M. B. NEIMAN, A. A. MEDZHIDOV, E. G. ROZANTSEV, L. A. SKRIPKO

1964

SovietRxiv

Abstract

Full Text

CHEMISTRY

M. B. NEIMAN, A. A. MEDZHIDOV, E. G. ROZANTSEV, L. A. SKRIPKO

A NEW REACTION FOR THE FORMATION OF STABLE WURSTER SALTS

(Presented by Academician A. A. Balandin, August 16, 1963)

A typical representative of this class of radical salts is "Wurster's Red," obtained by the oxidation of *p*-aminodimethylaniline with one equivalent of bromine

[scheme: oxidation of p-aminodimethylaniline by [Br]/ − e to resonance forms of the Wurster radical cation]

In an analogous manner, "Wurster's Blue" is obtained from tetramethyl-*p*-phenylenediamine ([1], [2]).

According to Michaelis, Schubert, and Granick ([3]), stable Wurster salts can be formed only in the presence of sufficiently high symmetry of the molecules of the corresponding *p*-phenylenediamines.

Whereas symmetrical tetramethyl-*p*-phenylenediamine and *p*-aminodimethylaniline form stable ion-radicals, N,N′-dimethyl-*p*-diaminodurene does not give a Wurster salt:

[structure of N,N'-dimethyl-p-diaminodurene]

For resonance stabilization of cation-radicals of this kind, the benzene ring, the nitrogen atoms, and the substituents at nitrogen must be coplanar, since participation of the quinonoid canonical structure restricts free rotation of the amino groups.

The simplest Wurster salts are stable also in the pH range from 3.5 to 6, since the greatest possibilities for resonance are realized only in the monopolar ion-radical, in contrast to the bipolar and neutral radicals:

[structures of the monopolar ion-radical and neutral radical]

We have found that, upon interaction of certain organic free radicals with N,N′-disubstituted-*p*-phenylenediamines in an acidic medium, a reaction takes place leading to the formation of stable Wurster salts:

[N,N'-disubstituted-p-phenylenediamine] + $\dot{\mathrm{R}}$ + H^+ → [corresponding Wurster radical cation] + RH

We observed this reaction in the example of 9 different derivatives of *p*-phenylenediamine when using free radicals belonging to the class of aroxyls, diarylpicrylhydrazyl, iminoxyl, and also trialkylmethyl:

[chemical structures: aroxyl, diarylpicrylhydrazyl, iminoxyl, and trialkylmethyl radicals]

The reactions were carried out in ampoules evacuated of air, placed directly in the resonator of a radiospectrometer; a mixture of ethanol and acetic acid (1:1) was used as the medium.

The most stable solutions of ion-radicals were obtained by interaction of equal volumes of solutions of paraphenylenediamine derivatives (concentration 10^{-2} mol/l) and solutions of various radicals (concentration 10^{-3} mol/l) in a mixture of ethanol and acetic acid.

In the case of using equivalent amounts of diamine and free radical, the radical ions formed as intermediates perish according to the reaction:

[reaction scheme: oxidation of substituted *p*-phenylenediamine by an iminoxyl radical in acid, with formation of a diiminium cation-radical and hydroxylamine derivative]

Registration and analysis of the resulting cation-radicals were carried out on the domestic EPR-2 radiospectrometer of our institute.

[EPR spectrum]

Fig. 1. Formation with time of the cation-radical of N,N'-di-*n*-octyl-*p*-phenylenediamine and disappearance of the triacetoniminoxyl radical. The process of complete conversion took place over 10 min.

The process of formation of a new cation-radical, for example in the reaction of the triacetoniminoxyl radical with N,N'-di-*n*-octyl-*p*-phenylenediamine, is shown in Fig. 1, from which it is clearly seen that the triplet spectrum is gradually replaced by a multiplet spectrum belonging to the cation-radical of N,N-di-*n*-octyl-*p*-phenylenediamine. With a decrease in the pH of the medium, the rate

the reaction increases noticeably, whereas in a neutral medium the process almost completely stops.

The EPR spectrum of the cation-radical formed after completion of the reaction is shown in Fig. 2. The hyperfine structure of the spectrum is explained by an approximately equal interaction of the unpaired electron with two nuclei of nitrogen atoms, with two protons of the amino groups, with four protons of the

n-octyl radicals closest to the amino groups, and also by an interaction, three times smaller, with four protons of the aromatic ring.

Fig. 2. EPR spectrum of the cation-radical of N,N′-di-*n*-octyl-*p*-phenylenediamine after completion of the reaction

The theoretically calculated spectrum should contain 35 components; however, owing to the low intensity, the outer components of the spectrum are at the "noise"level, and therefore the experimental spectrum includes only 33 HFS lines. The interpretation of the spectrum is in agreement with the interpretation of the EPR spectrum of "Wurster' s blue" ([4]).

Fig. 3. EPR spectrum of the cation-radical of N,N′-di-sec-octyl-*p*-phenylenediamine. The arrow indicates a component of the residual EPR signal of the triacetone aminoxyl radical

It can be seen from Fig. 3 that the spectrum of the ion-radical of N,N′-di-sec-octyl-*p*-phenylenediamine is due to an approximately equal interaction of the unpaired electron with two nuclei of nitrogen atoms, with two protons of the amino groups, with two protons of the methine groups of the alkyl radicals, and to an interaction, approximately three times smaller, with four protons of the aromatic ring.

Figure 4 presents the EPR spectrum of the ion-radical obtained by the interaction of N-phenyl-N′-*n*-octyl-*p*-phenylenediamine with 2,2,6,6-tetramethylpentamethylene aminoxyl, comprising 9 groups of lines with a weakly resolved hyperfine structure formed as a result of an almost equal interaction of the unpaired electron with two nitrogen atoms and two protons of the amino groups.

Fig. 4. EPR spectrum of the cation-radical of N-phenyl-N′-*n*-octyl-*p*-phenylenediamine

Table 1

Some new free cation-radicals studied by the EPR method

R	R′	Color	EPR spectrum: theoretical number of lines	EPR spectrum: splitting constants
$CH_2-CH_7-H_{15}$	$-CH_2-C_7H_{15}$	Red	35	$a_1 = 6.2$ oersted$a_2 =$ 2.0 oersted
$-CH(CH_3)-C_6H_{13}$	$-CH(CH_3)-C_6H_{13}$	Red	29	$a_1 = 6.3$ oersted$a_2 =$ 2.0 oersted

R	R′	Color	EPR spectrum: theoretical number of lines	EPR spectrum: splitting constants
$-CH_2-C_7H_{15}$	phenyl	Blue	9 groups	$a_N = 5.0$ oersted$a_H =$ 5.7 oersted

The cation-radical has the general form

$$R-NH-C_6H_4^+-\dot{N}H-R'$$

Table 1 presents several of the new Wurster salts studied by us in greatest detail and their radiospectroscopic characteristics.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
10 VIII 1963

REFERENCES

1. C. Wurster, R. Sendtner, Ber., **12**, 1803 (1879).
2. C. Wurster, E. Schobig, Ber., **12**, 1807 (1879).
3. L. Michaelis, M. Schubert, S. Granick, J. Am. Chem. Soc., **61**, 1981 (1939).
4. J. Bolton, A. Carrington, J. dos Santos-Veiga, Mol. Phys., **5**, No. 6, 615 (1962).

Note: Figure translations are in progress. See original paper for figures.