

ANODIC FLUORINATION OF BENZENE

I. N. Rozhkov, A. V. Bukhtiarov,
and I. L. Knunyants

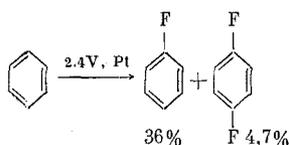
UDC 542.944:546.16:547.532

The oxidation of naphthalene on platinum in solutions, containing either F^- or $H_nF_{n+1}^-$ anions, leads to the formation of fluorinated naphthalene derivatives [1, 2]. The mechanism of this reaction apparently consists in the initial oxidation of the aromatic molecule to the cation-radical, which then reacts with the fluorine anion, with a simultaneous transfer of a second electron (the so-called ECE mechanism [3]). The comparatively low oxidation potential of naphthalene [$E_{1/2} = 1.54$ V (standard calomel electrode)] [4] makes it possible to definitely consider the primary process to be oxidation, and the subsequent process to be fluorination. The oxidation of benzene requires more positive potentials. Employing the method of cyclic voltamperometry it was shown that benzene is oxidized by the EC mechanism (one-electron oxidation with subsequent rapid chemical reaction) at a potential of 2.5 V (s.c.e.) [5]. Oxidation is observed at $E_{1/2} = 2.38$ V (s.c.e.) when $NaClO_4$ is used as the support [4].

The transition to such high values of the anode potentials markedly complicates the anodic oxidation process, since the progress of other processes becomes possible, and primarily the oxidation of the solvent and the discharge of the support. This apparently explains the unsuccessful attempt to prepare the cyano derivative of benzene by the oxidation of benzene on Pt in methanol solution on a KCN support at $E = 2.0-3.5$ V (s.c.e.) [6].

In the present paper was studied the possibility of using the oxidative fluorination method at high values of the anode potential. The acetonitrile used by us previously [2] is suitable for operation at anode potentials < 2.0 V. This acetonitrile can be purified by oxidizing the impurities by electrolysis under potentiostatic conditions at 2.9 V (s.c.e.). Analysis of the gaseous electrolysis products failed to disclose the presence of fluorinated gases, the formation of which could be expected when the F^- anion is oxidized on a Pt anode. In this connection it should be mentioned that on nickel the oxidation of F^- in $KF-CH_3COOH$ solution was observed even at 2.5 V (s.c.e.), which led to the formation of a mixture of CF_4 and CHF_3 [7]. Evidently, on Pt (in acetonitrile) the overvoltage for the oxidation of F^- is much higher than in the case of Ni (in CH_3COOH). The oxidation of F^- , if it does occur, takes place at potentials > 3.0 V.

A rise in the polarization curve is observed (Fig. 1) when benzene is added to a solution of $(C_2H_5)_4NF \cdot 3HF$ in acetonitrile (subjected to preliminary polarization at 2.9 V until the current ceases to drop) at $E = 2.0-2.1$ V (s.c.e.), which suggests the start of benzene oxidation. On the basis of these data we ran the preparative electrolysis at $E = 2.4$ V (s.c.e.), which led to the formation of fluorobenzene and 1,4-difluorobenzene in a total yield of 40%



In an analogous manner, difluorobenzene is formed from fluorobenzene in 21% yield under these conditions.

The performed coulometric measurements disclosed that the value of the current of the support electrolyte decreases sharply when benzene is added. At $E = 2.4$ V (s.c.e.), practically all of the current

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 5, pp. 1130-1133, May, 1972. Original article submitted August 26, 1970.

© 1972 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.

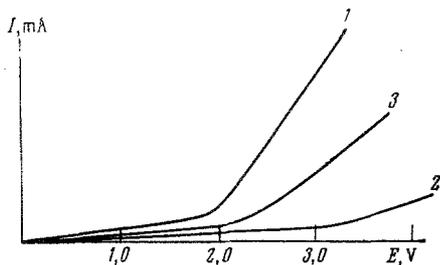
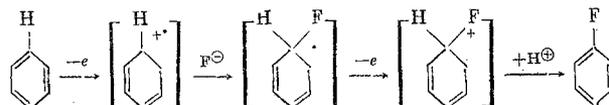


Fig. 1. Anodic oxidation of benzene on Pt in acetonitrile on a $(C_2H_5)_4NF \cdot 3HF$ support: 1) solution of $(C_2H_5)_4NF \cdot 3HF$ before electrolysis; 2) after preliminary electrolysis at 2.9 V (s.c.e.); 3) solution of 1.0 g of benzene and 5.0 g of $(C_2H_5)_4NF \cdot 3HF$ in 30 ml of acetonitrile after preliminary anodic polarization.

passed through is consumed for the oxidation of benzene (the electrolyte contained $\sim 20\%$ of unreacted benzene after passing through 80% of the current when calculated on the basis of a two-electron process).

The obtained data on the anodic replacement of the hydrogen in benzene by fluorine apparently testify in support of the ECE mechanism, analogous to the mechanism proposed by us earlier for naphthalene [2]



Fluorination, associated with the initial oxidation of the F^- , seems improbable. Thus, benzene forms only tarry products in the Simons electrochemical process [8]. The electrochemical fluorination of benzene derivatives in HF proceeds exhaustively and leads to the corresponding perfluorocyclohexanes [9].

