[CONTRIBUTION OF THE CHEMISTRY DEPARTMENT, OHIO UNIVERSITY]

The Kolbe Electrolysis as a Source of Free Radicals in Solution

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RECEIVED MARCH 14, 1959

The electrolysis of methanolic solutions of potassium acetate has been carried out in the presence of both butadiene and isoprene. Examination of the products indicated the addition of both methyl and acetoxy free radicals to the acceptor molecules.

For many years the Kolbe electrolysis has been known as a useful method of producing symmetrical alkanes from aliphatic carboxylic acids. The mechanism of the reaction has been discussed at some length,[1] and it is now generally accepted that in non-aqueous solvents such as acetic acid or methanol the reaction proceeds through the discharge of the carboxylate anion to form an acyloxy free radical.[1b,c] The subsequent reactions of this intermediate account for the variety of products frequently found in the Kolbe electrolysis.

The question of whether or not the Kolbe electrolysis may serve as a useful source of free radicals in solution has been only partially answered. It has been reported that the electrolysis of sodium acetate in acetic acid containing trinitrotoluene leads to the formation of a small amount of trinitro-*m*-xylene.[2] Similarly, 4-phenylpyridine has been found in small amounts during the electrolysis of benzoic acid in pyridine.[3] Wilson and Hayashi[4] have reported 30% yields of *o*- and *p*-acetoxyanisoles formed by the electrolysis of potassium acetate in a mixture of acetic acid and anisole. These latter data have been interpreted as indicating a finite life time for the acetoxy free radical in the reaction.[1c]

Of particular interest is the observation by Goldschmidt and co-workers that the electrolysis of sodium acetate in acetic acid and styrene produced 2,3-diphenylhexane and a low molecular weight polystyrene.[5] In addition, a fraction corresponding to $C_{19}H_{22}O_2$, a mixture of isomeric diphenylpentyl acetates, was isolated. Apparently the yields of these low molecular fragments were quite small. Similar results were obtained in a series of probing experiments in this Laboratory just prior to the publication of the work in Germany. It is evident from these results that both acetoxy and methyl free radicals are being produced in the electrolysis and that both are then attacking the radical acceptor styrene.

Kharasch and co-workers[6] have shown that butadiene and isoprene may both serve as exceptionally good radical traps. Furthermore, dimeric dibasic acids have been reported as products when potassium ethyl malonate was electrolyzed in the presence of butadiene.[7] In order to extend our knowledge of the Kolbe electrolysis as a source of free radicals in solution we have carried out the electrolysis of potassium acetate in methanolic solutions containing either butadiene or isoprene.

Discussion

The data existent in the literature[2-5] suggest that the electrolysis of acetate ions in the presence of butadiene should lead to products formed by the attack of both acetoxy and methyl free radicals upon the radical acceptor. The two possible intermediates will have the resonance hybrid structures A–B and C–D, respectively (see Chart I). Subsequent reactions of these intermediates with other methyl or acetoxy radicals, with the solvent or with each other will produce products containing either one or two acceptor units per molecule. These various possibilities are enumerated in Chart I. The twenty-one compounds listed here by no means exhaust all of the possibilities for the radical intermediates above may themselves add to butadiene to produce new radicals containing a higher number of butadiene units. However, this latter course of reaction would not be expected to be very important, for the radical intermediates A–B and C–D are no doubt sufficiently stabilized by resonance to make further attack on butadiene unlikely. Furthermore, it is reasonable to expect that the environment about the electrode has a particularly high concentration of radicals which would be expected to react preferentially with each other.

The electrolysis of potassium acetate in a methanolic solution of butadiene was carried out according to the procedure usual for the Kolbe electrolysis.[8] Vapor phase chromatography (V.P.C.) of the reaction product indicated the presence of at least ten different products. The reaction product was subdivided into two fractions on the basis of boiling point. All material boiling below 70° (approximately 75 wt. % of the product) was collected in fraction I, while all material boiling above 70° was similarly placed into fraction II.

