BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (3), 1043—1044 (1975)

The Dimerization of the Phenoselenazine and Benzo[*c*]phenoselenazine Cation-radicals

Yoshio Matsunaga and Tomio Tanaka
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received October 7, 1974)

Synopsis. The equilibrium constants and the heats of dimerization and the monomer and dimer spectra were determined for the phenoselenazine and benzo[*c*]phenoselenazine cation-radicals in aqueous sulfuric acid (1: 1 by volume).

In connection with our work on the phenoselenazine-iodine complex,[1] attempts were made to measure the ESR absorption spectrum of the phenoselenazine cation-radical produced in sulfuric acid at various dilutions and temperatures, but all without success. During the course of such attempts, however, a reversible color change from brown to pink occurred upon warming, suggesting that the cation-radical is in the monomer-dimer equilibrium. As the monomer and dimer spectra are important tools for speculating on the mode of intermolecular interaction in solid ion-radical salts,[2] we analyzed the temperature- and concentration-dependences of the solution spectrum.

The phenoselenazine and its semiquinoid bromide employed here were prepared in our previous work.[1] The preparation of benzo[*c*]phenoselenazine was carried out by a method analogous to that for phenoselenazine reported by Müller *et al.*[3] The phenoselenazine bromide was dissolved in aqueous sulfuric acid (1: 1 by volume). The absorption spectra of eight solutions, ranging from 5.05×10^{-5} to 6.12×10^{-4} mol/l, were recorded on a Beckman DK 2A spectrophotometer at 20, 35, and 50 °C with the aid of a temperature-regulated cell holder. As the composition of the oxidation product of benzo[*c*]phenoselenazine with bromine did not agree with the calculated one, the compound was directly dissolved in concentrated sulfuric acid. Then, one volume of the solution was slowly diluted, avoiding excessive heating, with one volume of water. For this radical, we prepared fifteen solutions, the concentrations of which were in the range from 1.27×10^{-5} to 1.64×10^{-3} mol/l. The spectra were then examined at 20, 35, 50, and 65 °C. The spectral change in the phenoselenazine cation-radical was found to be slightly irreversible if the solution was heated to 65 °C.

Upon heating, the intensities at 400, 475, and 733 nm in the spectrum of the phenoselenazine radical become weaker and those at 433 and 513 nm become stronger. The locations of the six isosbestic points observed are as follows: 358, 411, 438, 493, 559, and 868 nm. We assumed that the observed spectral change can be interpreted in terms of the monomer-dimer equilibrium; that is, $2(A^+)\rightleftarrows(A_2)^{2+}$. This formula does not exclude the possibility of the presence of an anionic species in the dimer. Since the absorption bands assignable to the monomer and dimer overlap considerably, the values of the true extinction coefficient of the monomer, ε_M, and that of the dimer, ε_D, were determined by the extrapolation procedure described by Boyd and Phillips.[4] The monomer band at 513 nm and the dimer band at 733 nm were chosen for this purpose. The best sets of values of ε_M and ε_D were as follows:

$$\varepsilon_M = 9.50\times10^3,\ \varepsilon_D = 5.55\times10^3 \text{ at 513 nm and}$$

$$\varepsilon_M = 0.75\times10^3,\ \varepsilon_D = 11.0\times10^3 \text{ at 733 nm.}$$

The average equilibrium constants evaluated from the data at the monomer and dimer bands were $K(20\ ^\circ\mathrm{C}) = 3.7\times10^3$, $K(35\ ^\circ\mathrm{C}) = 1.6\times10^3$, and $K(50\ ^\circ\mathrm{C}) = 0.72\times10^3$ l/mol. From the temperature dependence of K, the heat of dimerization of the phenoselenazine cation-radical was estimated as −9.9 kcal/mol.

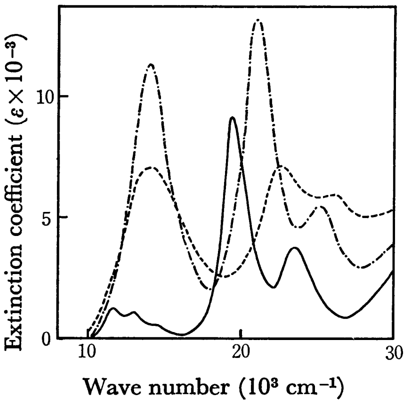

Fig. 1. Absorption spectra of the monomer (——) and dimer (-----) of phenoselenazine cation-radical and reflection spectrum of the semiquinoid bromide (-·-·-).

