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THE KOLBE ELECTROLYSIS AS A SOURCE OF FREE RADICALS IN SOLUTION—V

THE ELECTROLYSIS OF POTASSIUM ACETATE IN THE PRESENCE OF 3,3-DIMETHYL-1-BUTENE

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Abstract—The electrolysis of potassium acetate has been carried out in methanol solutions of 3,3-dimethyl-1-butene. Twelve compounds were identified as reaction products. Among these were a number which resulted from molecular rearrangements. The implications of these regarding the mechanism of the reaction are discussed. The bulk of the products arise from attack of a Me free radical on the terminal olefin carbon and the subsequent reactions of the resultant free radical.

INTRODUCTION

DURING the course of the past several years a series of experiments has been carried out on the electrolysis of potassium acetate in the presence of various substrates which were potentially capable of reacting with the species formed at the electrode. Among the various substrates have been butadiene and isoprene,[1,2] cyclohexadiene,[3] vinyl acetate and methyl methacrylate,[4] acrylic acid,[5] cyclohexene and both *cis* and *trans* 2-butene,[6] and a variety of aromatic compounds.[7]

The electrolysis of methanol solutions of potassium acetate at smooth platinum electrodes yields mainly 2-methylcyclohexyl acetate with smaller amounts of 3-acetoxycyclohexene, and 3-methylcyclohexene when cyclohexene was used as the substrate.[6] Similarly the electrolysis in the presence of *trans*-2-butene gave mainly 2-acetoxy-3-methylbutane plus smaller amounts of 2-methyl-2-butene, 2,3-dimethylbutane, methyl 3-methyl-2-butyl ether, 3-acetoxy-1-butene, 2-acetoxy-2-butene, and 2,3-diacetoxybutane.[6]

During the work with cyclohexadiene, evidence for methyl ether formation was obtained.[4] Methyl ethers were also found with aromatic substrates.[7] These observations are most readily accommodated by mechanisms involving cationic intermediates which attack the solvent methanol.

The formation of carbonium ions by the electrolysis of carboxylate ions now seems well established[8,9] and occurs in many cases where the normal Kolbe coupling product is not observed. If carbonium ions are important in the reactions described above, then they are presumably formed by a second oxidation step of some first formed intermediate. Such a proposal has been made previously by Eberson, *et al.*[10] who electrolyzed acetic acid solutions of potassium acetate in the presence of cyclooctatetraene and found the 7-methyl-8-acetoxybicyclo[4.2.0]octa-2,4-dienes among the products.

To test the hypothesis of carbonium ion intermediates the electrolysis of methanolic potassium acetate has now been carried out in the presence of 3,3-dimethyl-1-butene.

The addition of either a methyl or acetoxy free radical to this olefin will produce neopentyl-like radicals. While such radicals undergo normal addition and disproportionation reactions, they do not rearrange.[11, 12] In contrast, oxidation of neopentyl radicals to neopentyl cations would be expected to lead to typical rearrangement products. Thus, the examination of the reaction products should provide evidence on the importance of organic cations in these reactions.

RESULTS AND DISCUSSION

The electrolysis of methanol solutions of potassium acetate in the presence of 3,3-dimethyl-1-butene was carried out for various times and with various amounts of added acetic acid. The conditions are described in the Experimental, and the products are recorded in Tables 1 and 2. It is evident that the reaction products form a complex mixture and, bearing in mind the relative nature of the per cent distributions as determined by VPC, only large changes should be considered significant. The most obvious of these are the distinct decrease in the amount of 2,3,3-trimethylpentane as the acidity of the reaction mixture is decreased and the concomitant increase in the amount of 2,3,3-trimethyl-1-butanol (presumably derived from its acetate or methyl carbonate precursors).

Large amounts of rearranged products were found in all cases. All of these involved the addition of some moiety at the C-1 position of the substrate, rearrangement of the original carbon skeleton, and then either addition or elimination to form the rearranged product.