The analysis of fraction I was accomplished by a combination of vapor phase chromatography and infrared spectral analysis. Wherever possible a direct comparison was made with authentic samples of suspected reaction components. The details of the analysis are given in the Experimental section. Suffice it to say here that the following products were established as composing this fraction: 1-pentene, 22 mole %; 3-methyl-1-

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[1] (a) S. Glasstone, "Introduction to Electrochemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1942, pp. 516–519. (b) B. C. L. Weedon, *Quart. Revs.*, **6**, 380 (1952); (c) C. L. Wilson and W. T. Lippincott, THIS JOURNAL, **78**, 4290 (1956).

[2] L. F. Fieser, R. C. Clapp and W. H. Daudt, *ibid.*, **64**, 2052 (1942).

[3] F. Fichter and H. Stenzel, *Helv. Chim. Acta*, **22**, 970 (1939).

[4] C. L. Wilson and T. Hayashi, Abstracts of Papers Presented at the 126th Meeting of the American Chemical Society, New York, N. Y., 1954, p. 78-O.

[5] (a) S. Goldschmidt and E. Stockel, *Chem. Ber.*, **85**, 630 (1952); (b) S. Goldschmidt, *Angew. Chem.*, **69**, 132 (1957).

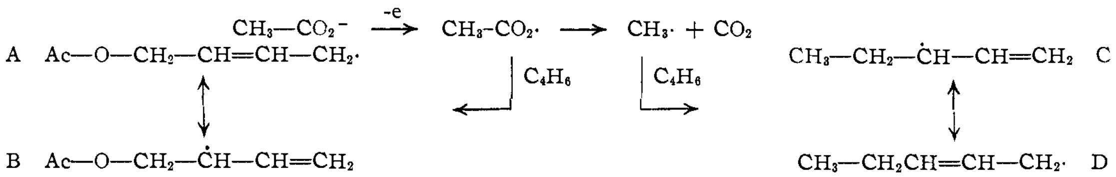
[6] M. S. Kharasch, P. G. Holton and W. Nudenberg, *J. Org. Chem.*, **19**, 1600 (1954).

[7] R. V. Lindsey and M. L. Peterson, U. S. Patent 2,680,713, June 8, 1954; *C. A.*, **48**, 9847 (1954).

[8] F. Fichter and R. E. Meyer, *Helv. Chim. Acta*, **16**, 1408 (1933).

CHART I

PROBABLE PRODUCTS FROM THE ELECTROLYSIS OF POTASSIUM ACETATE IN THE PRESENCE OF BUTADIENE



Monomeric products

1. A + $\cdot$O-Ac → $AcOCH_2CH{=}CHCH_2OAc$
2. B + $\cdot$O-Ac → $AcOCH_2CH(OAc)CH{=}CH_2$
3. C + $\cdot$OAc → $CH_3CH_2CH(OAc)CH{=}CH_2$
4. D + $\cdot$OAc → $CH_3CH_2CH{=}CHCH_2OAc$ ← $CH_3\cdot$ + A
5. A + Y-H[a] → $AcOCH_2CH{=}CHCH_3$
6. B + Y-H → $AcOCH_2CH_2CH{=}CH_2$
7. C + Y-H → $CH_3CH_2CH_2CH{=}CH_2$
8. D + Y-H → $CH_3CH_2CH{=}CHCH_3$
9. C + $CH_3\cdot$ → $CH_3CH_2CH(CH_3)CH{=}CH_2$
10. D + $CH_3\cdot$ → $CH_3CH_2CH{=}CHCH_2CH_3$
11. B + $CH_3\cdot$ → $AcOCH_2CH(CH_3)CH{=}CH_2$

