

POLAROGRAPHIC BEHAVIOUR OF SOME NEW
 N¹-ISONICOTINOYL-N²-DISUBSTITUTED HYDRAZINES
 AND DETERMINATION THEIR STRUCTURE

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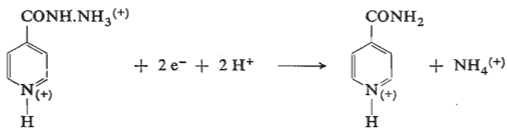
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The general polarographic behaviour of six new N¹-isonicotinoyl-N²-disubstituted hydrazines has been studied and compared with the corresponding behaviour of isonicotinamide and three in literature known N¹-isonicotinoyl-N²-monosubstituted hydrazines. The structure of the new compounds has been determined by means of their syntheses, their polarographic behaviour, and the result obtained by controlled-potential electrolysis on the first cathodic wave.

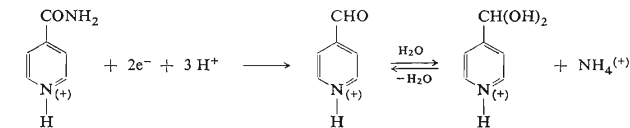
N¹-Isonicotinoyl-disubstituted hydrazines were prepared by three different ways¹. The compounds have been obtained by addition of N¹-isonicotinoyl hydrazine (Isoniazid) to the corresponding derivatives of acrylic acid, or from Isoniazid and derivatives of β-chloropropionic acid. The third way is by ammonolyses of the compounds obtained by the reaction of one mol Isoniazid and two mol of methyl acrylate with the corresponding amines.

Polarographic behaviour of these new compounds has been compared with the polarographic behaviour of similar compounds, which had previously been investigated. Isonicotinamide was studied by several authors²⁻⁵. Lund⁵ has determined the nature of its electrode reaction. The mechanisms of the electrode reactions of Isoniazid have also been established by the same author⁶. Quite a number of other authors⁷⁻²⁰ have also investigated the polarographic behaviour of Isoniazid. N¹-Isonicotinoyl-N²-(β-benzil propionamide)hydrazine (Niamid) has been studied polarographically by Schlitt and coworkers¹⁷ and by Brandys²¹.



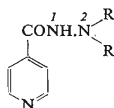
SCHEME 1

According to Lund^{5,6,19} the first cathodic wave of Isoniazid, in strongly acid solution, was found to be caused by a reductive splitting of the nitrogen–nitrogen bond (Scheme 1). The second cathodic wave of Isoniazid is caused by the reduction of isonicotinamide, formed in the first reduction, and the reaction proceeds according to Scheme 2.

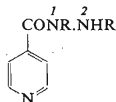


SCHEME 2

As the new synthesized N¹-isonicotinoyl-disubstituted hydrazines, according to their elementary analysis, could have the structure *A* or the structure *B*, we attempted to determine which structure corresponds to them. For this purpose their

*A*

- I*, R = $-(\text{CH}_2)_2\text{CONH}_2$
II, R = $-(\text{CH}_2)_2\text{CONHNH}_2$
III, R = $-(\text{CH}_2)_2\text{COOCH}_3$

*B*

- IV*, R = $-(\text{CH}_2)_2\text{CONH}(\text{CH}_2)_2\text{OH}$
V, R = $-(\text{CH}_2)_2\text{CONH}(\text{CH}_2)_3\text{OH}$
VI, R = $-(\text{CH}_2)_2\text{CONHCH}_2\text{C}_6\text{H}_5$

polarographic behaviour have been studied. Furthermore, the structure of the compound obtained by controlled-potential electrolysis on the first cathodic wave of the compound *III*, have been determined.

EXPERIMENTAL

Compounds

New compounds *I*–*VI* were prepared in the department of synthetic chemistry of the Pharmaceutical and Chemical factory "Galenika", Beograd-Zemun. Their melting points and the results of elementary analysis are the following:

I: m.p. 208–209°C (ethanol). For C₁₂H₁₇N₅O₃ (279.2) calculated: 51.60% C, 6.00% H, 25.00% N; found: 51.85% C, 6.18% H, 24.74% N.

