VOLTAMMETRIC STUDY OF REACTIONS OF TRIPHENYLPHOSPHITE OZONIDE

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The electrochemical characteristics of reduction of triphenylphosphite ozonide at a stationary platinum electrode were determined in acetonitrile at between −30 and −11°C. The feasibility of employing voltammetric methods to investigate the reactions of phosphite ozonides was demonstrated in a model study of the kinetics of the thermal decomposition of $(C_6H_5O)_3PO_3$ and its reaction with triphenylphosphite.

Keywords: kinetics, decomposition, ozonide, triphenylphosphite, ozonation, voltammetry.

Electrochemical methods are utilized in analyzing peroxides and studying their reactions [1, 2]. However, no research of this sort has been conducted for phosphite ozonides.

The present investigation used $(C_6H_5O)_3PO_3$ as a model for voltammetric study of the kinetics of the thermal decomposition of ozonide and its reaction with triphenylphosphite.

EXPERIMENTAL

The methods used to synthesize and purify the $(C_6H_5O)_3P$ (1) were described in [3]. The acetonitrile was purified and thoroughly dried by the techniques of [4]. We obtained the ozonide $(C_6H_5O)_3PO_3$ (2) by treating 0.25-0.35 mmole of 1 in 5-10 ml of dry CH_3CN with an O_3–O_2 mixture (the $[O_3]$ at the ozonizer outlet was $\approx 2 \cdot 10^{-4}$ mol/liter, and the delivery rate for the O_3–O_2 mixture was 20 ml/min) by the method of [5]. After ozonation was complete, dry Ar was passed through the solution, and the content of compound 2 was determined by a procedure analogous to that in [6].

Cyclic and differential pulsed volt–ampere curves were determined in an RA-3 polarographic analyzer (Czechoslovakia) with scan rates of 10-500 mV/s. The working electrode was a platinum electrode with S = 1.81 mm^2, while the auxiliary electrode was a platinum plate with S = 80 mm^2. The reference electrode was a silver wire immersed in a 0.1 M solution of $AgNO_3$ in CH_3CN. The reference electrode was connected to the cell through a semipermeable membrane bridge filled with a solution of the $(C_4H_3)_4NClO_4$ background electrolyte. The cell was temperature-controlled at the experimental level.

The thermal decomposition kinetics of 2 were studied in CH_3CN solution at from −30 to −11°C. A portion of 5-10 ml of dry CH_3CN and a weighed portion of the background electrolyte were placed in the polarographic cell, dry Ar was passed through it, and the volt–ampere curves were determined. We then added 0.3 mmole of 2 to the cell. The reaction was considered to start when the ozonide was introduced. Differential pulsed volt–ampere curves were determined at definite intervals, and their peak heights established.

The kinetics of the reaction between 2 and 1 were studied from the amount of 2 consumed in a 3:1 acetonitrile–toluene mixture at 30°C. The toluene was added to improve the solubility of the 1. We added 0.1-0.5 mmole of 1 to a cell containing 0.01 mmole of 2 in an Ar atmosphere. The reaction was assumed to begin when the 1 was introduced.

Dummy experiments showed that the 1 and the breakdown products of the 2 (triphenyl phosphate and O_2) were reduced over the potential range investigated.

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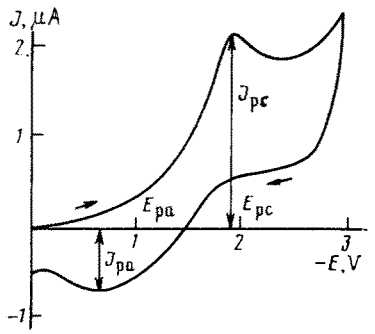

Fig. 1

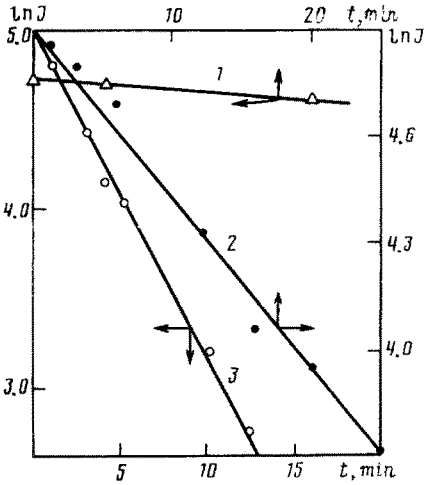

Fig. 2

Fig. 1. Cyclic volt-ampere curve for $3.48 \cdot 10^{-2}$ mol/liter 2 in CH_3CN at −35°C. Potential sweep speed of 500 mV/s.

Fig. 2. Anamorphoses of critical consumption curves for 2 during thermal decomposition (1, 2) and in presence of 1 (3). CH_3CN as solvent. 1) −30°C, $[2]_0 = 3.48 \cdot 10^{-3}$ mol/liter; 2) −11°C, $[2]_0 = 3.11 \cdot 10^{-3}$ mol/liter; 3) −30°C, $[2]_0 = 1 \cdot 10^{-3}$ mol/liter, $[1]_0 = 20 \cdot 10^{-3}$ mol/liter.