The monomer and dimer spectra were constructed by plotting the measured apparent extinction coefficient, ε, at about thirty wavelengths *versus* the fraction of the stoichiometric concentration existing as a monomer calculated from the above-mentioned equilibrium constants for each concentration. They are presented in Fig. 1, along with the spectrum of the solid semiquinoid bromide, as measured by the diffuse-reflectance method. The similarity between the dimer spectrum and the solid-state spectrum provides strong evidence that the intermolecular interaction in the solid bromide is predominantly pair-by-pair.

Although phenothiazine bromide dissolved in aqueous sulfuric acid shows a spectrum essentially the same as the monomer spectrum given in Fig. 1, the dimerization has been demonstrated by Kagiya *et al.* at temperatures as low as −70 °C in an ethanol–ether–sulfuric acid solution.[5] The enthalpy change estimated by them is about −5 kcal/mol. There seems to be appreciably more shift of the equilibrium towards the dimer in the phenoselenazine cation-radical as compared with

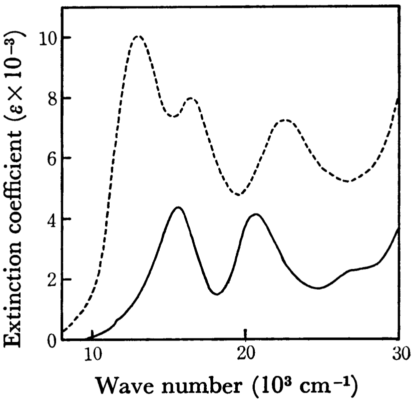

Fig. 2. Absorption spectra of the monomer (——) and dimer (-----) of benzo[*c*]phenoselenazine cation-radical.

the sulfur-analogue. A similar marked difference in the dimerization behavior between the cation-radical of phenoxathiin and that of phenoxaselenine, as judged from the spectral and magnetic properties, has been reported by Hillebrand *et al.*[6]

Upon the introduction of an extra benzene nucleus into phenoselenazine, the temperature-dependence of the spectrum of the cation-radical becomes less pronounced. The extrapolation procedure could be applied only to the dimer band appearing at 788 nm. We obtained the following values; $\varepsilon_M=1.25\times10^3$, $\varepsilon_D=9.95\times10^3$, $K(20\ °C)=9.9\times10^4$, $K(35\ °C)=3.4\times10^4$, $K(50\ °C)=1.3\times10^4$, and $K(65\ °C)=0.48\times10^4$ l/mol. The heat of dimerization of -13.3 kcal/mol estimated for this cation-radical is about 30% higher than that of the phenoselenazine cation-radical; that is, the heat is approximately proportional to the size of the molecules within this pair. For such a comparison, it may be more appropriate to use the heat of the dimerization of the phenoselenazine cation-radical, evaluated only on the basis of the data taken at the dimer band. The required value is a little larger than the aforementioned value—that is, -10.7 kcal/mol. The constructed spectra of the monomeric and dimeric benzo[*c*]phenoselenazine cation-radical are presented in Fig. 2. The difficulty in analyzing the spectrum of this radical apparently arises not only from the large equilibrium constant but also from the overlap of the monomer and dimer spectra.

We attempted to extend our study to the dibenzo[*c,h*]phenoselenazine cation-radical; however, the dilution of a concentrated sulfuric acid solution in the desired range of concentration with an equal volume of water resulted in the formation of a dark green precipitate, and the recording of the spectrum was not possible.

The authors wish to express their thanks to Mr. Yukio Suzuki for providing them with the results of his preliminary spectral measurements of the phenoselenazine cation-radical.

References

1) Y. Matsunaga and Y. Suzuki, This Bulletin, **45**, 3375 (1972).

2) Y. Iida and Y. Matsunaga, *ibid.*, **41**, 2615 (1968).

3) P. Müller, N. P. Buu-Hoï, and R. Rips, *J. Org. Chem.*, **24**, 37 (1959).

4) R. H. Boyd and W. D. Phillips, *J. Chem. Phys.*, **43**, 2927 (1965).

5) T. Kagiya, K. Nakai. S. Nakayama, and K. Suzuki, Paper presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970.

6) M. Hillebrand, O. Maior, and V. E. Sahini, *Rev. Roum. Chim.*, **16**, 1489 (1971).