In any system as complex as the one investigated here the problem is not so much in selecting a reaction mechanism or mechanisms but rather in defending one's choice among the many possibilities. The Kolbe electrolysis is an old and well explored reaction. Yet it can be truthfully said that it is only in the past few years that the details of the electrode process have begun to become clear.

It is known that in aqueous solutions the current density-potential curves for carboxylic acids are sigmoids with more or less well defined inflection points which signal the onset of the Kolbe coupling reaction. Based on studies of this critical potential and on charging curve phenomena, Dickinson and Wynne-Jones[13] have proposed that oxygen evolution occurs primarily below the critical potential. As the anode potential is increased the anode becomes covered with adsorbed acetate radicals produced by the discharge of acetate ions. When all of the discharge sites are covered, oxygen evolution is hindered and acetate ions begin to discharge upon already occupied sites.

Eberson has criticized the concept that acetate radicals could be sufficiently stable to exist for any finite life time even in an adsorbed state.[14] Conway and Dzieciuch have characterized the critical potential as being due to the buildup of a passive film of intermediates on the anode.[15] Arguing from the results of thermodynamic calculations of the electrode potentials for a variety of possible electrode reactions, Eberson[14] has postulated that the direct discharge of acetate ions to methyl radicals and carbon dioxide should be the preferred mode of reaction. Methyl radicals accordingly are proposed as the adsorbed intermediate.

Lund[16] has measured the oxidation potentials of a series of aromatic compounds in acetonitrile, and Eberson and Nyberg[17] have done the same in the acetic acid–acetate system. It now seems certain that acetoxylation of aromatic hydrocarbons occurs largely, if not exclusively, by prior oxidation of the aromatic hydrocarbon.[17] We have found the yields of acetoxylation products to increase in the order benzene < toluene < anisole paralleling the decrease in oxidation potentials for these substrates.[7]

No similar measurements of oxidation electrode potentials are available for the alkenes. A plot of Lund's data[16] against the electron impact ionization potentials for a series of aromatic compounds gives a good linear relation. If one assumes that alkenes such as ethylene and propylene may be placed on the same line using their ionization potentials, then one concludes that alkene oxidation potentials are probably above the calculated potential for acetate discharge (ca. 2·2 V). Thus, it seems unlikely that any primary oxidation of the olefin at the electrode is important here though one can not exclude the possibility.

Recently, Mango and Bonner[18] have electrolyzed sodium acetate in the presence of 1,1-diphenylethylene and *trans*-stilbene respectively. They concluded from the stereochemistry of the products formed from the latter both in anhydrous and moist acetic acid that a cyclic acetoxonium ion served as an intermediate in the reaction. They proposed that this intermediate might arise either through the attack of an acetoxy radical on an absorbed olefin with the transfer of an electron to the anode, i.e. two one-electron transfer steps, or by a concerted attack of an acetate ion on the absorbed olefin with the delivery of two electrons to the electrode.

It is apparent from the data in Tables 1 and 2 that under acidic conditions the additions of methyl radicals across the double bond in 3,3-dimentyl-1-butene is an important reaction. Presumably, the reaction is stepwise:

TABLE 1. ELECTROLYSIS PRODUCTS WITH INCREMENTAL ADDITION OF ACETIC ACID

Compounds	Per cent	Analytical methods*
1. *trans*-4,4-Dimethyl-2-pentene	6·7	I and II
2. 2,3-Dimethyl-1-pentene	4·4	I and II
3. 2,2,3-Trimethylpentane	45·6	II and IV
4. 2-Methoxy-2,2-dimethylpentane	8·0	I and II
5. 3-Acetoxy-2,2-dimethylpentane	2·1	I and II
6. 3,3-Dimethyl-1-butyl acetate	1·6	I
7. 4-Acetoxy-2,3-dimethyl-1-butene	10·6	All
8. 1-Acetoxy-2,3,3-trimethylbutane	12·3	All
9. Methyl 2,3-dimethyl-3-butenyl carbonate	2·5	All
10. Methyl 2,3,3-trimethyl-1-butyl carbonate	6·2	All

