the reduction step but the process as a whole is irreversible since $E_{1/2}$ varies noticeably with concentration (Fig. 3).

When $p\mathrm{H} > 9$ a pronounced diminution in diffusion currents occurs. Apparently the diazotate ion, $\mathrm{R{-}N{=}N{-}O^-}$, reverts so slowly to the diazohydroxide that measurable concentrations of the latter cannot be maintained in the vicinity of the dropping electrode. The diazotate ion does not discharge at potentials available for study in solutions containing sodium ion.

A similar analysis may be applied to the results obtained with the diazotized aminobenzoic acids. In these cases, however, $E_{1/2}$ for the first wave becomes more negative with increasing $p$H. We ascribe this increasing difficulty of reduction of $\mathrm{RN_2^+}$ to the appearance of negative poles as the carboxyl groups become ionic with increasing $p$H.

In conclusion it must be pointed out that while the present work explains the formation of diphenylmercury in the coulometric analysis and in previous large scale electrolyses[4] and possibly explains an isolated case in which biaryl has been formed by an electrolytic method,[14] polarography cannot explain the formation of phenylhydrazine and its reduction products.[4,15,16,17,18] In the cited cases large scale reductions were performed using cell potentials above 5 v. and currents as high as 7 amp. Under these conditions hydrogen was evolved, thus rendering an examination of this potential region by the polarograph impossible.

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## Summary

1. Diazo compounds derived from aniline and the three isomeric aminobenzoic acids exhibit two polarographic waves in the range of 0 v. to −1.5 v. *vs.* S.C.E. $E_{1/2}$ values for the four compounds do not differ significantly from one another.
2. At a single $p$H or over a limited range of $p$H diffusion currents are proportional to concentration of diazo compounds. When $p\mathrm{H} > 9$ diffusion currents decrease markedly and in strongly basic solutions no waves are observed.
3. In general, $E_{1/2}$ values become more negative with increasing $p$H.
4. Coulometric analysis indicates that 1 electron/mole $\mathrm{RN_2X}$ is involved at all potentials.
5. The first wave is assigned to a slow irreversible reduction of the diazonium ion, $\mathrm{RN_2^+}$ (B); the second wave to a rapid irreversible reduction of the diazohydroxide, $\mathrm{R{-}N{=}N{-}OH}$ (C). The equilibrium $\mathrm{RN_2^+} \rightleftarrows \mathrm{R{-}N{=}N{-}OH}$ is mobile, while $\mathrm{R{-}N{=}N{-}OH} \rightleftarrows \mathrm{R{-}N{=}N{-}O^-}$ is slow.

DURHAM, N. H. RECEIVED SEPTEMBER 16, 1949

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# Hydrogen Fluoride as a Condensing Agent. III. Nuclear Alkylation of Thiophenes in the Presence of Hydrogen Fluoride[1]

BY VIKTOR WEINMAYR

The action of hydrogen fluoride upon thiophene has been discussed in the literature on several occasions; Fredenhagen,[2] and Klatt[3] reported that hydrogen fluoride polymerized thiophene violently, Kutz[4] stated that hydrogen fluoride produced resinous products when used as an alkylating catalyst for thiophene.

We have discovered that thiophene did not polymerize at the instant it came in contact with hydrogen fluoride, but that a short, yet discernible time of stability existed. Although this period of stability was short it was sufficient to allow alkylation, and to convert the unstable, unsubstituted thiophene to the much more stable alkylthiophenes.

Because two competing reactions, the polymerization and the alkylation, could take place, it was necessary, with the thiophenes that polymerized easily, to use olefins as the alkylating agents rather than the less reactive alcohols or ethers.

Thiophene has been reported to be more reactive than benzene, hence benzene had been used as a solvent for acylations of thiophene.[5] However, when a solution of thiophene in benzene was alkylated with hexene-1 it was the benzene rather than the thiophene which was alkylated.

The constitution of the compounds obtained was not determined but was postulated upon

[1] For the previous paper of this series see Calcott, Tinker and Weinmayr, THIS JOURNAL, **61,** 1010 (1939).