Dimeric products

12. A + A → $AcOC_4H_6C_4H_6OAc$
13. B + B → $AcOCH_2CH(CH{=}CH_2)CH(CH{=}CH_2)CH_2OAc$
14. A + B → $AcOC_4H_6CH(CH{=}CH_2)CH_2OAc$
15. C + C → $CH_3CH_2CH(CH{=}CH_2)CH(CH{=}CH_2)CH_2CH_3$
16. D + D → $CH_3C_4H_6C_4H_6CH_3$
17. D + C → $CH_3C_4H_6CH(CH{=}CH_2)CH_2CH_3$
18. A + C → $AcOC_4H_6CH(CH{=}CH_2)CH_2CH_3$
19. A + D → $AcOC_4H_6C_4H_6CH_3$
20. B + C → $AcOCH_2CH(CH{=}CH_2)CH(CH{=}CH_2)CH_2CH_3$
21. B + D → $AcOCH_2CH(CH{=}CH_2)C_4H_6CH_3$

[a] The symbol Y-H denotes some source of hydrogen in the reaction. Whether this is the solvent or atomic hydrogen produced at the electrode is not known.

pentene, 16 mole %; *trans*-3-hexene, 56 mole %; and a mixture of methanol and methyl acetate, 6 mole %. The above quantities were determined from the areas under the V.P.C. curve, and it is recognized that they are only approximate values. A specific search for *cis*-3-hexene produced negative results.

The behavior of fraction II on distillation indicated the futility of this mode of separation. Examination of each fraction obtained by V.P.C. showed the presence of several components in each. Consideration of the boiling points, infrared spectra and the list of possible products in Chart I suggested that this fraction was composed primarily of a mixture of C_{10}-hydrocarbons and C_6-acetate esters. The complication of *cis–trans*-olefin isomers in interpreting the V.P.C. and infrared data was eliminated by hydrogenating this fraction until completely saturated. Separation of the ester material from the hydrocarbon component was effected by first reducing the esters with lithium aluminum hydride to the corresponding alcohols followed by chromatography over alumina. The hydrocarbon fraction was eluted with petroleum ether and designated as fraction II′. The alcoholic component was obtained by elution from the column with methanol and was collected as fraction II″.

Fractional distillation of II′ failed to effect any appreciable separation; the major fraction boiling over the range 140–147°. Analysis of this fraction for carbon and hydrogen and by means of molecular weight agreed with the assignment $C_{10}H_{22}$. Fractionation by V.P.C. produced three bands. The first band off the column was small and cleanly separated from the following two large bands which tailed together badly. Attempts to resolve these latter bands at different conditions of temperature and flow rate of eluting helium failed to produce a better separation. A comparison of the retention times of these two bands with those of several likely C_{10}-hydrocarbons suggested that they were 3-ethyloctane and *n*-decane, respectively. The infrared spectrum of fraction II″ was found to contain the characteristic bands of each of these compounds. The presence of three additional bands in the spectrum of the reaction product was indicative of an additional substance in the mixture in keeping with the V.P.C. data. No evidence for 2,3-diethylhexane was found in either the V.P.C. or infrared examination of this fraction.

Fraction II″ was examined in essentially the same fashion. The combination of boiling point. infrared data and V.P.C. data supported the view that this fraction consisted of a mixture of C_4^- and C_5^-alcohols. A survey of retention times of known alcohols suggested by the possibilities listed in Chart I was carried out. The three major bands formed by fraction II″ on V.P.C. were found to agree in retention times with those of *n*-butyl alcohol, 2-methyl-1-butanol and *n*-amyl alcohol. A rough calculation of the amounts of these components was carried out from the areas under the various curves. The amounts of each were, respectively: 6 mole %, 62 mole % and 32 mole %. The infrared spectra of a synthetic mixture of these alcohols was in agreement with this analysis of the mixture. Confirmation was obtained by converting samples of the reaction product and the synthetic mixture to their corresponding acetate esters. The infrared spectra and V.P.C. analysis were again in agreement regarding the composition of the unknown.

The electrolysis of potassium acetate in the presence of isoprene yielded approximately the same amount of high boiling reaction product as in the case of butadiene. In view of the dissymmetry of the radical acceptor the number of potential products is greatly increased. Examination of the reaction products was carried out in essentially the same fashion as before. From the low boiling hydrocarbon fraction it was possible to obtain pure *cis*-3-methyl-3-hexene, produced by the 1,4-addition of methyl radicals to isoprene. Examination of the reaction product failed to reveal the presence of any of the corresponding *trans* isomer.

