Russian Journal of General Chemistry, Vol. 73, No. 5, 2003, pp. 695–696. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 5, 2003, pp. 735–736.

Polarographic Behavior of Phosphorus Tribromide

L. M. Kisil', I. M. Osadchenko, and A. P. Tomilov

State Research Institute of Organic Chemistry and Technology, Moscow, Russia

Received April 26, 2001

Abstract — Phosphorus tribromide gives a one-electron reduction wave at $E_{1/2}$ –0.6 V on a mercury drop cathode in acetonitrile in the concentration range 0.05–0.5 mM, applicable for analytical purposes. It is proposed that the cathodic process gives rise to an unstable species particle PBr which is adsorbed on the mercury surface.

Continuing studies on the polarographic behavior of phosphorus halides [1, 2] we turned to the electrochemical reduction of phosphorus tribromide on a mercury drop electrode in acetonitrile.

The studies were carried out on an R-60 polarograph. Capillary characteristics: m 1.65 mg/s, τ 3.6 s at an open circuit and a mercury column height of 45 cm. Phosphorus tribromide was prepared according to [3]. All measurements were performed in an 0.08 M acetonitrile solution of tetraethylammonium perchlorate prepared according to [4]. Acetonitrile was dried over phosphoric anhydride and twice distilled. Oxygen was purged off with helium for 30 min. Under these conditions, one reduction wave of phosphorus tribromide with a half-wave potential of –0.60 V (against bottom mercury) is observed.

The general view of the polarogram is presented in the figure. In the concentration range 0.05–0.5 mM, the limiting current is linear via the concentration of phosphorus tribromide, which can be used for analytical purposes. The limiting current is duffusion in nature, as evidenced by its direct relation to the square root of the mercury column height and to the slope of the straight line in the coordinates $\log I_l - \log H$, close to 0.5. The number of electrons taking part in the potential-determining stage, calculated by the Il'kovich equation is near 1 (the diffusion coefficient calculated by the Stokes–Einstein equation [5] is 1.55×10^{-4} cm^2/s), which agrees with the microcoulometric data according to [6].

Logarithmic analysis of the polarographic wave in the $\log [I/(I_l - I)] - E$ coordinates permits us to propose that the process is irreversible.

The resulting datcan be explained in terms of the following reduction scheme.

$$PBr_3 + e \longrightarrow PBr_2 + Br^-.$$

The radical formed undergoes disproportionation.

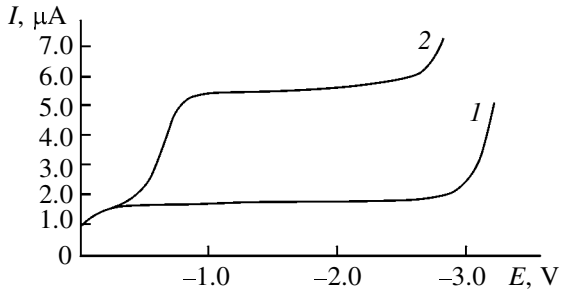
$$2PBr_2 \longrightarrow PBr_3 + PBr.$$

Further transformations are evidently connected with reaction of phosphorus monobromide with the cathode material.

$$PBr + Hg \longrightarrow P(HgBr).$$

The possibility of PBr_3 formation has been reported in [7].

Evidence for the proposed scheme was obtained by preparative electrolysis of phosphorus tribromide. It was found that in the course of electrolysis a red-brown film formed on the cathode surface. Elemental analysis showed that it contained 17.0% of phosphorus, 14.3% of bromine, 30.0% of mercury, 32% of oxygen and 4.0% of hydrogen, or (in atomic fractions) one bromine atom, one mercury atom, and 11 mol of water per three phosphorus atoms. Thus the



Polarogram of phosphorus tribromide in acetonitrile on the background of 0.08 M $(C_2H_3)_4NClO_4$. (*1*) Background and (*2*) in the presence of PBr_3 (0.33 mM).

1070-3632/03/7305-0695 $25.00

composition of the precipitate can be presented by the empirical formula $P_3(HgBr) \cdot 11H_2O$.

REFERENCES

1. Filimonova, L.F. and Tomilov, A.P., *Zh. Vses. Khim. O–va,* 1970, vol. 15, no. 3, p. 352.
2. Kisil', L.M., Osadchenko, I.M., and Tomilov, A.P., *Zh. Vses. Khim. O–va,* 1975, vol. 46, no. 2, p. 243.
3. Karyakin, Yu.V. and Angelov, I.M., *Chistye khimicheskie veshchestva* (Pure Chemical Substances), Moscow: Khimiya, 1974.
4. Kolthoff, I. and Cootzee, J., *J. Am. Chem. Soc.,* 1957, vol. 79, no. 3, p. 870.
5. Kolthoff, I.M. and Lingane, J.J., *Polarography,* New York: Interscience, 1946.
6. Stribert, A.G. and Markalyova, T.M., *Zh. Fiz. Khim.,* 1954, vol. 28, no. 4, p. 671.
7. Wazer, J.R. van, *Phosphorus and Its Compounds,* New York: Interscience, 1958.