

Electrochemical Amination: IX.¹ Effectiveness of the Process

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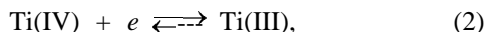
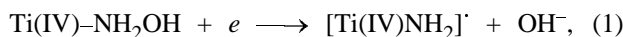
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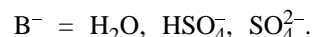
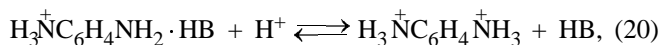
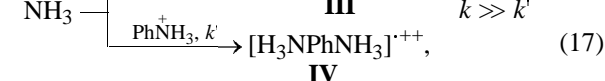
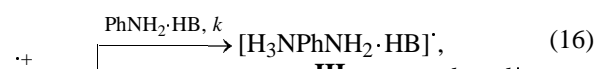
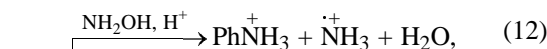
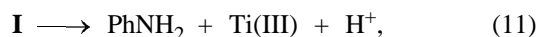
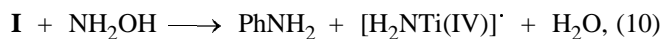
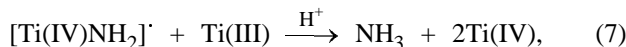
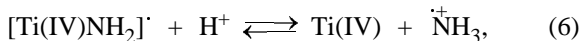
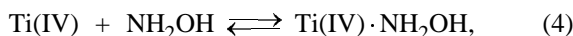
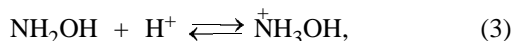
Abstract—Electrochemical amination of aromatic compounds with hydroxylamine in sulfuric acid in the presence of transition metal ions occurs by a chain mechanism. Electrolysis of the system Ti(IV)–NH₂OH–C₆H₆ in 11 M H₂SO₄ and 5 M CH₃COOH leads to formation of aniline and isomeric phenylenediamines with a total current yield of 137%. The role of acetic acid in the electrochemical process is not limited to aiding in solution of the aromatic compound. Acetic acid affects the mechanism of amination and can serve as one of the factors controlling the relative rate and selectivity of substitution.

Amination of benzene and its derivatives with hydroxylamines and transition metal ions (one-electron reducing agents) yields under certain conditions mono- [2–4] and diamines [5]. The proposed scheme of the electrochemical process in sulfuric acid media, for the system Ti(IV)–NH₂OH–PhH as an example, can be presented by Eqs. (1)–(20) [5–9]:

Catode:



Catholyte:



At a given current density the composition and yield of the amination product is determined by the relative rates of such key stages of the electrochemical process as reduction of aminyl radicals to ammonia [Eq. (7)], reaction of aminyl radicals and amine cations with the aromatic substrate [Eqs. (8) and (9)] and its monoamino derivatives [Eqs. (16) and (17)], and rearomatization of mono- [Eqs. (10)–(13)] and diaminocyclohexadienyl radicals [Eqs. (18) and (19)].

Evidently, the conditions for increased effectiveness of substitution in aqueous solutions are suppression of the competing reaction of ammonia formation and the high rate of oxidation of intermediates I–IV. To meet these conditions, electrolysis of the system Ti(IV)–NH₂OH–ArH is expedient to perform in sufficiently acidic electrolytes [4, 5, 10] at high concentrations of aromatic compounds. In this case the major aminating agent will be the most electrophilic radical cation $\overset{+}{\text{N}}\text{H}_3$ [Eq. (6)], and the rate of reaction (9), the selectivity of substitution, as well as

¹ For communication VIII, see [1].

Table 1. Isomeric compositions of phenylenediamine at various concentrations of sulfuric acid^a

[H ₂ SO ₄], M	<i>ortho</i> , %	<i>meta</i> , %	<i>para</i> , %
9	27 (26)	1 (~0)	72 (74)
10	24 (22)	1 (~0)	75 (78)
11	20 (18)	2 (~0)	78 (82)
12	14 (12)	5 (1)	81 (87)
13	7 (6)	11 (3)	82 (91)

^a Values in parentheses are the percentages in the absence of acetic acid [5].

the oxidation potential of Ti(IV) ions [10] will be increased. The problem of the low solubility of some aromatic substrates in aqueous media can be solved by addition to the electrolyte of an organic solvent comparatively inert to radical intermediates, such as acetic acid [8, 11] which we already used in experiments in 1.3 [8] and 12.8 M sulfuric acid [12]. Proceeding with these studies, in the present work we considered the effect of acetic acid on the effectiveness and mechanism of substitution in media with varied protogenic activity and gained a general notion