* I. Retention time;
II. IR;
III. NMR;
IV. Refractive index;
All. I, II, III, and IV.

$$\mathrm{Me_3CCH = CH_2 + Me^{\bullet} \rightarrow \underset{I}{Me_3C\dot{C}HEt}}$$

$$\mathrm{I + Me^{\bullet} \rightarrow Me_3CCH(Me)Et}$$

Subsequent oxidation of I yields a neopentyl-like cation which rearranges to give 2,3-dimethyl-1-pentene and 2-methoxy-2,3-dimethylpentane. The failure to observe

TABLE 2. ELECTROLYSIS PRODUCTS FROM INITIAL ADDITION OF ACETIC ACID ONLY

Run No.	I	II	III	IV[a]	V	VI
Acetic acid in grams	84	57	49	49	31	0
Conditions[b]	A–A	A–N	A–B	A–B	N–B	B–B
Yield in grams	3·3	2·9	2·4	7·2	3·6	6·1
Products	Per cent composition					
1. *trans*-4,4-Dimethyl-2-pentene	6·9	9·5	9·0	1·1	1·8	1·6
2. 2,3-Dimethyl-1-pentene	3·0	5·8	6·0	0·5	1·2	0·4
3. 2,2,3-Trimethylpentane	29·0	41·8	40·5	13·0	13·6	4·4
4. 2-Methoxy-2,3-dimethylpentane	14·0	7·5	11·6	3·5	8·6	2·8
5. 3-Acetoxy-2,2-dimethylpentane	3·1	1·9	1·3	t[c]	t[c]	t[c]
6. 3,3-Dimethyl-1-butyl Acetate	1·8	1·2	1·0	t	t	t
7. 4-Acetoxy-2,3-dimethyl-1-butene	15·8	11·9	4·6	1·7	2·3	4·8
8. 1-Acetoxy-2,3,3-trimethylbutane	16·3	10·3	6·8	0	0	0
9. Methyl 2,2-dimethyl-3-pentyl Carbonate	0·8	0·8	1·8	7·7	22·4	12·5
10. 2,3,3-Trimethyl-1-butanol	1·0	1·2	0·3	59·0	22·2	52·5
11. Methyl 2,3-dimethyl-3-butenyl Carbonate	2·1	1·7	3·3	2·7	4·5	2·2
12. Methyl 2,3,3-trimethyl-1-butyl Carbonate	4·7	3·1	12·8	5·0	18·9	9·0
13. Miscellaneous unknowns	1·5	3·3	1·0	5·8	4·5	9·8

[a] Run IV was electrolyzed for 48 hr rather than 24 hr as in other cases.

[b] Initial and final acidity as determined by moistened pH test paper; A, acid; B, basic; and N, neutral.

[c] t means trace.

2-acetoxy-2,3-dimethylpentane is curious but understandable in that various attempts to synthesize this compound (including one carbonium ion reaction) all failed.

The formation of 4-acetoxy-2,3-dimethyl-1-butene may arise from primary attack of an acetoxy radical on the olefin, subsequent oxidation to the carbonium ion, followed by rearrangement and elimination. The formation of a cyclic acetoxonium ion and its subsequent rearrangement can not be excluded. However, the observation of 1-acetoxy-2,3,3-trimethylbutane and 3,3-dimethyl-1-butyl acetate strongly supports the concept of acetoxy radical addition. Whether this occurs freely in the solution or in the complex milieu at the electrode surface is a moot point.

The observation of the three methyl alkyl carbonates among the products is apparently the first report of such compounds in an electrochemical reaction, and their formation presents a mechanistic enigma. Similar products had not been observed in any of our previous studies. Subsequent to their discovery here this point was rechecked for the electrolysis in the presence of *trans*-2-butene. No indications of methyl butyl carbonates could be found.

