HYDRAZONES

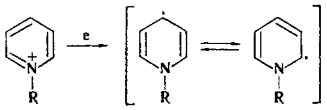
XXXIX.* POLAROGRAPHIC STUDY OF N-BENZYLIDENEIMINOPYRIDINIUM IODIDES

Yu. P. Kitaev, T. V. Troepol'skaya,
and L. N. Orlova

UDC 547.821.3: 543.253

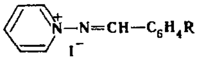
The polarographic behavior of a number of N-benzylideneiminopyridinium iodides in aqueous alcohol buffer solutions was studied over a wide range of pH values. The mechanism of their reduction on a dropping mercury electrode and the factors affecting the cleavage of the N–N bond are discussed. The reduction product – the pyridinium ion – induces the catalytic evolution of hydrogen.

The polarographic behavior of N-alkylpyridinium salts has been described in quite some detail. On a dropping mercury electrode (DME) they form one-electron reversible diffusion reduction waves that correspond to the formation of a radical [2].



The half-wave potential and the wave height are independent of the pH. The radical that arises dimerizes or reacts with the solvent, as a result of which the nitrogen atom loses its ammonium character and becomes capable of accepting a proton, thereby inducing catalytic hydrogen currents. The catalytic waves on the polarograms of alkylpyridium salts have been examined in detail in a number of papers [3-5].

In a polarographic respect, the previously uninvestigated N-benzylideneiminopyridinium iodides (I) that we studied in the present research should be closer to hydrazones than to alkylpyridinium salts. However, one should also note several differences, inasmuch as compounds (I) have a positively charged nitrogen atom included in a heteroring of aromatic character, while arylhydrazones should be protonated at the more basic imine nitrogen atom.



I

R = H, p and m-CH_3, p and m-NO_2, m-Cl, p OCH_3, p-Br, p $N(CH_3)_2$, p $CH(CH_3)_2$.

In fact, with respect to their behavior on a DME, salts (I) display a great similarity to both arylhydrazones [6] and to 1,2,4-triazolylimines of the benzaldehyde series [7]. In acid buffer solutions they all form two two-electron waves of equal height (the number of electrons going into the reduction of the investigated compounds was established from the Il'kovich equation).

The $E_{1/2}$ value of these waves depends on the pH, and this attests to prior protonation of the compounds. It can be assumed that the protonation center is the nitrogen atom of the C=N bond, although one

---

*See [1] for communication XXXVIII.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR, Kazan'. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 666-669, May, 1974. Original article submitted February 13, 1973.

cannot exclude protonation at both nitrogen atoms. The first of these waves, which has a more positive $E_{1/2}$ value, has a constant height at pH ~ 4, which rapidly decreases to zero as the pH is increased further, while the second wave increases simultaneously on its own account, reaching the height of a four-electron wave. This sort of phenomenon has also been observed for some arylhydrazones, dimethylhydrazones, and 1,2,4-triazolylimines [6, 7]. It can evidently be explained by a change in the mechanism of the electrode reaction – by transition from a two-step reduction with the intermediate formation of an imine as a kinetically independent particle to almost simultaneous addition of four electrons of the depolarizer molecule as the electrode reaches a sufficiently negative potential due to a decrease in the pH of the medium. In both cases the final products are the same.

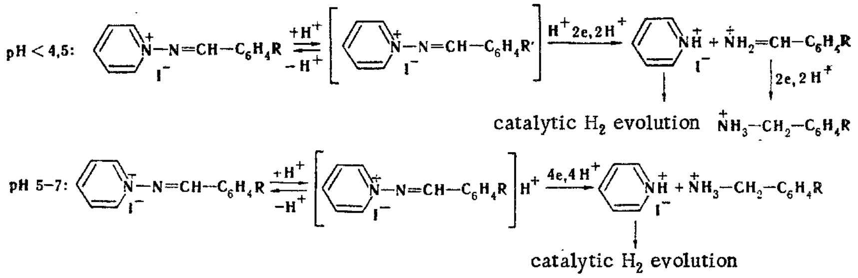
In some cases [(I), R = p-Br, m-Cl, and m-NO_2], the overall height of these waves was somewhat depressed, although hydrolysis did not take place in acidic media (in contrast to 1,2,4-triazolylimines). In these instances, substantial kinetic limitations were observed: specifically, the temperature coefficients exceeded the values characteristic for purely diffusion processes. Because of the high adsorbability of the depolarizer on the DME, its desorption as the temperature rises could even lead to a negative temperature coefficient. Phenomena of this type have been observed for arylhydrazones [6] and were explained by the kinetics of the dehydration of these compounds in acidic media, which precedes the strictly electrode process. It can be assumed that the positively-charged nitrogen atom in (I) promotes their hydration in aqueous solutions, shifting the electron density on the carbon atom of the C=N bond toward the positive center.

An analysis of the graph of the dependence $I_{lim}/\sqrt{H} = f(\sqrt{H})$ (I_{lim} is the limiting current and H is the height of the mercury reservoir) provided evidence for the kinetic character of the first wave. The second wave proved to be a diffusion wave. For it, $I_{lim}/\sqrt{H}$ = const. The kinetic limitations imposed by the dehydration reaction apparently also reduce the maximum limiting currents of reduction for (I) as well. As one should have expected, these phenomena are most distinctly seen in compounds with electron-acceptor R substituents that decrease the electron density on the carbon atom of the azomethine grouping.