The high boiling material was again separated into a hydrocarbon and alcohol fraction by first reducing the acetates to their corresponding alcohols followed by chromatography over alumina. Distillation of the hydrocarbon fraction so obtained gave a fraction which agreed in properties with that reported by Kharasch, Holton and

Nudenberg for the reaction of methyl iodide with magnesium in the presence of isoprene.[8] This fraction has been shown to consist of a mixture of $C_{12}H_{20}$ diolefins produced by the addition of methyl radicals to isoprene followed by dimerization through coupling of these intermediate free radicals.

$$CH_3\cdot + C_5H_8 \longrightarrow CH_3{-}C_5H_8\cdot$$
$$2CH_3{-}C_5H_8\cdot \longrightarrow CH_3{-}C_5H_8{-}C_5H_8{-}CH_3$$

The attempt to identify the components of the alcohol fraction was abandoned after a preliminary examination revealed the complexity of the mixture.

In keeping with the observations in the literature, it is evident from our data that both methyl and acetoxy free radicals are attacking the radical acceptors butadiene and isoprene. Of the various paths outlined in Chart I for the attack on butadiene, evidence now exists for the operation of paths 4, 5 and/or 6, 7, 9, 10, 11, 16 and 17. A careful search of the reaction products failed to produce any evidence for the operation of paths 2, 3, 8 and 15. While no decision regarding the non-operation of the remaining paths is possible, it is evident that they play no significant role in the course of the reaction.

The failure to observe any *cis*-3-hexene from the reaction with butadiene or any *trans*-3-methyl-3-hexene from the reaction with isoprene raises a point of some interest. It is reasonable to expect that if the intermediate C–D or its isoprene analog existed free in the reaction, then mixtures of *cis–trans* isomers would result. The observed stereospecific mode of addition suggests that the reaction intermediate is held on the electrode surface in some position preferential to the formation of the observed products. Support for the supposition of a chemisorbed intermediate is given by formation of 1-pentene (path 7) to the exclusion of 2-pentene (path 8) in the reaction with butadiene. Whether this product arises through the attack of the intermediate C–D on the solvent or by reaction with atomic hydrogen produced at the electrode is a matter of speculation. This result suggests, however, that C–D is not free in solution to react at will, but rather is bound in some way precluding the formation of any of the 2-isomer. In the absence of additional outside evidence the above discussion must be recognized as being of a speculative nature.

There would seem to be no *a priori* reasons for predicting the operation of certain paths in Chart I to the complete or nearly complete exclusion of other possible paths. Questions regarding the concertedness of the radical additions, the role of steric factors in the addition and, finally, of chemisorption of radical intermediates on the electrodes must await further studies of the Kolbe electrolysis as a means of producing free radicals in solution. Such studies are currently being pursued in this Laboratory.

NOTE ADDED IN PROOF.—After submission of this material for publication R. V. Lindsey and M. L. Peterson (THIS JOURNAL, 81, 2073 (1959)) reported that the electrolysis of methanolic solutions of potassium acetate in the presence of butadiene produces 3-hexene as well as various decadienes. When isoprene was the diene, 3-methyl-3-hexene was reported as well as higher molecular weight hydrocarbons.

Acknowledgment.—This research was supported by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

Experimental

All infrared spectra were recorded on a Perkin–Elmer model 21 infrared spectrophotometer.[8a] Vapor phase chromatography (V P.C.) was carried out using a Fisher-Gulf partitioner. The standard column (tricresyl phosphate on firebrick) furnished with the instrument was used in each case. Temperatures and flow rates of eluting helium are recorded below. Molecular weights were determined by the lowering of the freezing point of benzene.

The Electrolysis of Potassium Acetate in the Presence of Butadiene.—The reaction was carried out in a flask fitted with a Dry Ice condenser, dropping funnel, and a pair of electrodes mounted to glass tubes fitted through a rubber stopper and mounted in the center hole of the flask. The electrodes were pieces of smooth platinum 1.25 inches square and space 0.25 inch apart.

