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Two reduction waves of oximes and imine formation in acidic media

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Abstract

The separation of the two two-electron waves in acidic media in solutions of some aromatic aldoximes and ketoximes is attributed to differences between the pK_a-values of oximes (which are smaller than about 1.0) and those of protonated forms of corresponding imines. Dependences of half-wave potentials on pH show that the lower limit pK_a of imine varies from −0.25 for *p*-formylbenzaldehyde oxime to 2.2 for *p*-fluorobenzaldehyde oxime. For the benzaldehyde and acetophenone oximes bearing substituents, which have pK_a higher than −1.50, a good agreement was observed for pK_a-values obtained spectrophotometrically and pK_{ox} values obtained from the change in the slope of $E^1_{1/2} = f(H_0)$ plots. Past misrepresentations of the electroreduction mechanism of protonated forms of imines is attributed to insufficiently controlled compositions of supporting electrolytes. The reduction potential of protonated forms of oximes in the more positive wave i_1 is affected by the concentration of halides in the supporting electrolyte. This is attributed to an ion-pair formation, between these anions and protonated forms of oximes. The reduction of the protonated form of imines at acidity, where in the bulk predominates the same protonated form that is reduced, is independent of the nature and concentration of anions of the supporting electrolyte.

Keywords: Oximes; Electroreduction; Polarography; Imine intermediate; Ionic strength; Halide ions

1. Introduction

The four-electron reduction of oximes and its dependence on pH has been recognized early [1,2] and reviewed more recently [3–5]. The four-electron process may be in principle initiated either by the hydrogenation of the azomethine bond or by the cleavage of the N–O bond. In his seminal paper Lund [6] proposed that the second alternative is the first step. This proposition was based on the known electrochemical behavior of the two possible reduction intermediates—the imine and a hydroxylamine derivative. The only experimental evidence was indirect and based on identification of testosterone propionate as an electrolysis product of testosterone propionate oxime. The isolated ketone was assumed to be formed by hydrolysis of the testosterone propionate imine [6].

It has been demonstrated recently [7] that, at pH higher than 2.0 and lower than about 7.0 or 8.0, aromatic oximes are reduced in diprotonated form. In the resulting grouping $>C{=}NH^+OH_2{}^+$ the cleavage of the N–O bond is facilitated by the presence of OH_2 as a good leaving group as well as by the positive charge on the azomethine nitrogen. Similar diprotonated form has been identified as the reducible species also in the reduction of hydrazones [8].

For the reduction of related hydrazones the formation of imines as intermediates in their four-electron reduction has recently been proved [9]. The proof has been made possible by comparison of current–voltage curves of hydrazones of benzophenone and fluorenone with those of corresponding imines, that are sufficiently stable between pH 6 and 10. Comparison of reduction potentials confirmed formation of imine intermediates.

For oximes Lund [10] reported a similar approach, based on comparison of the oximes with the imine of 2,4-dihydroxybenzophenone at pH < 3.0. The reported stability of the imine at these acidities is remarkable, since the imine of unsubstituted benzophenone underwent acid catalyzed hydrolysis [9] already at pH < 4.6.

Hence for the proof of formation of an imine intermediate in the reduction of oximes, another kind of experimental evidence

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was needed. Such evidence is confirmed in this contribution based on behavior of oximes at $pH < 3.0$. In these acidic solutions some oximes are reduced in two two-electron waves. Such separation of the four-electron process was first reported by Lund [10] for 2,4-dihydroxybenzophenone oxime, who correctly attributed the second step to the reduction of the imine, and later also reported for 2,4-dihydroxyacetophenone oxime [11] and for oximes of 2-carboxybenzophenones [12] substituted in position 4. In this later contribution, the separation of two waves was attributed to formation of hydrogen bond between the azomethine nitrogen and the oxygen of the hydroxy or carboxy group. Nevertheless, the observation that in 0.1 M $HClO_4$ such separations were observed for 4-fluoro- and 4,4′-difluorobenzophenone [13] and were reported also for methyl *p*-tolylketoxime in 10–50% H_2SO_4 and for unsubstituted benzophenone oxime in 50% H_2SO_4 [2], ruled out this interpretation.