The $N-N^+$ bond in N-benzylideneiminopyridinium iodides is cleaved more readily than the N–N bond in benzaldehyde arylhydrazones because of its greater polarity (its disintegrative character). The overall height of the waves of the investigated compounds reaches a maximum at pH 5–6 and then decreases rapidly to approximately the two-electron level. The reduction also occurs in alkaline solutions. An adsorption wave with $E_{1/2}$ from –0.8 to –1.0 V is observed for pH > 6.

In the case of some of the slightly soluble substances (R = p-Br, p-NO_2), at pH ~ 4.0 there appears a small elongated wave (caused by a change in the capacity of the DME because of desorption of a large portion of the depolarizer from the electrode surface [6]) with $E_{1/2}$ from –1.2 to –1.6 V, which is masked by the base electrolyte at lower pH values. It reaches a maximum and then decreases in neutral media. The dependence of the height of this wave on the pressure on the dropping mercury and the temperature indicates its kinetic character. Anomalously high catalytic waves for hydrogen evolution with $E_{1/2}$ = –1.73 V, which merged with the base electrolyte at pH < 3 and vanished at pH ~ 7.0, were observed for all of the compounds in acidic media.

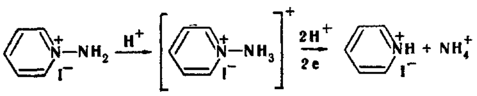
The overall scheme of the reduction of N-benzylideneiminopyridinium iodides in acidic media can be represented in the following manner:



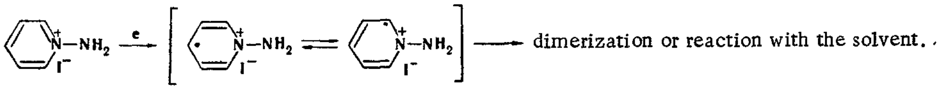
The unprotonated form of these compounds at pH > 7.0 is also reduced. However, we were unable to detect the signal of a free radical in $C_2H_5N^+NH_2I^-$ and $(C_5H_5N^+N{=}CH-C_6H_5)I^-$ solutions at pH 9.2 by means of ESR spectroscopy. The one-electron wave of the first compound apparently corresponds to the formation of a radical that is not sufficiently stable under these conditions.

All of the investigated compounds also have an anode wave at -0.24 V, which is due to the formation of an insoluble mercury salt with the iodide anion. In the case of compounds that contain a polarographically active NO_2 group, one also observes its reduction waves, which have already been adequately studied and are therefore not described here.

The reduction of the starting N-aminopyridinium iodide may, to a certain degree, serve as a model of the first step in the electrode reaction with the participation of its derivatives (I). This compound is reduced in acidic buffered media via one two-electron wave of diffusion character, the $E_{1/2}$ value of which depends substantially on the pH ($\Delta E_{1/2}/\Delta pH = 90$ mV/pH unit). This $\Delta E_{1/2}/\Delta pH$ value can be explained by the participation in the electrode reaction of a larger number of protons than electrons as a consequence of protonation of the amino group.



When pH > 6.0, the wave falls rapidly to the one-electron level with $E_{1/2} = -1.6$ V. It is possible that the unprotonated N-aminopyridinium iodide undergoes one-electron reduction in alkaline media to give a free radical, as described for N-alkylpyridinum salts [2].



It is interesting to note that maxima (suppressed by gelatin), which are apparently associated with the greater adsorbability of the dimers as compared with the starting depolarizer (see [8]), appear on the polarograms at pH > 6.0. An anode wave from interaction of the iodide ion with the electrode material and a catalytic wave of hydrogen evolution are also observed for N-aminopyridinium iodide.

EXPERIMENTAL

The methods for the preparation of the investigated compounds and their spectral and physicochemical characteristics have been described in a previous communication [1]. The polarograms of 20% ethanol–water Britton–Robinson buffer solutions with pH 1.7-11 were recorded with a Metrohm Polarecord polarograph; the depolarizer concentration in the cell was $5 \cdot 10^{-4}$ mole/liter. The comparison electrode was a silver chloride electrode. The dropping mercury electrode has the following characteristic: $t^{1/6}m^{2/3} = (1.554 \text{ mg/sec})^{2/3} \cdot \text{sec}^{1/6} = 1.342$.

LITERATURE CITED

1. T. V. Troepol'skaya and Yu. P. Kitaev, Khim. Geterotsikl. Soedin., 1219 (1973).
2. P. Tompkins, Anal. Chem., 21, 64 (1949).
3. S. G. Mairanovskii, Dokl. Akad. Nauk SSSR, 110, 593 (1956).
4. S. G. Mairanovskii, Dokl. Akad. Nauk SSSR, 114, 1272 (1957).
5. L. Floch, M. S. Spritzer, and P. J. Elving, Anal. Chem., 38, 1074 (1966).
6. Yu. P. Kitaev and T. V. Troepol'skaya, Izv. Akad. Nauk SSSR, Ser. Khim., 1903 (1967).
7. Yu. P. Kitaev, I. M. Skrebkova, and L. I. Maslova, Izv. Akad. Nauk SSSR, Ser. Khim., 2194 (1970).
8. S. G. Mairanovskii, J. Electroanal. Chem., 12, 547 (1966).