One hundred grams of potassium acetate was dissolved in a mixture made up of 440 ml. of methanol and 100 g. of butadiene. The current was adjusted to 2.0–2.1 amps. The reaction was allowed to proceed for 12–14 hr. with stirring. During this period 35 g. of acetic acid was added in portions in such a way that the *p*H of the reaction mixture, as measured by touching a small drop to a piece of moistened *p*H test paper, was maintained between 6–8.

At the end of the reaction period the butadiene was allowed to evaporate. The remaining solution was then poured into an equal volume of water. The oily layer which formed was dried over anhydrous magnesium sulfate. In those experiments in which only the high boiling reactions were to be examined the reaction mixture was further extracted with several portions of ether. The yield of crude product, containing appreciable amounts of dissolved butadiene, was 25–30 g.

The reaction product was distilled through a semi-micro column. All material boiling below 70° (8 g.) was retained in fraction I. Material boiling above 70° (4 g.) was designated as fraction II.

(a) **Examination of Fraction I.**—Fractional distillation of the material boiling below 70° through a spinning band column gave material boiling continuously over the range of 24–64°. By careful refractionation it was possible to isolate material with b.p. 62–64°, $n^{25}\mathrm{D}$ 1.3910; reported[9] for *trans*-3-hexene, b.p. 67°, $n^{20}\mathrm{D}$ 1.3943. The infrared spectra of this material indicated that it was pure *trans*-3-hexene.[10a]

The composition of fraction I was further examined by means of V.P.C. at 80°. At a flow rate of 50 ml. helium per min. these three major bands were found; retention times: 7, 13 and 18 min. In addition, a very small double band was found at 25–28 min. This latter doublet was identified as a trace of methanol and methyl acetate by comparison of retention times with known samples. By the use of a Dry Ice trap it was possible to freeze out a portion of the 18-min. band. The infrared spectrum identified this material as *trans*-3-hexene.

In the same fashion a sample of the material appearing at 13 min. was obtained. The infrared spectrum of this material showed all of the characteristic bands of 3-methyl-1-pentene when compared with that of an authentic sample.[11] It was further evident from the spectrum that the sample was somewhat contaminated with *trans*-3-hexene. The retention time (V.P.C.) of the authentic sample was in complete agreement with the 13-min. band in the reaction product.

[8a] The authors acknowledge with gratitude the financial aid provided by the National Science Foundation for the purchase of the Perkin–Elmer model 21 infrared spectrophotometer used in this study (NSF-G 3912).

[9] M. C. Hoff and C. E. Boord, *Am. Petroleum Inst. Research Project* **45**, Monthly Reports, 75 (1949).

[10] "Catalog of Infrared Spectral Data," Am. Petroleum Inst. Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa. (1947); (a) serial no. 621 (1947); (b) serial no. 1816 (1956).

[11] A sample of 3-methyl-1-pentene was generously supplied by Dr. W. D. Huntsman.

The band appearing at 7 min. was identified as 1-pentene by comparison of the retention time and band shape with that of an authentic sample.

Determination of the area under the V.P.C. curve allowed the following rough estimation of the composition of fraction I: 1-pentene, 22 mole %; 3-methyl-1-pentene, 16 mole %; *trans*-3-hexene, 56 mole %; and methanol–methyl acetate, 6 mole %.

(b) **Examination of Fraction II.**—Careful fractionation of the material boiling above 70° produced no pure fractions; the boiling point rose continuously from 100–170°. Examination of the various samples collected by means of infrared spectroscopy, molecular weight determinations and V.P.C. suggested that this material was a mixture of unsaturated hydrocarbons and acetate esters.

The fraction II material from four different runs was collected (total 31 g.). It was first hydrogenated over Adams platinum with a small amount of added acetic acid until no further test for unsaturation was given.

The material from the hydrogenation was washed with water, dil. sodium bicarbonate, then again with water, and dried over anhydrous magnesium sulfate.