II: m.p. 184–185°C (ethanol). For C₁₂H₁₉N₇O₃ (309.2) calculated: 46.61% C, 6.14% H, 31.71% N; found: 46.35% C, 6.10% H, 31.50% N.

III: m.p. 84–85°C (ethylacetate). For C₁₄H₁₉N₃O₅ (309.2) calculated: 54.39% C, 6.15% H, 13.59% N; found: 54.58% C, 6.18% H, 13.71% N.

IV: m.p. 156–157°C (ethanol). For $C_{16}H_{25}N_5O_5$ (367.2) calculated: 52.33% C, 6.87% H, 19.07% N; found: 52.46% C, 6.88% H, 18.95% N.

V: m.p. 177–178°C (ethanol). For $C_{18}H_{29}N_5O_5$ (395.2) calculated: 54.69% C, 7.36% H, 17.74% N; found: 54.85% C, 7.32% H, 17.74% N.

VI: m.p. 215–216°C (ethanol). For $C_{26}H_{29}N_5O_3$ (459.3) calculated: 67.98% C, 6.31% H, 15.25% N; found: 68.10% C, 6.20% H, 15.42% N. The physical properties of compounds used for comparing agreed with those given in literature.

Methods

In the d.c. polarographic measurements a Sargent Model XV Recording polarograph, with a polarographic cell containing a separated calomel and a dropping mercury electrode, was used. For the current–voltage curves, from which the temperature coefficients have been calculated, a special thermostated cell was used. The current–voltage curves were recorded with the normal vertical dropping mercury electrode (for $h = 50$ cm, $m = 2.18$ mg s⁻¹ and $t = 3.02$ s at the potential of the limiting current on the first reduction wave). Controlled-potential electrolysis were made with the Wenking potentiostat.

TABLE I

Limiting Currents i_d (in μ A) of Isonicotinamide, N¹-Isonicotinoyl-N²-monosubstituted Hydrazines and N¹-Isonicotinoyl-disubstituted Hydrazines as a Function of pH Values

Buffer	pH	Isonicotinamide	Isoniazid		N ¹ -Isonicotinoyl-N ² -(β -methoxy-carbonyl-ethyl)hydrazine		Niamid	
			I w.	II w.	I w.	II w.	I w.	II w.
1M-H ₂ SO ₄	—	4.95	4.10	4.38	3.70	3.90	3.26	3.25
Acetate	4.75	10.64	4.40	9.10	3.62	7.56	3.37	6.66
Phosphate	6.83	8.16	4.90	7.80	4.00	6.30	3.30	5.56
Borate	9.20	4.70		9.12	3.84	3.80	3.50	3.48
Britton–Robinson	1.72	6.10	4.66	7.54	3.78	6.36	3.28	4.67
Britton–Robinson	2.00	8.30	4.46	7.92	3.80	6.66	3.32	5.46
Britton–Robinson	3.20	9.70	4.30	8.90	3.70	7.54	3.28	6.32
Britton–Robinson	4.05	10.20	4.40	9.10	3.50	7.90	3.36	6.78
Britton–Robinson	5.25	9.54	4.30	8.80	3.80	7.26	3.08	6.20
Britton–Robinson	6.15	8.82	4.50	8.00	3.98	6.54	3.10	5.70
Britton–Robinson	7.32	7.52	4.38	6.36	4.20	5.00	3.14	4.68
Britton–Robinson	8.15	5.21		9.00	4.34	3.40	3.18	3.43
Britton–Robinson	9.92	4.60		9.10		7.17	3.52	3.02

The polarographic behaviour of all ten compounds were examined in 1M-H₂SO₄, acetate buffer, phosphate and borate buffer and in Britton-Robinson universal buffer over the range pH 1.72 to pH 9.92.

