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Reduction of diprotonated form of aryl hydrazones

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Abstract

Hydrazones derived from aromatic aldehydes and ketones are reduced at pH 2 to about 8 in a four-electron step. The species reduced in this step bears two positive charges on adjacent nitrogen atoms. This has been proved by the pH-dependence of half-wave potentials of *N*,*N*,*N*-trialkylhydrazonium ions, which indicates a protonation of the azomethine nitrogen prior to the first electron uptake. Similar species with two adjacent positive charges is generated by diprotonation of hydrazones, adsorbed at the electrode surface. The existence of such species as reactive intermediates at electrode surface has been in some instances confirmed, based on steep plots of $i_{max}/i_d = f(pH)$. The steep shape of these plots has been confirmed for acetophenone (II) and fluorenone (III) hydrazones using conventional buffers and for benzophenone hydrazone (IV) after extrapolation of buffer concentration to zero. The shape of the $i_{max}/i_d = f(pH)$ can be namely achieved by protonation not only by H^+ ions, but also by acid buffer components, as in general acid catalysis.

Keywords: Hydrazones; *N*,*N*,*N*-trialkylhydrazonium ions; Electroreduction; Diprotonation; Adsorption; Polarography

1. Introduction

Most hydrazones derived from aromatic aldehydes and ketones are reduced at pH lower than about 7 or 8 in a single four-electron step [1,2]. It has been proposed and recently confirmed [3] that the reduction involves an initial cleavage of the N–N bond followed by a reduction of the imine.

Limiting currents of arylhydrazones, which are up to about pH 7 pH-independent, decrease gradually at higher pH-values. This behavior resembles that of the more extensively studied oximes [3–6] and was attributed [1–6] to a proton transfer preceding the uptake of the first electron. Nevertheless, no evidence was presented for the number of protons transferred. The role of an antecedent protonation of the azomethine bond was also indicated by the observation of the pH-dependence of reduction potentials of quarternized hydrazones [7].

It is the aim of this contribution to demonstrate that the reduction of arylhydrazones can occur in the dicationic form, with two positive charges on two adjacent nitrogen atoms. Such species are generated at pH lower than about 8 in a heterogeneous process at or close to the surface of the electrode – either by the diprotonation of hydrazones unsubstituted on the amino nitrogen, or by the protonation of the azomethine nitrogen in *N*,*N*,*N*–trialkylhydrazonium ions.

2. Experimental

2.1. Instrumentation

Current–voltage curves were recorded by using Sargent Model 4001 Polarograph and IBM EC/225 Voltammetric Analyzer combined with IBM 7424 MT X-Y-T Recorder as well as capillary electrodes with characteristics of $m = 2.5\ mg\ s^{-1}$, $t_1 = 3.0\ s$ at $h = 64\ cm$. A two-electrode electrolytic cell is used with a S.C.E. separated by a liquid junction (Kalousek cell).

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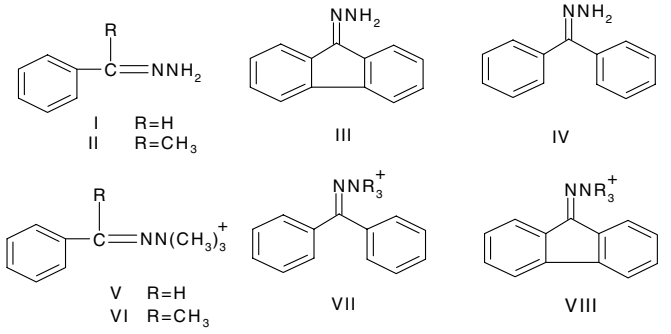
2.2. Chemicals

Benzaldehyde hydrazone (I) was prepared in solution in situ by reacting 0.2 mM solution of benzaldehyde with 2 mM solution of hydrazine in an acetate buffer, pH 5.7, for 60 min. Under these conditions the formation of azine was negligible. Prepared reaction mixture was used as a stock solution in electroanalytical experiments. Acetophenone hydrazone (II), fluorenone hydrazone (III) and benzophenone hydrazone (IV) were supplied by Aldrich. Benzaldehyde *N*,*N*,*N*-trimethyl hydrazonium iodide (V), acetophenone *N*,*N*,*N*-trimethyl hydrazonium iodide (VI), benzophenone *N*,*N*,*N*-trimethyl hydrazonium iodide (VII) and fluorenone *N*,*N*,*N*-trimethyl hydrazonium perchlorate (VIII) were prepared at the Department of Organic Chemistry at the University of Aarhus (Denmark) by reaction of the dimethylhydrazones with methyl iodide in acetonitrile.