The crude material was then treated with 5 g. of lithium aluminum hydride in 250 ml. of ether. The reaction mixture, after stirring at room temperature overnight, was treated with 15 ml. of 10% potassium hydroxide. The ether solution was decanted from the slurry which was then washed repeatedly with more ether. The combined ether extracts were dried over magnesium sulfate. The ether was boiled off, and the residue material was chromatographed over 250 g. of chromatographic grade alumina made up in petroleum ether. The hydrocarbon component (fraction II′) of the mixture was eluted from the column with one liter of low boiling petroleum ether which was then distilled off through a Widmer column (yielded 7.5 g.). The alumina was then washed with one liter of methanol which was distilled away from fraction II″ (4.8 g.).

Slow distillation of fraction II′ through the spinning band column gave the following cuts: 1, 35–138°, $n^{25}\mathrm{D}$ 1.4090 (1.4 ml.); 2, 140–143°, $n^{25}\mathrm{D}$ 1.4140 (4.5 ml.); 3, 143° to temperature drop, $n^{25}\mathrm{D}$ 1.4143 (3.0 ml.); residue (0.4 ml.). Examination of fractions 2 and 3 by means of V.P.C. indicated that they were of the same composition. At 126° and a flow rate of *ca.* 150 ml. of helium per min. three bands were produced. The first (retention time, 7 min.) was quite small and was not examined further. The second and third bands (retention times, 10 and 12 min., respectively) were large, and the second band tailed badly into the third. A search for more advantageous conditions for separation failed to produce any better resolution of these bands. The carbon-hydrogen analysis[12] of fraction 3 was carried out.

Anal. Calcd. for $C_{10}H_{22}$: C, 84.41; H, 15.59. Found: C, 84.62; H, 15.34; mol. wt., 142.

An examination of the infrared spectrum of this fraction suggested that it was primarily a mixture of *n*-decane and 3-ethyloctane. A comparison was made with the spectra of authentic samples of these compounds. In addition to the usual bands found in common with all alkanes, bands were found at 8.27, 8.45, 9.32, 11.88 and 12.60 μ (these bands are characteristics of *n*-decane). Other bands at 8.12, 8.36, 8.70, 9.50 and 10.44 μ were found in agreement with the spectrum of authentic 3-ethyloctane. A synthetic mixture of authentic *n*-decane and 3-ethyloctane produced a spectrum which was virtually superimposable upon that of fraction 3. The spectrum of reaction product showed additional bands at 11.55, 12.21 and 13.40 μ indicating that the fraction was not completely pure. These bands may have been due to the small amount of the material which appeared in the first bands of the V.P.C. tracing.

Further evidence was obtained for the existence of *n*-decane and 3-ethyloctane in the reaction product for the retention times of authentic samples of these compounds on V.P.C. were in complete agreement with those found for the reaction product in fraction 3 above; the band at 10 min. corresponded to 3-ethyloctane while the one at 12 min. agreed with the time for *n*-decane.

A specific search was made for the presence of *n*-nonane and 2,3-diethylhexane among the reaction products. Comparison of the V.P.C. retention times and the infrared spectra of authentic samples of these materials with the corresponding data from the reaction product failed to produce any evidence for their formation in the reaction.

Fraction II″ was analyzed in essentially the same fashion. Careful fractional distillation indicated the presence of a small amount of methanol in this fraction. The major component was found to have b.p. 92–93°, $n^{25}\mathrm{D}$ 1.4067 (yield 1.1 ml.). The V.P.C. of this fraction at 136° and a flow rate of 120 ml. of helium per min. produced three bands with retention times of 8.8, 12.7 and 15.5 min., respectively. The last two bands were not completely resolved. A comparison of the retention times and infrared spectra of a number of authentic samples of C_4- and C_5-alcohols with the data from the unknown fraction suggested that this material was a mixture of *n*-butyl alcohol, 2-methyl-1-butanol and *n*-amyl alcohol. From the areas under the V.P.C. curves it was estimated that these components were present in approximately the following amounts: 6 mole %, 62 mole % and 32 mole %, respectively. A synthetic mixture of this composition was made up. The V.P.C. graph and the infrared spectra were in complete agreement with those of the reaction product. As a further check a sample of the reaction product and the synthetic mixture of alcohols were each converted to the acetate esters by a Fischer type esterification. Again the V.P.C. curves and the infrared spectra of the known and unknown mixtures were in complete agreement.