RESULTS AND DISCUSSION

The typical cyclic volt-ampere curve of 2 is depicted in Fig. 1. The volt-ampere curve parameters, i.e., the ratio of the anodic and cathodic peaks $I_{pa}/I_{pc} \approx 0.15$ and the potential difference between the cathodic and anodic peaks $\Delta E = E_{pa} - E_{pc} \approx 1.6$ V, indicated irreversibility of the electrochemical reduction of 2 [7]. This conclusion was also confirmed by the significant peak half-width ($W_{1/2} \approx 600$ mV) for the differential pulsed volt-ampere curve and the manner in which it depended on the modulation amplitude.

Triphenylphosphite ozonide undergoes reduction at ≈−1.7 V. The similarity of the reduction potentials for 2 and oxygen under the conditions in question (≈−1.8 V) somewhat complicated the measurements, but use of differential pulsed voltammetry enabled us to distinguish them. The dependence of ΔI on the concentration of 2 was linear over the range investigated (r = 0.98):

$$\Delta I = (1.06 \pm 0.18) \cdot 10^{-4} + (5.21 \pm 0.58) \cdot 10^{-3} [(C_6H_5O)_3PO_3],$$

which enabled us to use a standard curve for quantitation of 2. The lower limit of the determinable triphenylphosphite ozonide concentration ($\approx 5 \cdot 10^{-4}$ mol/liter) a product of the superimposed O_2 peak, while the upper limit ($\approx 5 \cdot 10^{-2}$ mol/liter) was dictated by the limited solubility of 2 in CH_3CN at low temperature.

The analytic signal amplitude for the peak ΔI varied as a function of time during thermal decomposition of 2 in accordance with the equation (Fig. 2):

$$\ln(\Delta I) = \ln(\Delta I)_0 - k_0 t, \quad (1)$$

where ΔI_0 and ΔI (μA) are the peak currents at the starting time and time t and k_0 is a constant. Since ΔI is linearly related to the concentration of 2, we have

$$\ln(\Delta I)/(\Delta I)_0 = \ln([2]/[2]_0), \quad (2)$$

where [2] and $[2]_0$ are the instantaneous and initial ozonide concentrations (mol/liter).

It can be seen from Eqs. (1) and (2) that the consumption of 2 followed a first-order rule, which held over the entire temperature and ozonide concentration ranges investigated. The dependence of k_0 on temperature:

T, °C	−30	−26	−20	−15	−4
$k_0 \cdot 10^{-4}$, s^{-1}	0.9	1.5	3.6	7.5	8.3

yielded:

$$\lg k_0 = (9.64 \pm 1.90) - (15.18 \pm 1.38)/Q,$$

with Q = 9.6·RT (kJ/mol).

The activation parameters in CH_3CN were close to those found in CH_2Cl_2: log A = 9.17 and E = 58.9 ± 7.5 kJ/mol [8] and log A = 10.50 ± 0.61 and E = 64.7 ± 3.0 kJ/mol [9].

The reaction of 2 with 1 was studied for $[1]_0 \gg [2]_0$. When excess 1 was present, consumption of 2 was by a pseudo-first-order rule with effective rate constant k_{ef} (see Fig. 2). The increase in ozonide consumption rate in the presence of phosphite was due to the fact that decomposition of 2 competed with its reaction with 1. According to Fig. 2, $k_{ef} = 2.9 \cdot 10^{-3}$ s^{-1}, and the second-order rate constant for the reaction of 2 with 1 was consequently k = 0.14 liter/mol·s (we assumed $k_0 = 0.9 \cdot 10^{-4}$ s^{-1} in making the calculations).

The above examples show that the voltammetric method can be used to study the reaction kinetics of phosphite ozonides.

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LITERATURE CITED

1. V. L. Antonovskii and M. M. Buzlanova, Analytic Chemistry of Organic Peroxides [in Russian], Khimiya, Moscow (1978), p. 308.
2. D. Swern, Organic Peroxides, Vol. 2, Wiley-Interscience, New York (1971), p. 568.
3. H. B. Gottlieb, J. Am. Chem. Soc., 54, 748 (1932).
4. A. Weissberger, E. Proskauer, J. Riddick, and E. Toops, Jr., Organic Solvents — Physical Properties and Methods of Purification, Interscience (1955).
5. Q. Thompson, J. Am. Chem. Soc., 73, 548 (1961).
6. V. V. Shereshovets, N. M. Korotaeva, and R. K. Yanbaev, React. Kinet. Catal. Lett., 38, 243 (1989).
7. A. M. Bond, Polarographic Methods in Analytic Chemistry [in Russian], Khimiya, Moscow, (1983), pp. 118, 160.
8. R. Murray and M. Kaplan, J. Am. Chem. Soc., 91, 5358 (1969).
9. V. V. Shereshovets and N. M. Korotaeva, Izv. Akad. Nauk SSSR, Ser. Khim., No. 6, 1228 (1988).