2.3. Buffers used

For the initial information about the dependence of current–voltage curves of studied hydrazones on pH, a set of buffers was used denoted in text below as ''common buffers''. Instead of universal buffers sometimes used, which present some disadvantages for mechanistic studies, a series of simple buffers were used (Table 1). Each of these buffers contained only a single weak acid component. The chemicals used for preparation of buffers were of analytical quality.

For quantitative evaluation of the role of concentration of buffer components, that act as proton donors in the electroreduction of hydrazones, several series of buffers were prepared (Table 2). In each series the analytical concentration of the buffer was varied, but the ratios of concentrations of the acid and base component of the buffer was kept constant. Ionic strength was kept constant by addition of a solution of sodium chloride. Thus the pH in each series remained constant.

2.4. Procedure

The stock solutions (0.01 M) were prepared for compounds IV, VI and VII in water, for compounds II, III, V, and VIII in acetonitrile. Simple buffer solutions (phosphate, acetate, borate, veronal, ammonia–ammonium ions and glycine) were used. Recording of *i*–*E* curves was carried out in buffered solutions containing concentrations of acetonitrile lower than 30%. Presence of acetonitrile up to 30% v/v as a co-solvent was needed to secure the solubility of 0.02–0.2 mM solutions of some of the investigated hydrazones. The pH-values were measured using a glass electrode standardized with using buffers containing 15% and 30% acetonitrile [8]. A stock solution of the investigated hydrazone derivative was added to the buffered solution after deaeration, with gelatin added in some cases to prevent streaming maxima. The following final concentrations were used: For the investigation of compound I the reaction mixture prepared as described above was diluted 10-fold by the individual buffer solution to have a hydrazone concentration of 0.02 mM. For compound II 0.02 mM in 30% acetonitrile–water mixture, for III 0.05 mM in 15% acetonitrile–water mixture, for IV 0.2 mM in water, for V 0.1 mM in water with 0.004% gelatin and 1% acetonitrile, for VI 0.2 mM in water with 0.005% gelatin, for VII 0.1 mM in 15% acetonitrile–water mixture with 0.005% gelatin and for compound VIII 0.05 mM in the presence of 15% acetonitrile. After brief final purging by nitrogen the current–voltage curves were recorded. Unless otherwise stated, highest mean current (i_{max}) was measured.

Table 1
Composition of common buffers used

pH	Acid	[Acid] (M)	Base	[Base] (M)
3.10	H_3PO_4	0.010	NaH_2PO_4	0.160
3.60	CH_3COOH	0.250	CH_3COONa	0.025
4.20		0.200		0.063
4.70		0.100		0.100
5.20		0.050		0.160
5.70	NaH_2PO_4	0.300	Na_2HPO_4	0.050
6.10		0.150		0.050
6.30		0.150		0.075
6.50		0.100		0.100
6.70		0.060		0.100
7.10		0.030		0.100
7.25		0.020		0.100
8.00	BarbH[a]	0.033	$Barb^-$	0.033
8.35		0.020		0.080
8.50	H_3BO_3	0.095	$H_2BO_3^-$	0.015
9.10		0.100		0.050
9.30		0.075		0.075
9.75		0.036		0.140
8.00	NH_4Cl	0.100	NH_3	0.100
8.90		0.100		0.032
9.25		0.100		0.010
10.4	H_3BO_3	0.012	$H_2BO_3^-$	0.137
10.8	Na_2HPO_4	0.100	Na_3PO_4	0.020
11.2		0.100		0.063

[a] Barbital.

3. Results and discussion

The first evidence of a hydrazone derivative bearing two positive charges on adjacent nitrogen atoms is based on pH-dependence of half-wave potentials of the reduction of *N*,*N*,*N*-trialkylhydrazonium ions. The shift of half-wave potentials ($E_{1/2}$) of such compounds has been mentioned