A specific search for 3-pentanol failed to indicate any evidence for the presence of this compound among the reaction products.

The distillation of fraction II″ left a small amount of high boiling residue. The boiling point of this material was determined by the melting point capillary method as 193–195° with decomposition. The spectrum of this component resembled to a certain degree that of *n*-nonyl alcohol. However, it was not possible to make a definite identification. Examination of the spectrum of 1,2-butanediol ruled out the possibility of the presence of this compound in the high boiling alcoholic residue.

Comparison Compounds.—The following compounds were prepared so that their infrared spectra and behavior on V.P.C. could be compared with the products of the above reaction; *n*-decane, 3-ethyloctane, 3,4-diethylhexane, *n*-nonane and 3-pentanol. Each was prepared by a method existent in the literature. The physical properties in each case were in agreement with the reported values.

The Electrolysis of Potassium Acetate in the Presence of Isoprene.—The electrolysis of potassium acetate in the presence of isoprene was carried out in a fashion completely analogous to that reported above for butadiene. After dilution of the reaction mixture with water the oily layer was drawn off and dried. The isoprene was then stripped off, and the residue distilled through a semi-micro column. All material boiling below 100° was placed in fraction I while material boiling above 100° was designated as fraction II. The yield of crude product was about 12 g.

Distillation of fraction I (1–2 g.) gave a small amount of methanol and methyl acetate. The major portion distilled between 89 and 93° and was slightly contaminated with ester. Purification was carried out by treating this material with a small portion of lithium aluminum hydride. The hydrocarbon component was recovered in the usual fashion; b.p. 91–92.5°, $n^{25}\mathrm{D}$ 1.4075 (reported[13] for *cis*-3-methyl-3-hexene, b.p. 100.47, $n^{20}\mathrm{D}$ 1.4083). This material gave a molecular weight of 98 and 106 for two determinations and a hydrogen equivalent of 92; calcd. for C_7H_{14}, 98. The infrared spectrum of this substance showed all of the bands of *cis*-3-methyl-3-hexene.[10b] In addition, several bands attributable to vinyl absorption were also present.

As previously described, fraction II (10–11 g.) was treated with lithium aluminum hydride and then chromatographed over alumina. The hydrocarbon component (6.5 g.) was eluted with petroleum ether. Distillation of this material through a spinning band column produced a fraction b.p. 81–87° (14 mm.), $n^{25}\mathrm{D}$ 1.4520 (reported by Kharasch, *et al.*, for $C_{12}H_{22}$ fraction from the action of methyl iodide on magnesium in the presence of isoprene; b.p. 75–80° (14 mm.), $n^{20}\mathrm{D}$ 1.4542[6]). The molecular weight was determined as 165 (calcd. for $C_{12}H_{22}$, 166). The hydrogenation equivalent was found to be 84 (calcd. for $C_{12}H_{22}$, 83).

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[12] Analysis performed by the Galbraith Laboratories, Knoxville, Tenn.

[13] W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 413–434 (1945).

Elution of the chromatographic column with methanol gave a mixture of alcohols (4.0 g.) boiling continuously over the range 80–194°. No attempt was made to identify materials in this fraction due to the large number of isomers potentially present.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS]

Participation by *ortho* Substituents in the Dissociation of Iodobenzene Dichlorides

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RECEIVED APRIL 25, 1959

The dichlorides of 2-iodoacetanilide, 2-iodobenzanilide, 2-iodobenzyl alcohol and 2′-iodobenzanilide, like those of 2-iodobenzoic acid and its methyl ester, equilibrate with their component iodobenzenes and chlorine in acetic acid much more rapidly than do their *para* isomers. It is suggested that the substituents *ortho* to the iodine atom in these dichlorides promote the reaction through a neighboring group type participation which involves electron release to the iodine atom. The *o*-$OCOCH_3$, *o*-$OCOC_6H_5$ and *o*-COCl groups, which are closely related structurally to those substituents that so strongly enhance the reactivity of iodobenzene dichloride, are ineffective as *ortho* participants in this reaction.

