classified in terms of the initial steps involving the substrate, and the following five may be distinguished:

1. Hydrogen atom abstraction from the ring. Although hydrogen abstraction is more probable from the α-position of the side chain than from the ring, as shown by the fact that the relative reactivities of abstraction by methyl radicals from toluene and benzene favor the former by a factor of 19 in solution[27] and of 14 in the gas phase,[28] it is, nevertheless, possible to abstract a hydrogen atom from the ring. The radical so


(6)

generated could combine with methyl or acetoxyl to give final product. A perhaps less likely possibility, because of the instability of the cation produced, would be the further anodic oxidation of the above aromatic radical to form a carbonium ion, which could then react to give a ring acetoxylation product.

2. Hydrogen atom abstraction from the side chain. When a hydrogen atom is removed from carbon α to the aromatic ring, the odd electron is delocalized owing to contributing structures with that electron at the *ortho* and *para* positions of the ring. Such abstraction may, therefore, result finally in ring substitution as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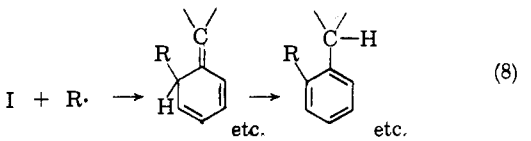
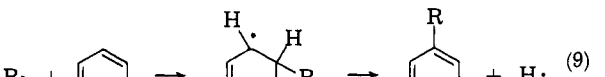
I


(8)

In this case, too, the intermediate oxidation of I to a carbonium ion may result finally in ring acetoxylation.

3. Radical addition to the ring. This may involve only radicals or an ionic intermediate as indicated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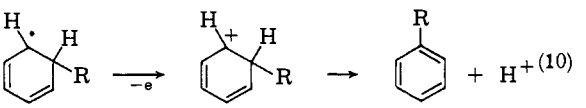
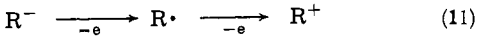
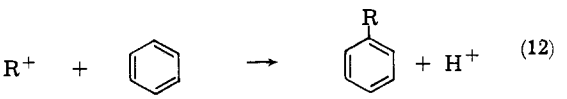
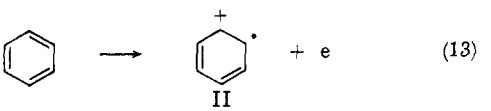

(10)

4. Electrophilic substitution. A two-electron change at the anode may generate an electrophilic species which substitutes the aromatic ring.


(11)


(12)

5. Discharge of the substrate on the anode. If the aromatic substrate is adsorbed on the anode and transfers an electron to it, a radical ion, II, will be formed. This process may be represented as


(13)

II

(25) L. Eberson, *Acta Chem. Scand.*, **17**, 2004 (1963).

(26) E. J. Corey, N. L. Bauld, R. T. LaLonde, J. Casanova, Jr., and E. T. Kaiser, *J. Am. Chem. Soc.*, **82**, 2645 (1960); E. J. Corey and J. Casanova, Jr., *ibid.*, **85**, 165 (1963); L. Eberson, *Acta Chem. Scand.*, **17**, 1196 (1963).

(27) F. G. Edwards and F. R. Mayo, *J. Am. Chem. Soc.*, **72**, 1265 (1950).

(28) A. F. Trotman-Dickenson, *Quart. Rev.* (London), **7**, 198 (1953).

A species such as II might be capable of either reacting with a nucleophile to give a radical or combining with a radical to give a carbonium ion. Alternatively, it might lose a hydrogen atom to form an aromatic cation or a proton to give a radical. Any one of the intermediates so generated could result finally in a ring-substituted product.

This reaction path, first suggested by Eberson,[25] is attractive, because there is a parallelism between the degree to which a given substrate inhibits the normal anodic reactions of acetate ion and its ionization potential.[29] In addition to the compounds listed in Table I, we have studied gassing rates, but not the products formed, with acetophenone and with anisole. The former gives $94.6 \pm 2.0\%$ of the theoretical Kolbe anode gas. The latter shows only 5% of the theoretical anode gas initially, and anodic gassing rises steadily to 72.2% at 38 hr. of electrolysis. Thus addends of high ionization potential, *e.g.*, benzene and acetophenone, show the highest anodic gassing rates, and those of lowest ionization potential, anisole and naphthalene, give the lowest rates. The remaining compounds in Table I give rates which are bunched closely together but, nevertheless, in the order of their ionization potentials.