All experiments, except those designed to investigate the effect of concentration, and controlled-potential electrolysis, were carried out with solutions that were $2 \cdot 10^{-4}$ M with respect to the depolarizers. Since Niamid and compound VI are only slightly soluble in water, their stock solutions were made in dimethylformamide. The solutions to be examined were prepared by mixing 0.4 ml of the stock solution ($5 \cdot 10^{-3}$ M in dimethylformamide) with 9.6 ml of the buffer solution. The stock solutions of other eight compounds were made in water ($1 \cdot 10^{-3}$ M). Their examined solutions were prepared by mixing 2.00 ml of the water stock solution with 8.00 ml of the buffer solution. The buffer solution was twice as concentrated as in the original prescription of Britton-Robinson (*i.e.* each acid was 0.08M and 0.4M-NaOH was added).

Controlled-Potential Electrolysis of III

Controlled-potential electrolysis on the first cathodic wave was carried out with $1 \cdot 10^{-3}$ M concentration of the depolarizer (Compound III), in 0.1M-H₂SO₄. After the electrolysis, which

TABLE I
(Continued)

I		II		III		IV		V		VI	
I w.	II w.	I w.	II w.	I w.	II w.	I w.	II w.	I w.	II w.	I w.	II w.
3.62	3.66	2.98	3.10	3.40	3.32			3.06	3.00	2.82	2.96
3.68	7.02	3.18	6.40	3.34	6.74	3.32	6.74	3.00	5.90	3.04	5.78
3.42	6.50	3.02	3.80	3.22	5.80	3.16	5.72	3.00	5.00	2.78	3.86
	7.18	3.04	3.50	3.10	3.32	3.18	3.40	3.00	2.90	2.70	2.54
3.70	5.86	3.36	4.30	3.40	5.00	3.30	4.82	3.00	4.32	2.90	4.16
3.60	6.06	3.30	4.74	3.40	5.94	3.36	5.30	3.00	4.90	2.92	4.48
3.76	7.00	3.38	5.90	3.40	6.54	3.38	6.22	3.00	5.70	2.90	5.57
3.70	7.00	3.20	6.32	3.32	6.70	3.30	6.60	2.94	5.80	2.93	5.72
3.50	7.06	3.10	6.28	3.30	6.72	3.22	6.60	2.80	5.72	2.85	5.57
3.24	6.30	3.18	5.52	3.28	5.92	3.20	5.86	2.80	5.00	2.83	4.36
3.12	5.42	2.96	4.50	3.20	4.70	3.00	4.81	2.80	3.70	2.80	3.00
3.00	4.10	2.90	3.70	3.06	3.66	2.90	3.48	2.90	2.90	1.50	1.50
	7.04	3.18	3.26	3.60	2.80	3.10	3.20	2.80	2.62	1.21	1.33

had not to be carried out completely, the solution was made slightly alkaline with ammonia and evaporated *in vacuo*. The residue was extracted with methanol. Thin-layer chromatography was used for separating the compounds after the electrolysis. As the adsorbent silica gel HF₂₅₄ acc. to Stahl was used. Chloroform-methanol (8:2) was used as the developing system. The separated compounds were identified either, according to R_F values, which were compared with those of the appropriate standards (isonicotinic acid, R_F 0.05, isonicotinamide, R_F 0.47, compound III, R_F 0.83), or chromatopolarographically. (Under short wavelength UV-light spot areas (about 1 . 10 cm) were scraped from the chromatoplate and extracted with methanol. The extract was evaporated to dryness, the residue was dissolved in water, transferred into a polarographic cell and recorded the polarogram, using phosphate buffer pH about 7 as a supporting electrolyte).