Recently a number of cases have been reported of reactions at an aromatic side chain which are subject to intense acceleration when certain *ortho* substituents are present.[1–4] Presumably these substituents, through participation as neighboring groups, substantially reduce the activation energy required for reaction. This interpretation has been applied in explaining the observation that carboxyl and carbomethoxy groups in *ortho*, but not in *para*, positions very sharply enhance the rate of equilibration of iodobenzene dichloride with its components in acetic acid.[5] It has been suggested, from what is known of the influence of various solvents on the kinetics of the dichloride equilibration process, that the iodine atom is positively polarized in the activated complex.[6] An *o*-carboxyl (or carbomethoxy) substituent apparently is favorably located so that it can facilitate the activation process by donating electrons to the neighboring iodine. For reasons outlined previously it seems unlikely that the bulk of the *o*-substituent can be an important rate-influencing factor in this type of reaction.[7]

If the proposed explanation for the carboxyl and carbomethoxy effects is correct, it may be anticipated that other appropriately located substituents with nucleophilic properties may also increase the reactivity of iodobenzene dichloride. As a result of this investigation, in which the equilibration rates of a number of likely *o*-substituted dichlorides and their *p*-isomers have been studied, four additional participating substituents can be reported.

Experimental

Materials.—The solvents were purified as described previously.[5–7] Except as specified all substituted iodobenzenes which were used were from Eastman Organic Chemicals.

The 2-iodoacetanilide, m.p. 109–111°, was prepared from the free amine and acetic anhydride and recrystallized from water. The 2-iodobenzanilide, m.p. 137–139°, and 4-iodobenzanilide, m.p. 217–219°, were prepared by the Schotten–Baumann method and recrystallized from ethanol. Samples of 2′-iodobenzanilide, m.p. 142–143°, and 4′-iodobenzanilide, m.p. 212–213°, were prepared from 2- and 4-iodobenzoyl chlorides and aniline and were recrystallized from ethanol.[8]

The benzoates of 2- and 4-iodophenol[9] were prepared by standard techniques[10,11] and were recrystallized from methanol. Their respective melting points were 36° and 118–120°. The acetates of 2- and 4-iodophenol were prepared as described previously.[10,12] The latter melted at 29–30°. The former, b.p. 110° (22 mm.), contained a trace of 2-iodophenol as indicated by a faint positive ferric chloride test and by the presence in its infrared spectrum of a band at 2.85 μ (OH stretch) as well as a band at 5.62 μ (which is characteristic of the ester).

The 2- and 4-iodobenzyl alcohols were prepared by lithium aluminum hydride reduction of the iodobenzoic acids by essentially the same procedure which has been used in preparing *o*-chlorobenzyl alcohol.[13] The crude products were recrystallized from water. The melting points[14] of the *o*- and *p*-isomers were, respectively, 87–89° and 72–74°.

Samples of 4-iodobenzoyl chloride,[15] m.p. 71–72°, and of 2-iodobenzamide,[8] m.p. 183–186°, were prepared as described previously.

The dichlorides were precipitated by adding chlorine to 0.1–0.2-g. samples of the substituted iodobenzene in 5 ml. of the appropriate solvent. In most cases acetic acid was used as the solvent, but in a few instances (because the iodobenzene was insoluble or the dichloride was extensively soluble) other media were used. Carbon tetrachloride was employed in preparing the derivatives of 2-iodophenyl benzoate, 2-iodophenyl acetate, and 2- and 4-iodobenzoyl chlorides. An equal volume mixture of chloroform and carbon tetrachloride was used in preparing the dichloride of 2-iodobenzanilide, and the derivative of 2′-iodobenzanilide was precipitated from an equal volume mixture of acetic acid and carbon tetrachloride. Chloroform was used in preparing the iodobenzyl alcohol dichlorides.

The yellow precipitates were filtered, washed with carbon tetrachloride and air-dried for a short time. The iodometric equivalent weights were determined as described previ-

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