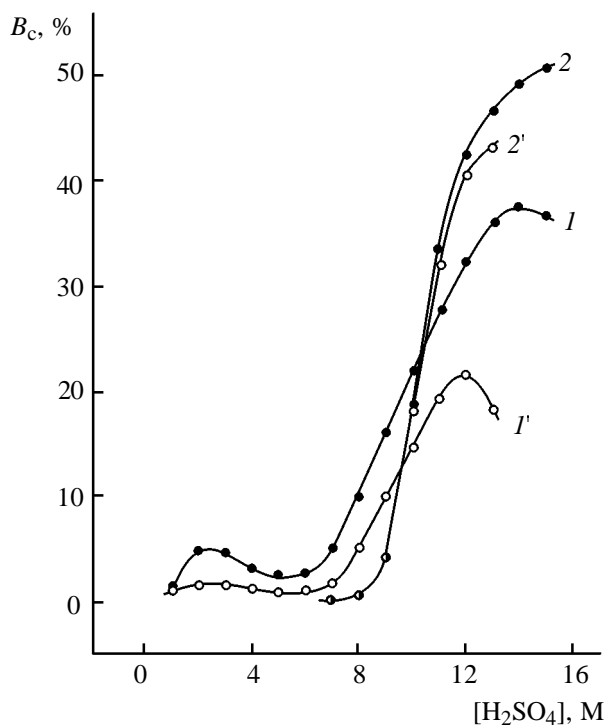


Fig. 1. Effect of the concentration of sulfuric acid on (*I*, *I'*) the current yield of aniline and (*2*, *2'*) the total current yield of isomeric phenylenediamines (*I*, *2*) in the presence and (*I'*, *2'*) in the absence [5] of 1.25 M acetic acid. [Ti(IV)] 0.25 M, 40°C.

of amination in sulfuric acid electrolytes containing the organic solvent.

For the model system we used Ti(IV)–NH₂OH–PhH, and the effectiveness of the process was measured by the total current yield of the target amines. For comparable results of benzene amination in the presence and in the absence of acetic acid, we used the experimental conditions described in [5].

Introduction of 1.25 M acetic acid in dilute and concentrated solutions of sulfuric acid much increases the current yield of aniline but does not exert such a significant effect on the total yield and the composition of isomeric phenylenediamines. In terms of the existing notion of the mechanism of the amination process (see scheme), this reaction result can be explained by the fact that the small amount of acetic acid introduced in the solution instead of water considerably increases the solubility of benzene in the electrolyte but only slightly affects the molar ratio of sulfuric acid and water, which determines the concentration of the associates PhNH₂·H₂O and hence the relative rates of formation of intermediates **III** and **IV**, whose subsequent oxidation gives either *ortho*- and *para*-phenylenediamines or the *meta* isomer, respectively.

Our studies were performed in 11 M H₂SO₄, where side reactions of aminocyclohexadienyl radicals are completely suppressed [10] and no sulfonation of the aromatic substrate occurs. Moreover, for convenient experimentation and for preparing electrolytes with increased contents of acetic acid, the concentration of

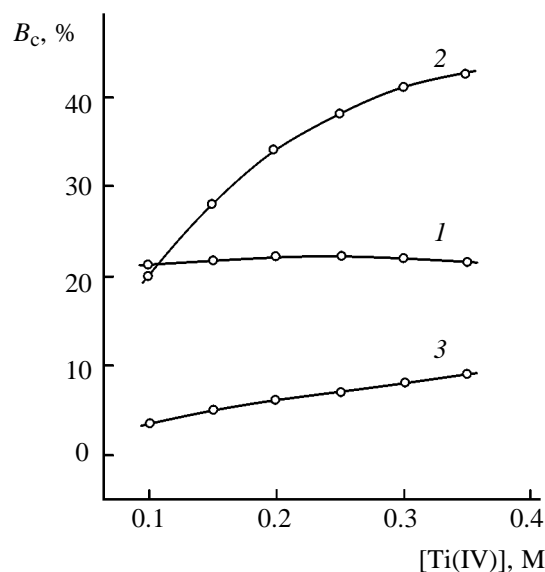


Fig. 2. Plots of the current yields of (*1*) aniline, (*2*) *para*-phenylenediamine, and (*3*) *ortho*-phenylenediamine vs. Ti(IV) concentration.