One is tempted to postulate the formation of these substances by the attack of a carbonium ion on carbon dioxide with formation of an oxocarbonium ion which then reacts with the solvent. The observation of methyl 2,3-dimethyl-3-butenyl carbonate and the failure to observe methyl 2,3-dimethyl-2-pentyl carbonate argues against this pathway. No further comment on this matter is possible at this time other than the observation that neither the acetate products nor alcohols act as precursors to the methyl carbonates.

EXPERIMENTAL

All VPC was carried out on an F& M Model 500 instrument using a 12 ft column of 20% Ucon lubricant on 60–80 mesh Chromosorb P. Perkin–Elmer Infracord and a Varian A-60 instruments were used for IR and NMR spectra respectively. All NMR spectra were run as dilute solns in CCl_4 with TMS as an internal standard. Hydrogen analyses were carried out by NMR as described elsewhere.[19]

Starting materials and comparison compounds

3,3-*Dimethyl-1-butene*. Pinacolyl acetate was prepared from pinacolyl alcohol by the usual acetylation procedure utilizing pyridine and Ac_2O. The ester was pyrolyzed by passage in a stream of N_2 through a vertical column 1·6 ft long filled with glass beads and heated to 450°. The condensate was washed with dil $NaHCO_3$aq and dried over $MgSO_4$. Distillation of the product from 136 g of ester gave 51 g (64%) of 3,3-dimethyl-1-butene, b.p. 39–42°; reported [20] b.p. 41·2°. This material checked as pure on several VPC columns.

2,2-*Dimethyl-3-pentyl acetate** *and methyl carbonate*. 2,2-Dimethyl-3-pentanol was prepared from t-BuMgCl and propionaldehyde by the procedure of Gaylord and Caul.[21]

A mixture of 31·2 g of the alcohol, 47 g of isopropenyl acetate, and 4 drops of conc H_2SO_4 was very slowly distilled. The forerun up to 157° amounted to 19·3 g. A fraction (22 g) boiling from 157–159·5° was collected and freed from starting alcohol by washing through an alumina column using pet. ether as the eluant. Distillation produced a 52% yield of 2,2-dimethyl-3-pentyl acetate, b.p. 157–159·5°, n_D^{22} 1·4110. The IR spectrum showed a strong band at 1750 cm^{-1}. The NMR spectrum showed a pair of doublets centered at 5·45 and 5·60 τ (J = 4 c/s, 1 proton), singlet 8·08 τ (acetate methyl, 3 protons), strong singlet at 9·16 τ and a complex multiplet between 8·2–9·3 τ (total of 14 protons). (Found: H, 11·19. Calc. for $C_9H_{18}O_2$: H, 11·36%.)

2,2-Dimethyl-3-pentanol (5·4 g) and 11·1 g of pyridine were stirred and cooled by an ice bath. Methyl chloroformate (14 g) was added dropwise over a 15 min period. The mixture was stirred overnight at room temp then poured into a 1:3 AcOH–water. The oily layer was separated, washed, and dried over $MgSO_4$. Pure methyl 2,2-dimethyl-3-pentyl carbonate was isolated by VPC trapping, n_D^{28} 1·4101. The IR spectrum showed an ester band at 1750 cm^{-1}, and the NMR spectrum had a pair of doublets centered at 5·50 and 5·60 τ (J = 5 c/s. 1 proton), singlet at 6·28 τ (3 protons), sharp singlet at 9·12 τ among a complex multiplet spaced from 8·2–9·2 τ (total 14 protons). (Found: H, 10·82. Calc. for $C_9H_{18}O_3$: H, 10·42%.)