TABLE II

$E_{1/2}$ (in V) as a Function of pH of Isonicotinamide, N¹-Isonicotinoyl-N²-monosubstituted Hydrazines and N¹-Isonicotinoyl-disubstituted Hydrazines

Buffer	pH	Isonicotinamide	Isoniazid		N ¹ -Isonicotinoyl-N ² -(β-methoxy-carbonyl-ethyl)hydrazine		Niamid	
			I w.	II w.	I w.	II w.	I w.	II w.
1M-H ₂ SO ₄	—	-0.63	-0.50	-0.63	-0.43	-0.64	-0.42	-0.65
Acetate	4.75	-0.96	-0.81	-0.98	-0.79	-0.97	-0.75	-0.98
Phosphate	6.83	-1.15	-1.04	-1.15	-1.00	-1.16	-0.98	-1.16
Borate	9.20	-1.27		-1.26	-1.20	-1.29	-1.14	-1.27
Britton-Robinson	1.72	-0.73	-0.54	-0.74	-0.54	-0.74	-0.52	-0.75
Britton-Robinson	2.00	-0.75	-0.57	-0.76	-0.57	-0.77	-0.56	-0.81
Britton-Robinson	3.20	-0.83	-0.66	-0.84	-0.67	-0.86	-0.66	-0.87
Britton-Robinson	4.05	-0.93	-0.77	-0.94	-0.76	-0.94	-0.75	-0.96
Britton-Robinson	5.25	-1.03	-0.92	-1.08	-0.88	-1.05	-0.88	-1.06
Britton-Robinson	6.15	-1.11	-1.03	-1.19	-0.97	-1.14	-0.97	-1.15
Britton-Robinson	7.32	-1.18	-1.10	-1.23	-1.06	-1.20	-1.04	-1.23
Britton-Robinson	8.15	-1.23		-1.23	-1.11	-1.24	-1.10	-1.27
Britton-Robinson	9.92	-1.31		-1.31		-1.28	-1.21	-1.35

RESULTS

Polarographic Behaviour

Polarographic behaviour of six N¹-isonicotinoyl-disubstituted hydrazines has been compared with the polarographic behaviour of isonicotinamide, Isoniazid, Niamid, and N¹-isonicotinoyl-N²-(β -methoxycarbonyl)ethyl)hydrazine. In the whole investigated pH region the new compounds have the same number of cathodic waves as Isoniazid, Niamid and N¹-isonicotinoyl-N²-(β -methoxycarbonyl)ethyl)hydrazine (*cf.* Fig. 1*b* - *f**). In strongly acid solution the first wave corresponds to a two-electron reduction. With increasing pH the wave-height remains nearly constant as far as, in slightly alkaline solution, for some compounds, it has been combined with the second wave. The second wave of the investigated hydrazines and hydrazines used for comparing are both alike, with respect to limiting currents and to half-wave potentials (Table I

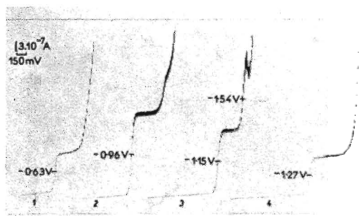
TABLE II
(Continued)

I		II		III		IV		V		VI	
I w.	II w.	I w.	II w.	I w.	II w.	I w.	II w.	I w.	II w.	I w.	II w.
-0.45	-0.64	-0.52	-0.64	-0.45	-0.64			-0.44	-0.65	-0.47	-0.66
-0.83	-0.97	-0.82	-0.97	-0.81	-0.98	-0.82	-0.99	-0.81	-0.97	-0.84	-0.99
-1.03	-1.16	-1.01	-1.15	-0.93	-1.08	-1.02	-1.16	-1.01	-1.15	-1.02	-1.19
	-1.24	-1.19	-1.29	-1.19	-1.28	-1.18	-1.28	-1.17	-1.27	-1.16	-1.29
-0.57	-0.73	-0.63	-0.75	-0.59	-0.74	-0.57	-0.75	-0.58	-0.75	-0.61	-0.78
-0.61	-0.78	-0.65	-0.78	-0.62	-0.76	-0.61	-0.78	-0.62	-0.78	-0.63	-0.81
-0.71	-0.87	-0.72	-0.85	-0.70	-0.86	-0.69	-0.85	-0.69	-0.87	-0.72	-0.89
-0.80	-0.94	-0.81	-0.95	-0.78	-0.95	-0.79	-0.96	-0.77	-0.95	-0.82	-0.97
-0.93	-1.05	-0.90	-1.06	-0.89	-1.05	-0.93	-1.14	-0.92	-1.11	-0.92	-1.07
-1.00	-1.14	-0.97	-1.12	-0.99	-1.15	-1.02	-1.21	-1.01	-1.19	-1.00	-1.14
-1.07	-1.20	-1.05	-1.19	-1.05	-1.19	-1.08	-1.25	-1.06	-1.20	-1.06	-1.21
-1.14	-1.23	-1.12	-1.23	-1.11	-1.23	-1.14	-1.28	-1.10	-1.23	-1.08	-1.21
	-1.29	-1.23	-1.32	-1.23	-1.31	-1.21	-1.30	-1.20	-1.30	-1.20	-1.32