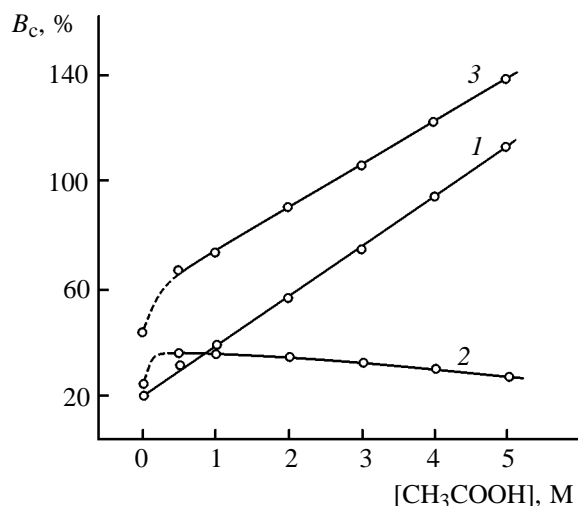


Fig. 3. Plots of (1) the current the yield of aniline and of the total current yields of (2) isomeric phenylenediamines and (3) all mono- and disubstituted products of benzene amination in 11 M H_2SO_4 vs. acetic acid concentration.

Ti(IV) ions was decreased to 0.1 M. Note that the total rate of formation of isomeric phenylenediamines in this case was considerably decreased (Fig. 2).

The products of benzene amination in 11 M sulfuric acid in the absence of the organic solvent are aniline and *ortho*- and *para*-phenylenediamines [5] (Figs. 3 and 4).

In the presence of 0.5 M CH_3COOH the current yield of all the amination products increases (Fig. 3) and traces of *meta*-phenylenediamine (Fig. 4) appear. With further increase in the concentration of acetic acid the overall effectiveness of the process also increases but the rate of formation of phenylenediamines (Fig. 3) slightly decreases with simultaneous increase in the fraction of the *meta* isomer (Fig. 4).

It is considered [2, 7, 15] that amination of aromatic compounds with $\text{M}^{n+}\text{-R}_2\text{NX}$ systems, where M^{n+} is transition metal ion (one-electron reducing agent), $\text{R} = \text{H, Alk}$; and $\text{X} = \text{Hlg, OH, and OSO}_3\text{H}$, occurs by a radical chain mechanism. However, we still have no evidence for the chain mechanism in systems where unsubstituted aminyl radicals are generated. The reported yields of amines with respect to current [16], hydroxylamine [2, 16], or hydroxylamine-*O*-sulfonic acid reach at best several tens percent. Only recently we managed to obtain aromatic amines in a current yield close to 100% [9]. In this context the results presented in Fig. 3 are good evidence in favor of the chain mechanism of electro-

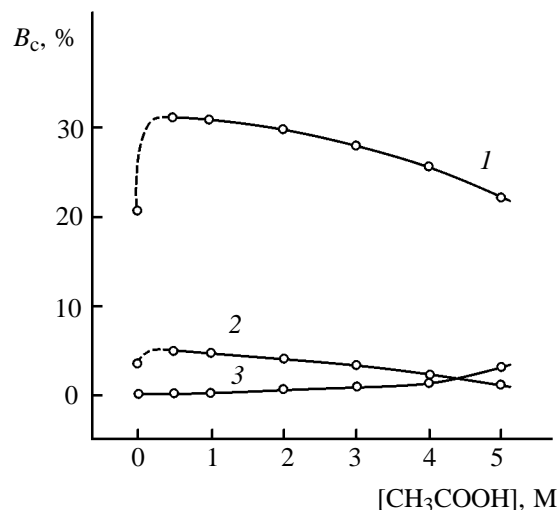


Fig. 4. Plots of the current yields of (1) *para*-phenylenediamine, (2) *ortho*-phenylenediamine, and (3) *meta*-phenylenediamine vs. acetic acid concentration for benzene amination in 11 M sulfuric acid.

chemical amination of aromatic substrates with hydroxylamine-based systems. The total current yields of amines in the electrolyses of the system Ti(IV)– NH_2OH –PhH at acetic acid concentrations of 3 M and more is higher than 100%. Thus, in the yield 5 M CH_3COOH is 137%.

The dependence of the isomeric composition of phenylenediamines on the concentration of acetic acid (Fig. 4) resembles the corresponding dependence on the concentration of sulfuric acid [5, 9]. In both cases increasing acid concentration gives rise to decreasing current yields of *ortho*- and *para*-phenylenediamines and increasing yields of the *meta* isomer. Since acetic acid additives in 11 M H_2SO_4 increased the sulfuric acid–water molar ratio, we performed a series of electrolyses of the system Ti(IV)– NH_2OH –PhH at increasing concentrations of acetic acid and a constant $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ molar ratio (Table 2); the concentration of Ti(IV) ions therewith decreased.

