EVOLUTION OF HYDROGEN FROM ACIDIC AQUEOUS AND AQUEOUS-ALCOHOLIC SOLUTIONS BY REDUCED FORMS OF ISOPOLYTUNGSTATES

S. S. Saidkhanov, E. N. Savinov, and V. N. Parmon

It was established in [1] that reduced polytungstates (PTs) and polymolybdates that are formed by the association of WO$_4^{2-}$ and MoO$_4^{2-}$ in acidic aqueous solutions are capable of spontaneous reoxidation, accompanied by the evolution of H$_2$, the same as the reduced forms of heteropolyacids (HPAs) [2-4]. The work reported in this article was aimed at determining the specific nature of the hydrogen-releasing PT species and investigating the features of H$_2$ evolution by this species.

EXPERIMENTAL

All experiments were performed in the pH interval 0-4. The acidity of the medium was adjusted by the addition of hydrochloric acid, Grade o.s.ch. ("ultrapure") or H$_2$SO$_4$, Grade kh.ch. ("chemically pure"). The PTs were prepared from normal Na tungstate. The concentration of the Na tungstate was varied from $10^{-4}$ to $10^{-2}$ M. The concentration of ethanol in the aqueous alcoholic solutions was 8.35 M.

In order to remove dissolved O$_2$, the samples were first purged with argon for 20 min. The PTs were reduced by Zn amalgam, after which the reduced forms were transferred to a reactor that did not contain amalgam; alternatively, the PTs were reduced by irradiation of aqueous-alcoholic solutions of the PT by soft UV light in the band corresponding to absorption of the PT (DRSh-1000 lamp with UFS-5 or UFS-6 filter).

The optical spectra and the kinetic curves were recorded at 22 ± 2°C in a Shimadzu UV-300 spectrophotometer; the ESR spectra were recorded at liquid-nitrogen temperature in an RE-1306 spectrometer. The redox titrations for the determination of the degree of reduction of the PTs were performed with (1-2)·$10^{-3}$ N KMnO$_4$. The quantity of H$_2$ evolved was determined in an LKhM-8 MD chromatograph.

DISCUSSION OF RESULTS

When WO$_4^{2-}$ solutions are acidified, various isopolytungstate species are formed; these may exist in solution in equilibrium with each other. The composition of the isopolytungstate mixture depends on such factors as the solution pH, the ionic strength, the temperature, and the concentration C of the original tungstate ions [5].

The mixture composition for these systems is commonly characterized as a function of the number Z, which is the ratio of the number of moles H$^+$ consumed in the reaction to the number of moles of WO$_4^{2-}$. In order to obtain solutions in which individual PT species predominate, we used procedure A of [6], which includes the addition of a 1 M NaCl solution to maintain the ionic strength. This procedure was used in preparing solutions containing the following PTs: [W$_6$O$_{20}$(OH)]$^{8-}$, designated paratungstate A (PT-A) with Z = 7/6 and C < 0.1 M; [H$_2$W$_{12}$O$_{42}$]$^{10-}$, paratungstate B (PT-B) with Z = 7/6 and C > 0.1 M; [W$_{10}$O$_{32}$]$^{4-}$, paratungstate Y (PT-Y) with Z = 16/10 and 5·10$^{-4}$ M < C < 10$^{-2}$ M. However, in a 1 M NaCl solution, the protons balancing the negative charge of the PT anion may be replaced by Na$^+$ cations. In the case of reduced HPA species, such replacement suppresses the reaction of H$_2$ evolution almost completely [7]. In solutions of PT-A, PT-B, and PT-Y prepared by procedure A and reduced by Zn amalgam or by the photochemical method, singly and doubly reduced PT species have been detected spectrophotometrically in the example of PT-Y [8]; however, no H$_2$ is released from the solution.

For this reason, the PTs were subsequently obtained by acidifying solutions containing WO$_4^{2-}$. Here, the values of the degree of acidification P (ratio of the acid normality to the WO$_4^{2-}$ concentration) were considerably greater (with the exception of the experiments at pH 4 and 3.4, at which Z is apparently close to 1.6, since the formation of PT-Y predominates) than the values of P corresponding to the PT conversion scheme of Glemzer [5]. The PTs prepared by such a method are reduced rapidly, either by Zn amalgam or photochemically (in aqueous-alcoholic solutions). The reduction of the PT is accompanied by the appearance of an intense band with a maximum at $\lambda$ 620 nm (Figs. 1a and 1b) and $\lambda$ 760 nm (Fig. 1c).

The observed absorption spectra correspond to the spectrum of a mixture of doubly and singly reduced forms of PT-Y (W$_{10}$O$_{32}^{6-}$ and W$_{10}$O$_{32}^{5-}$, respectively [8]). A calculation of the PT-Y concentration on the basis of known extinction coefficients ($\epsilon_{620} = 16,000$ and $\epsilon_{760} = 7500$ liters/mole·cm [8]) shows that only part of the WO$_4^{2-}$ anions introduced into the solution are present in the composition of the PT-Y. For example, in the solution for which the spectrum is shown in Fig. 1a, the concentration of doubly and singly reduced forms of PT-Y are 4.37·10$^{-4}$ and 2·10$^{-5}$ M, respectively. Thus, in the composition of the PT-Y there is only 7.37·10$^{-4}$ WO$_4^{2-}$ out of the original WO$_4^{2-}$ concentration of 10$^{-3}$ M. The quantity of WO$_4^{2-}$ anions present in the PT-Y polyanions will also depend on the pH of the solution.