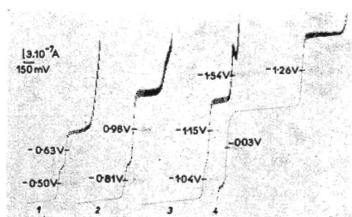
* See insert facing p. 368.

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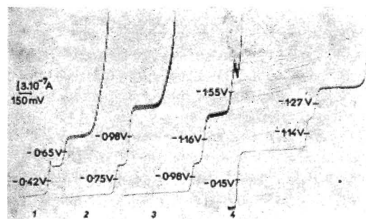
Polarographic Behaviour of Some New N¹-Isonicotinoyl-N²-disubstituted Hydrazines



a

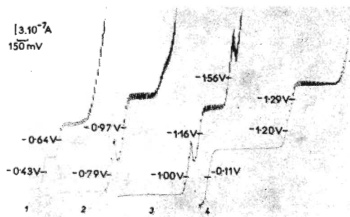


b

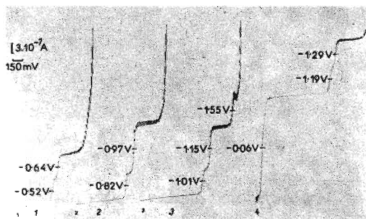


c

Polarographic Behaviour of Some New N^1 -Isonicotinoyl- N^2 -disubstituted Hydrazines



d

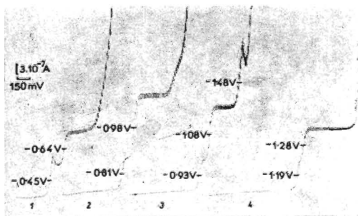


e

FIG. 1

Polarograms of Isonicotinamide (a), Isoniazid (b), Niamid (c), N^1 -Isonicotinoyl- N^2 -(β -methoxycarbonylethyl)hydrazine (d), Compound II (e) and Compound III (f)

In $1N\text{-H}_2\text{SO}_4$ (curves 1), acetate buffer pH 4.75 (curves 2), phosphate buffer pH 6.83 (curves 3), borate buffer pH 9.20 (curves 4). Concentration of depolarizer is $2 \cdot 10^{-4} \text{ M}$.



f

TABLE III
The $\Delta E_{1/2}/\Delta\text{pH}$ Values of N^1 -Isonicotinoyl- N^2 -monosubstituted- and N^1 -Isonicotinoyl-di-substituted Hydrazines

Compound	pH 1.72 to 6.15		pH 6.15 to 9.92	
	I wave	II wave	I wave	II wave
Isoniazid	-0.112	-0.102	-0.074	-0.032
Niamid	-0.102	-0.090	-0.090	-0.053
N^1 -Isonicotinoyl- N^2 - (β -methoxycarbonyl- ethyl)hydrazine	-0.097	-0.090	-0.082	-0.037
<i>I</i>	-0.097	-0.093	-0.077	-0.040
<i>II</i>	-0.077	-0.083	-0.069	-0.053
<i>III</i>	-0.090	-0.093	-0.064	-0.042
<i>IV</i>	-0.102	-0.104	-0.050	-0.024
<i>V</i>	-0.097	-0.099	-0.050	-0.029
<i>VI</i>	-0.088	-0.081	-0.053	-0.048

and Table II). In mineral acid solution this wave corresponds also to a two-electron reduction, but with the increasing pH it grows to a height of a four-electron reduction (between pH 4 and 5) and then decreases again with the increasing pH. The third wave of N^1 -isonicotinoyl- N^2 -monosubstituted hydrazines and N^1 -isonicotinoyl-disubstituted hydrazines appears at the same potentials as the second wave of isonicotinamide (Fig. 1).