As might be expected, there is a similar, but less completely documented, parallelism with the polarographic oxidation potentials of the substrates. The available data[30] do not include all of the substrates in the present study and were determined in acetonitrile at a rotating platinum electrode. We have made crude measurements of current as a function of applied anode potential (stationary Pt anode *vs.* Hg pool reference electrode) and have found a distinct lowering of the discharge potential when naphthalene is added to the potassium acetate–acetic acid system.

The available data do not permit any worthwhile assessment of the relative probabilities of the foregoing possibilities. It should be recognized that the stabilities and reactivities of the intermediate radicals may be significantly modified by the electrode and/or the field and by complex formation with the aromatic substrate.[31] In the present state of our knowledge these are recognizable but still largely intangible factors.

The difficulties in interpretation are illustrated by data on the production of methane, which can arise only from hydrogen atom abstraction. In the presence of ethylbenzene methane is produced at approximately twice the rate observed in its absence. This suggests that hydrogen abstraction may be an important step in initiating product formation from ethylbenzene. However, the total methane produced during the course of the electrolysis was 0.0085 mole. This is less than the 0.01348 mole of new product formed from the ethylbenzene. Furthermore, some hydrogen abstraction is from acetic acid, and all of the difference in methane production with ethylbenzene present and with ethylbenzene absent cannot be attributed with certainty to abstraction from the substrate. Also, where we have indicated loss of a hydrogen atom in the reaction schemes, this almost certainly involves a transfer to a radical and may result in methane production. On the other hand, there is no way to judge whether or not hydrogen atoms are being abstracted by acetoxyl radicals, since this would result in the formation of acetic acid, the solvent. In the face of these uncertainties, it may only be concluded that the role of hydrogen abstractions in product formation cannot be assessed quantitatively.

Some methyl acetate is also formed in these reactions, and, in the reaction with ethylbenzene added where special efforts were made to trap and detect it, approximately 0.006 mole was found. It might be argued that the formation of methyl acetate demonstrates the possibility of some finite existence for the acetoxyl radical under these reaction conditions.[32] Unlike the decomposition of acetyl peroxide in solution, radicals are here formed singly and not in pairs; there is no possibility for the ester arising from induced decomposition reactions and a normal cage effect is not operable. However, it is possible that most of the radicals formed undergo reaction before leaving the sphere of influence of the electrode and that this influence confers on these reactions some of the characteristics of reaction in a solvent cage. In addition, the possibility that methyl acetate arises from the anodic oxidation of an intermediate methyl radical to a carbonium ion cannot be completely eliminated even if it is relatively improbable.

Finally the striking difference in anodic gassing characteristics observed with naphthalene (Table II) compared to the other substrates (Table I) should be noted. This suggests that either different mechanisms or different distributions of mechanisms are operating in the two cases. It is hoped that further research focused on these differences will expand our understanding of these reactions.

(29) For a comprehensive review on ionization potentials and an excellent compilation of the pertinent data see A. Streitwieser, Jr., "Progress in Physical Organic Chemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1963, p. 1.

(30) E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1963).

(31) C. E. Boozer and G. S. Hammond, *ibid.*, **76**, 3861 (1954); G. S. Hammond, C. E. Boozer, C. E. Hamilton, and J. N. Sen, *ibid.*, **77**, 3238 (1955); G. A. Russell, *ibid.*, **80**, 4987 (1958); *Tetrahedron*, **8**, 101 (1960); C. Walling and M. F. Mayahi, *J. Am. Chem. Soc.*, **81**, 1485 (1959).

(32) For a discussion of the stability of the acetoxyl radical and arguments for and against its participation in product forming reactions see H. J. Shine and J. R. Slagle, *ibid.*, **81**, 6309 (1959); H. J. Shine, J. A. Waters, and D. M. Hoffman, *ibid.*, **85**, 3613 (1963); J. C. Martin and E. H. Drew, *ibid.*, **83**, 1234 (1961).