It was indicated [13] that the second reduction wave may correspond to the reduction of the imine and was observed that the $dE_{1/2}/dpH$ slopes of the first and second wave differ. That was erroneously attributed to changes in the reversibility of the reduction of the imine with acidity. Also the statement that the merging of the two waves with increasing pH "is determined by the difference in the degree of electroreduction reversibility of $>C{=}NH^+$ and $[>C{=}NOH]\ H^+$ groups" [5] is incorrect.

That none of the above offered satisfactory explanation for the separation of the two reduction waves of oximes in acidic media is due to insufficiently wide acidity range, particularly in the region where pH-scale is replaced by the acidity function H_0. The ionic strength in these studies was not kept constant and no attention has been paid to the role of the nature of and concentration of the anion of the strong acid. These factors are taken into consideration in the present contribution.

2. Experimental

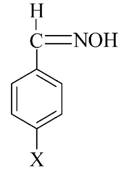
2.1. Instrumentation

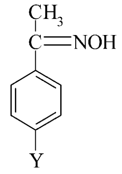
The polarographic current–voltage curves were recorded on an IBM EC/225 Voltammetric Analyzer combined with IBM 7424 MT X-Y-T Recorder as well as capillary electrodes with characteristics of $m = 2.5\ mg\ s^{-1}$, $t_1 = 3.0\ s$ at $h = 70\ cm$. A Kalousek cell [14] with a reference electrode separated by liquid junction was used for DC polarography. The reference electrode most cases was a saturated calomel electrode (SCE), in strongly acidic solutions were used Hg_2SO_4/H_2SO_4.

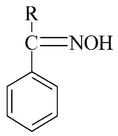
A Hewlett-Packard Agilent 8453 UV–vis spectrophotometer was used in recording the UV–vis absorption spectra. A 10 mm fused quartz cell was used during the measurements. A Denver Instrument Model UB-10 pH-meter was used with a glass electrode to determine the pH.

2.2. Chemicals

The compounds studied, benzaldehyde oxime (I) and 2-hydroxyimino-2-phenylacetonitrile (XIX) were supplied by Aldrich, acetophenone oxime (XI) by Alfa Aesar, and benzophenone oxime (XVIII) by Avocado Research Chemical Ltd. The rest of the oximes were prepared at the Department of Electrochemistry at J. Heyrovský Institute of Physical Chemistry (Czech Republic).







No.	X	No.	Y	No.	R
I	H	XI	H	XVIII	Ph
II	CH_3	XII	CH_3	XIX	CN
III	OCH_3	XIII	Cl	XX	CF_3
IV	$COOCH_3$	XIV	OH		
V	Br	XV	$COCH_3$		
VI	F	XVI	CF_3		
VII	CN	XVII	NO_2		
VIII	CF_3				
IX	CHO				
X	NO_2				

2.3. Procedures

The stock solutions (0.01 M) were prepared freshly for all studied compounds in acetonitrile. Simple buffer solutions (phosphate and acetate) were used, and ionic strength was kept constant by addition of a solution of sodium salts. In strongly acidic media solutions of sulfuric, perchloric, nitric and hydrochloric acids were used either without and or with an addition of a salt. Potentials measured in such solution against a mercurous sulfate electrode in concentrated sulfuric acid were corrected to SCE scale using the potential of Tl^+ (−0.450 V versus SCE). Acidity of these solutions was characterized using tabulated H_0 functions. The above reference electrode was used to minimize the liquid junction potential and to prevent diffusion of sulfuric acid into the investigated electrode compartment. Recording of *i–E* curves was carried out in the solutions containing concentrations of acetonitrile of about 1%. A stock solution of the investigated oxime derivative was added to the solution of supporting electrolyte after deaeration, with gelatin added in some cases to prevent streaming maxima. The final concentrations of studied oximes were 0.1 mM. After brief final purging by nitrogen the current–voltage curves were recorded.

3. Results and discussion

3.1. Reason for separation of two two-electron processes

The basic information about the nature of processes, resulting in separation of two two-electron waves in acidic media in the electroreduction of oximes (Fig. 1), is obtained from the dependence of half-wave potentials of individual waves on pH. For irreversible reduction processes a shift of potentials to more negative values indicate that the transfer of the electron is preceded by a rapidly established acid–base equilibrium, in which the conjugate acid is reduced. As long as the rate of protonation