The $\Delta E_{1/2}/\Delta\text{pH}$ values of the hydrazines, for the first and the second cathodic wave, from pH 1.72 to pH 6.15 and from pH 6.15 to pH 9.92, are tabulated in Table III.

The correlation between the height of the mercury head and the wave-height as well as the computed temperature coefficients²² (cf. Table IV) point to the fact that the first and the second cathodic wave of N^1 -isonicotinoyl- N^2 -monosubstituted- and N^1 -isonicotinoyl-disubstituted hydrazines and the first wave of isonicotinamide are diffusion-controlled over the investigated pH region.

It has been found for all N^1 -isonicotinoyl- N^2 -monosubstituted- and N^1 -isonicotinoyl-disubstituted hydrazines* that over the range $1 \cdot 10^{-4}$ to $2 \cdot 10^{-3}\text{M}$ the heights of the first and the second cathodic wave are a linear function of depolarizer concentration. Consequently, they can be utilized in polarographical analysis, in fact, at any desirable pH value. But for the determination it is better the use of the first

* Only for compound *VI* there is a linear function from $1 \cdot 10^{-4}$ to $1 \cdot 10^{-3}\text{M}$ (because of its slight solubility even in dimethylformamide).

TABLE IV

Temperature Coefficients (%) for the First and the Second Cathodic Wave of the Above Mentioned Compounds (Computed for the temperature range from 25° to 55°C Britton-Robinson universal buffer)

Compound	pH 4.25		pH 6.32		pH 8.36	
	I wave	II wave	I wave	II wave	I wave	II wave
Isonicotinamide	1.21		1.33		1.55	
Isoniazid	1.81	1.62	1.29	1.57		1.55 ^a
Niamid	1.67	1.55	1.60	1.41	2.27	1.22
N ¹ -Isonicotinoyl-N ² - (β-methoxycarbonyl- ethyl)hydrazine	1.39	1.19	1.14	1.44		1.34 ^a
<i>I</i>	1.65	1.58	1.43	1.31		1.46 ^a
<i>II</i>	1.35	1.34	1.18	1.27	1.73	1.19
<i>III</i>	1.41	1.31	1.23	1.27	1.57	1.28
<i>IV</i>	1.54	1.34	1.72	2.07	1.28	1.22
<i>V</i>	1.18	1.35	1.34	1.54	1.26	1.35
<i>VI</i>	1.57	1.59	1.62	1.60	1.98	2.13

^a First and second wave together.

cathodic wave (its height stay nearly constant with the changing of pH values), especially when the concentration has to be calculated from a calibration curve.

The diffusion coefficients *D*, have been computed from the height of the first cathodic wave under the assumption of two electrons, and making use of the uncorrected Ilkovič equation. The values obtained are given in Table V. They are in accordance with the size and the shapes of the molecules and may be compared with the values of *D* for various heterocyclic depolarizers²³ calculated in the same manner.

Besides, three cathodic waves have been found for all investigated compounds, in alkaline solution. Isoniazid^{6,18}, Niamid and N¹-isonicotinoyl-N²-(β-methoxycarbonyl)ethyl)hydrazine have been found to give a four-electron anodic wave (Fig. 1b, 1c, 1d). In the same medium compound *II* gives an eight-electron anodic wave (Fig. 1e). In general, the mechanism of electrode reaction for this kind of anodic waves is not known till now¹⁸.

For all four compounds, there is a linear dependence between wave-heights and concentrations of depolarizer, over the range from $1 \cdot 10^{-4}$ to $1 \cdot 10^{-3}$ M. As in an alkaline medium N¹-isonicotinoyl-N²-monosubstituted hydrazines give an anodic wave, in contrast to N¹-isonicotinoyl-disubstituted hydrazines,* according to de-

* The exception is compound *II* which has —CONHNH₂ groups.

creasing of this wave, it is possible to follow the chemical reaction from N^1 -isonicotinoyl- N^2 -monosubstituted- to N^1 -isonicotinoyl-disubstituted hydrazine, directly from the reaction mixture.