In contrast to naphthalene, benzene does not undergo profound fluorination. We were unable to obtain derivatives, containing more than two F atoms or with a quinoid structure. The fluorination of the 1, 2- and 1, 4-difluorobenzenes fails to take place under the same conditions. The ionization potentials of benzene, fluorobenzene and the difluorobenzenes are very close: 9.24, 9.195 and 9.3 eV [10]. Since the values of the ionization potential correlate well with the oxidation potentials [11], close values could also be expected for the oxidation potentials of these compounds. As a result, an anode potential of 2.4 V (s.c.e.) is sufficient to oxidize the molecules of difluorobenzenes to the corresponding cation-radicals. The absence of products with a quinoid structure of the tetrafluorodihydronaphthalene type is evidently associated with the greater energy of the aromatization of the benzene ring.

It should be mentioned that, the same as in the case of naphthalene, a distinct orientation during substitution is observed in the given process. In the fluorination of fluorobenzene the substitution goes only in the 4 position with the formation of 1, 4-difluorobenzene. 1, 2-Difluorobenzene was not detected.

EXPERIMENTAL METHOD

The purification of the acetonitrile and $(C_2H_5)_4NF \cdot 3HF$, and the analysis of the reaction products, were both carried out as described in [2]. The chromatographic separation of the benzene, fluorobenzene and 1, 4-difluorobenzene was carried out on Porapak Q at $170^\circ C$ and a column length of 2 m. The apparatus for electrolysis at a controlled potential, and the method used to plot the I vs. V curves, were analogous to those described in [2].

Electrolysis of $(C_2H_5)_4NF \cdot 3HF$ in Acetonitrile. A solution of 5.0 g of $(C_2H_5)_4NF \cdot 3HF$ in 30 ml of acetonitrile was oxidized at a controlled potential of 2.9 V (s.c.e.). The initial value of the current was 250 mA, after 1 h it was 35, and after 5 h it was 12 mA. The total amount of current passed through was 0.3 A-h. Analysis of the gaseous products during the electrolysis process failed to disclose the presence of CF_4 and CHF_3 ; the formation of tar on the anode surface was not observed.

Electrolysis in the Presence of Benzene. To the above obtained support electrolyte was added 1.0 g of benzene, after which a controlled potential of 2.4 V (s.c.e.) was applied to the anode. After the passage of 81% of the amount of electricity (when calculated on the basis of a 2-electron process) the electrolyte was treated with 50 ml of water and the reaction products were extracted with $CHCl_3$. The obtained solution was analyzed by GLC on Porapak Q, by the ^{19}F NMR method with accumulation, and mass-spectrometrically. The yield of fluorobenzene (based on the GLC data) was 36% , and that of 1, 4-difluorobenzene

was 4.7% when based on reacted benzene. ^{19}F NMR spectrum: two signals at 36.7 and 42.9 ppm relative to CF_3COOH . The mass spectrum disclosed the ions m/e 96 and 114. The electrolysis in the presence of fluorobenzene and the 1, 2- and 1, 4-difluorobenzenes was run in a similar manner. In the case of fluorobenzene the passage of 90% of the amount of electricity gave 1, 4-difluorobenzene in 21% yield; ^{19}F NMR spectrum: 6.3 ppm relative to fluorobenzene; the mass spectrum disclosed the ion m/e 114. In the case of the difluorobenzenes the above enumerated analysis methods failed to disclose the formation of further fluorination products.

The authors express their deep gratitude to E. M. Mysov for the mass-spectrometric analysis of the products, and to V. I. Dostovalova for studying the products by the ^{19}F NMR method.

CONCLUSIONS

1. A study was made of the possibility of fluorination at high values of the anode potential.
2. Benzene under these conditions is fluorinated to fluorobenzene and difluorobenzene. Fluorobenzene forms difluorobenzene, and further fluorination fails to occur.

LITERATURE CITED

1. I. L. Knunyants, I. N. Rozhkov, A. V. Bukhtiarov, M. M. Gol'din, and R. V. Kudryavtsev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1207 (1970).
2. I. N. Rozhkov, A. V. Bukhtiarov, N. D. Kuleshova, and I. L. Knunyants, *Dokl. Akad. Nauk SSSR*, **193**, 1322 (1970).
3. L. S. Marcoux, J. M. Fritsch, and R. N. Adams, *J. Am. Chem. Soc.*, **89**, 5767 (1967).
4. E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1963).
5. T. Osa, A. Yildiz, and T. Kuwana, *J. Am. Chem. Soc.*, **91**, 3994 (1969).
6. S. Andreades and E. W. Zahnow, *J. Am. Chem. Soc.*, **91**, 4181 (1969).
7. A. V. Bukhtiarov, I. N. Rozhkov, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 781 (1970).
8. G. I. Kokhanov and S. A. Per'kova, *Élektrokimiya*, **3**, 977 (1967).
9. *Fluorine Chem. Rev.*, Paul Tarrant (editor), Dekker, New York (1967), Vol. 1, p. 77.
10. V. I. Vedenev, L. V. Gurvich, V. N. Kondrat'ev, V. A. Medvedev, and E. L. Frankevich, *Cleavage Energy of Chemical Bonds. Ionization Potentials and Electron Affinity. Handbook* [in Russian], *Izd. AN SSSR* (1962).
11. J. W. Loveland and G. R. Dimmer, *Anal. Chem.*, **33**, 1196 (1961).