Based on the resulting data and taking into account that varied concentration of Ti(IV) ions in the electrolyte in the absence of acetic acid has no appreciable effect on the *p*-phenylenediamine:*o*-phenylenediamine ratio [Fig. 2; as the concentration of Ti(IV) ions decreases from 0.3 to 0.1 M, the *para*:*ortho* ratio varies within 5–6], we can state that the role of acetic acid in electrochemical aminations in sulfuric acid media is not limited to aiding in solution of the organic substrate. If the decrease in the current yield of *o*- and *p*-phenylenediamines with simultaneous increase in

the yield of the *meta* isomer (Table 2) can be explained in terms of decrease in the concentration of B^- and Ti(IV) with increasing concentration of acetic acid, then the effect of the concentration of the organic solvent on the *para/ortho* ratio implies participation of CH_3COOH in complex formation. In principle, solvent molecules can both react with the monoamination product and enter the coordination sphere of metal ions [1]. The alteration in the ligand surrounding of Ti(IV) ions may, in particular, influence the stage of rearomatization of intermediate III.

Hence, our present results show that acetic acid affects the mechanism of electrochemical amination and together with sulfuric acid it can serve as a tool for controlling the relative rate and selectivity of substitution.

EXPERIMENTAL

Quantitative analysis for aniline and isomeric phenylenediamines was carried out by GLC on a Chrom-4 chromatograph equipped with a flame-ionization detector and a glass column [2500×3 mm, 5% XE-60 on Chromaton N-AW-DMCS (0.160–0.200 mm)]. The column temperature was 150°C, and the carrier gas was helium at a flow rate of 30 ml/min.

Cathode-initiated amination of benzene was carried out in the three-electrode glass electrochemical cell described in [4, 9]. The cell was equipped with a reflux condenser and a ceramic diaphragm separating the cathode and anode spaces. The volume of the catholyte, aqueous sulfuric acid containing 0.2 M hydroxylamine and required concentrations of Ti(IV) ions and acetic acid, was 25 ml, and the volume of benzene was 10 ml. Before electrolysis the two-phase system was deoxygenated with argon. A highly dispersed emulsion of benzene in the electrolyte was maintained by means of magnetic stirring, in the course of amination argon was passed over the emulsion. The anode was a mercury electrode with a surface area of 12.3 cm². Electrolysis was carried out in the galvanostatic mode using a P-5848 potentiostat, cathodic current density 6 mA/cm², temperature 40°C. The working electrode potential was controlled by means of a Sch 4313 voltmeter–ammeter against a silver–silver chloride reference electrode. The anode and anolyte were a platinum wire and a sulfuric acid solution with a concentration equal to the acid concentration in the catholyte.

When electrolysis was complete, the catholyte was cooled, made weakly acidic with saturated aqueous sodium hydroxide, and neutralized with sodium

Table 2. Effect of the concentration of acetic acid on the yield and composition of the products of benzene amination at a constant H_2O/H_2SO_4 molar ratio of 2.7^a

[CH ₃ COOH], M	B _c , %					<i>para/ortho</i>
	PhNH ₂	(H ₂ N) ₂ C ₆ H ₄			Σ ^b	
		<i>ortho</i>	<i>meta</i>	<i>para</i>		
0	20.6	8.2	0.0	41.0	69.8	5.0
2	65.5	6.0	0.7	24.1	96.3	4.0
4	59.0	4.1	1.6	12.9	77.6	3.2
6	46.3	1.7	4.5	5.0	57.5	2.9
7	39.6	0.5	7.8	1.4	49.3	2.7
9 ^c	13.9	0.0	0.0	0.0	13.9	
10 ^c	10.4	0.0	0.0	0.0	10.4	

^a The concentration of Ti(IV) ions in the absence of acetic acid is 0.3 M. ^b Total current yield of the amination products.

^c Electrolysis occurs at the potentials of electrochemical formation of hydrogen.

hydrocarbonate. The amination products were extracted with chloroform.

We used a 15% solution of titanium(IV) sulfate in 2 M sulfuric acid (analytical grade), chemical grade sulfuric acid. Hydroxylamine sulfate was twice recrystallized. Isomeric phenylenediamines were purified by sublimation. Aniline was distilled in a vacuum over KOH. Chemical grade benzene, analytical grade chloroform, and chemical grade acetic acid were distilled. All solutions were prepared with twice distilled water.

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