TABLE V

Diffusion Coefficients D of N^1 -Isonicotinoyl- N^2 -monosubstituted- and N^1 -Isonicotinoyl-disubstituted Hydrazines (D , $\text{cm}^2 \text{s}^{-1}$, Britton-Robinson universal buffer)

Compound	pH 4.25	pH 6.32	pH 8.36
Isoniazid	$6.26 \cdot 10^{-6}$	$6.91 \cdot 10^{-6}$	—
Niamid	$4.19 \cdot 10^{-6}$	$4.04 \cdot 10^{-6}$	$3.79 \cdot 10^{-6}$
N^1 -Isonicotinoyl- N^2 -(β -methoxy-carbonylethyl)hydrazine	$5.40 \cdot 10^{-6}$	$6.86 \cdot 10^{-6}$	—
<i>I</i>	$4.79 \cdot 10^{-6}$	$4.25 \cdot 10^{-6}$	—
<i>II</i>	$3.40 \cdot 10^{-6}$	$3.32 \cdot 10^{-6}$	$3.57 \cdot 10^{-6}$
<i>III</i>	$4.00 \cdot 10^{-6}$	$3.64 \cdot 10^{-6}$	$3.79 \cdot 10^{-6}$
<i>IV</i>	$3.06 \cdot 10^{-6}$	$3.23 \cdot 10^{-6}$	$2.88 \cdot 10^{-6}$
<i>V</i>	$3.17 \cdot 10^{-6}$	$3.32 \cdot 10^{-6}$	$3.30 \cdot 10^{-6}$
<i>VI</i>	$3.28 \cdot 10^{-6}$	$3.14 \cdot 10^{-6}$	$2.59 \cdot 10^{-6}$

DISCUSSION

N^1 -Isonicotinoyl-disubstituted hydrazines have been prepared by three different ways. The first two ways were probably based on the labile bonds of both hydrogen atoms on the N^2 , behaving differently from the hydrogen atom on the N^1 (ref.²⁴) which pointed to structure *A*.

The other proves to confirm structure *A* have been: 1. The polarographic behaviour of N^1 -isonicotinoyl-disubstituted hydrazines. 2. Isonicotinamide — which has been identified after controlled-potential electrolysis on the first cathodic wave of compound *III* (compound *III* is the starting compound for other N^1 -isonicotinoyl-disubstituted hydrazines).

1. In strongly acid solution the first cathodic wave proceeds according to Scheme 1. As the result of this reduction, a compound with structure *A* would yield isonicotinamide and a compound with structure *B* would yield an N -substituted isonicotinamide with a larger substituent in the amide group. For isonicotinamide or amides with small substituents in the amide group, in this solution, a two-electron wave is characteristic, whereas amides with larger substituents in the amide group give a four-electron wave⁵. As in strongly acid solution the new compounds gave two

two-electron waves, it has been concluded that they must have structure *A*. Structure *A* was also confirmed by the following: The limiting current of the second wave of the new compounds depends on the pH in the same way as does the limiting current of the first wave of isonicotinamide. The half-wave potentials of the second wave of the new compounds are found at the same potentials as the first wave of isonicotinamide. The third wave of N¹-isonicotinoyl-disubstituted hydrazines appears at the same place and has the same nature as the second wave of isonicotinamide, and it is probably by catalytic evolution of hydrogen, due to isonicotinamide, which has been formed after the first two-electron reduction.

2. In strongly acid solution isonicotinamide has been formed by controlled-potential electrolysis on the first cathodic wave. Isonicotinamide has been proved chromatographically and chromatopolarographically.

We have concluded in accordance with the above mentioned results that N¹-isonicotinoyl-disubstituted hydrazines have structure *A*, and they could be designated as N¹-isonicotinoyl-N²-disubstituted hydrazines.

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