trans-4,4-*Dimethyl-2-pentene*. Following the above procedure, 2,2-dimethyl-3-pentyl acetate (46·7 g) was pyrolyzed to give 16·2 g of olefin, b.p. 74–80°; reported[20] for *trans*-4,4-dimethyl-2-pentene, b.p. 76·7°. Analysis by VPC produced two bands comprising 98% and 2% of the olefin mixture respectively. The major component was trapped off the VPC and was found to have an IR spectrum identical with that of *trans*-4,4-dimethyl-2-pentene.[22]

2,3-*Dimethyl-2-pentanol and compounds derived therefrom*. 2,3-Dimethyl-2-pentanol was prepared by the reaction of MeMgI with methyl 2-methylbutanoate following the method of Freundenberg *et al.*[23]

A sample of the alcohol (20 g) was dehydrated by slow passage through a 1 ft alumina column heated to 350°. The olefin yield was 103 g (61%), b.p. 79–88°. Analysis by VPC, trapping, and IR analysis indicated that the product consisted of 2,3-dimethyl-1-pentene (93%) and 2,3-dimethyl-2-pentene (7%). The reported b.p. for the former is 84·2°.[20]

2-Methoxy-2,3-dimethylpentane was prepared from the alcohol by a conventional Williamson ether synthesis. The ether, b.p. 133–134·5°, was collected in pure form by VPC trapping, n_D^{25} 1·4099. IR absorption was found to be strong at 1060 cm^{-1}. A OMe band in the NMR spectrum was found at 6·91 τ, (3 protons) plus a sharp band at 9·0 τ superimposed on a broad envelope spread from 8·2–9·3 τ (15 protons). (Found: H, 13·79. Calc. for $C_8H_{18}O$; H, 13·93%.)

Numerous attempts were made to prepare the unreported acetate ester of 2,3-dimethyl-2-pentanol. Among the conditions employed may be listed the following: 1. Acetylation of the alcohol with Ac_2O–pyridine; 2. Reaction of the alcohol with acetyl chloride–pyridine; 3. The sodium salt of the alcohol plus Ac_2O and acetyl chloride respectively; 4. The exchange of the alcohol with t-butyl acetate plus a trace of acid; 5. The reaction of the alcohol with isopropenyl acetate; 6. The reaction of 2,3-dimethyl-1-pentene with AcOH plus a small amount of conc H_2SO_4. In no case was any ester detected.

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* The nomenclature here and in related substances follows common practice and is quite explicit. A referee has pointed out that it does not follow the I.U.P.A.C. rules, but he recommended we simply note this fact.

2,3,3-Trimethyl-1-butyl acetate and methyl carbonate. 2,3,3-Trimethyl-2-butanol was prepared in 74% yield by the method of Huston and Barrett[24] from pinacolone and MeMgI. Dehydration of the alcohol over alumina as described above gave an 81% yield of 2,3,3-trimethyl-1-butene which was then converted to 2,3,3-trimethyl-1-butanol by the usual hydroboration procedure.[25] The yield of alcohol from olefin was 75%, b.p. 154–158°, n_D^{28} 1·4255; reported[26] b.p. 158–159°, n_D^{25} 1·4230.

The alcohol was converted to the acetate by the usual Ac_2O–pyridine method in 81% yield, b.p. 164–168°, n_D^{24} 1·4170; reported[20] 170–171°, n_D^{25} 1·4125.

The methyl carbonate of 2,3,3-trimethyl-1-butanol was prepared by the method above using 5·9 g alcohol, 9·8 g pyridine, and 9·5 g methyl chloroformate. Again the pure methyl carbonate was isolated by VPC trapping, n_D^{24} 1·4188, strong IR band at 1750 cm^{-1}. The NMR spectrum showed a sharp band at 6·40 τ (3 protons), a series of sharp bands (at least 7) was spread from 5·7–6·5 τ (2 protons), a broad envelope was found around 8·5 τ (1 proton), and a sharp spike with small shoulders on each side was found at 9·1 τ (12 protons). (Found: H, 10·20. Calc. for $C_9H_{18}O_3$: H, 10·42%.)