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TABLE I

ALKYL DERIVATIVES OF THIOPHENES

| Starting materials | | Mole ratio | Reaction products | Yield, % | B. p., °C. | Mm. | Sulfur, % Calcd. | Sulfur, % Found | $n^{20}D$ | $d^{20}_4$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Thiophene | Propylene | 1:1 | Isopropylthiophene | 19[a] | 153–154 | 760 | 25.0 | 24.70 | 1.5039 | 0.9634 |
| Thiophene | Propylene tetramer[b] | 1:0.8 | Dodecylthiophene | 77[a] | 75–143 | 2 | 12.8 | 12.76 | | |
| Thiophene | Hexene-1[c] | 1:1.5 | Hexylthiophene | 23 | 97–98 | 20 | 19.03 | 19.50 | 1.4969 | |
| | | | Dihexylthiophene | 6 | 98–100 | 2 | 12.69 | 13.00 | 1.4909 | |
| Thiophene | Diisobutylene | 1:2 | Tri-*t*-butylthiophene[d] | 11 | 94–95 | 2 | 12.69 | 12.40 | 1.4885 | .8565 |
| | | | Tetra-*t*-butylthiophene[e] | 62 | 125 | 2 | 10.38 | 10.60 | M. p. 28.4° | |
| 2-Methylthiophene | 2-Ethyl-1-butene | 1:1.2 | Hexyl-2-methylthiophene | 6 | 98–101 | 11 | 17.58 | 17.30 | 1.5025 | .9419 |
| | | | Dihexyl-2-methylthiophene | 16 | 150–152 | 10 | 12.02 | 11.64 | 1.4995 | .9214 |
| 3-Methylthiophene | Diisobutylene | 1:1.7 | 3-Methyloctylthiophene | 23 | 69–70 | 1 | 15.23 | 15.06 | 1.4969 | .9219 |
| | | | 3-Methyldioctylthiophene | 43 | 133–134 | 1 | 9.98 | 9.89 | M. p. 29.3°[f] | |
| 2-Chlorothiophene | Diisobutylene | 1:1.7 | 2-Chlorodibutylthiophene | 14 | 75–76 | 2 | 13.88 | 13.31 | Cl calcd.: 15.38<br>Found: 14.30 | |
| | | | 2-Chlorotributylthiophene | 15 | 136–138 | 1 | 11.17 | 10.6 | Cl calcd.: 12.38<br>Found: 10.6 | |
| 2-Thiophenecarboxylic acid | Isopropyl ether | 1:4 | Isopropyl-2-thiophencarboxylic acid | 30 | | | 18.82 | 18.43 | M. p. 81° | |

[a] Yield based on olefin. All other yields are based on the thiophenes. [b] A commercial product, b. p. 175–246°. [c] When equimolecular amounts of benzene and thiophene were alkylated with hexene-1 (0.75 mole per mole thiophene) the reaction product distilled from 98.5–100° (20 mm.); S, 2.81%. [d] This product could be sulfonated. [e] This product could not be sulfonated. [f] A mixed melting point with the tetra-*t*-butylthiophene showed a strong depression.

elementary analysis. The principal object of this paper was to show that hydrogen fluoride, in spite of previous reports, could be used very advantageously for the alkylation of thiophene.

The following thiophenes were alkylated: thiophene, 2-methylthiophene, 3-methylthiophene, 2-chlorothiophene, 2-bromothiophene and 2-thiophenecarboxylic acid, using as the alkylating agents propylene, isopropyl ether, propylene tetramer, hexene-1, 2-ethyl-1-butene and diisobutylene.

## Experimental

The experimental procedure was in general that described in a previous paper.[1] The essential part of a successful alkylation was the simultaneous addition of the thiophene and olefin to the hydrogen fluoride. Only in cases where the substituted thiophenes were stable in hydrogen fluoride could ethers or alcohols be used.

The experimental results are summarized in Table I.

## Summary

Hydrogen fluoride has been shown to be an effective condensing agent for the preparation of nuclear alkylated thiophenes.

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# The Fluorination of Sulfuryl Chloride

BY MARK M. WOYSKI

Volatile inorganic fluorides are frequently prepared by reaction of the corresponding chlorides with such agents as antimony trifluoride, zinc, lead, or sodium fluorides. In all but a few cases complete fluorination is achieved at moderate temperatures and pressures. An exceptional case is that of sulfuryl chloride,[1] which reacts with antimony trifluoride rapidly only at elevated temperatures and pressures and gives the chlorofluoride, $SO_2ClF$, as the only product. A second exception is carbon tetrachloride which is readily fluorinated only to the difluoro stage, $CCl_2F_2$.

Equilibrium in halogen exchange reactions has not been discussed in the literature. Available thermochemical data are summarized in Table I as differences of free energies of formation of chlorides and fluorides so that the algebraic difference of any two "couplets" gives the free energy of an exchange reaction. The table is therefore a list of fluorinating agents in order of decreasing thermochemical activity. Since some of these values may be in error by several thousand calories this table is presented only as a guide to investigators. Data for most of the volatile chlorides and fluorides are not available.

The free energy values given in the table have been calculated from heat of formation data recorded in the tables of Bichowsky and Rossini[2] and from entropy data given by Kelley.[3] Several values have also been deduced from experimental results published by Jahn-Held and Jellinek.[4] Advantage has also been taken of the observation that for many chloride fluoride couplets the entropy difference is nearly the same.

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