4-Acetoxy-2,3-dimethyl-1-butene and its 4-methyl carbonate analog. 4-Acetoxy-2,3-dimethyl-1-butene was prepared from trimethylethylene by a Prins reaction.[27] The NMR spectrum of the acetate consisted of an unresolved multiplet at 5·38 τ (2 protons), a pair of doublets at 6·12 and 6·22 τ (J = 3 c/s, 1 proton), a broad multiplet at 7·7 τ (1 proton), a singlet at 8·16 τ (3 protons), an unresolved multiplet at 8·40 τ (3 protons), and a doublet at 9·08 τ (J = 7 c/s, 3 protons). Hydrolysis of the acetate was carried out in alcoholic NaOH.[28]

Methyl 2,3-dimethyl-3-butenyl carbonate was prepared from 5·3 g of the crude alcohol, 10 ml pyridine, and 9 g methyl chloroformate by the usual procedure. The pure material was isolated by VPC, n_D^{25} 1·4262, strong IR bands at 1750, 1650, 1440, and 890 cm^{-1}. The NMR spectrum gave an unresolved multiplet at 5·37 τ (2 protons), a pair of doublets centered at 6·06 and 6·18 τ (J = 4 c/s, 1 proton), a singlet at 6·40 τ (3 protons), a broad multiplet spread about 7·6 τ (1 proton), a singlet at 8·30 τ (3 protons), and a doublet centered at 8·95 τ (J = 7 c/s, 3 protons). (Found: H, 9·17. Calc. for $C_7H_{12}O_3$: H, 8·92%.)

3,3-Dimethyl-1-butyl acetate. 3,3-Dimethyl-1-butene was converted to 3,3-dimethyl-1-butanol by hydroboration[25] and acetylated with Ac_2O–pyridine.[26]

The electrolysis of potassium acetate in a methanol solution of 3,3-*dimethyl-*1-*butene.* The electrolyses were carried out in two ways.

(a) *Incremental addition of acetic acid.* The electrolysis procedure has been described previously.[1] The electrodes were two pieces of smooth pt 1·25 inches square and spaced about 0·25 inches apart.

3,3-Dimethyl-1-butene (76 g) was added to a soln of 80 g of AcOK in 400 ml MeOH. A current of 1·5 amps was allowed to pass for 24 hr. During this period, 125 ml AcOH was added in portions in such a way that the pH was maintained at 6 to 7.

At the conclusion of the reaction period, the mixture was poured into 500 ml cold water. The oily layer was separated, dried over $MgSO_4$, and then distilled through a semimicro column. The distillation was stopped at a head temp of 42°. The amount of distillate was 51 g and was shown to be nearly pure 3,3-dimethyl-1-butene by VPC. The residue of 3·6 g was found to contain at least 12 components. The 10 major bands were trapped from the VPC and identified by a comparison of the retention volume, index of refraction, IR spectrum, and NMR spectrum with those of the known compounds prepared previously. These results are given in Table 1 in order of increasing retention volume.

(b) *Initial addition of acetic acid only.* Six electrolyses were carried out as described above except that all of the AcOH was added at the start of the reaction. In each case, 30 g AcOK, and 200 ml MeOH was used. The product was worked up as before. The conditions used and the product analyses are given in Table 2.

In one experiment, the electrolysis was carried out in an H-cell with the compartments separated by a glass frit. The product spectrum was the same as above. Product was found only in the anode compartment.

Electrolysis of potassium acetate in the presence of 2,3,3-*trimethyl-*1-*butyl acetate.* Two experiments were carried out in which AcOK was electrolyzed in MeOH solns of 2,3,3-trimethyl-1-butyl acetate. The conditions were essentially as described previously. In the first experiment AcOH was added in increments. Only unreacted ester was recovered. In the second, an initial amount of acetic acid was added, and the electrolysis continued until the reaction mixture was basic. The recovered product consisted of starting ester and the corresponding alcohol. No evidence of methyl carbonate formation was found in either case.

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