

# Pyridine catalyzed decomposition of triphenylphosphite ozonide

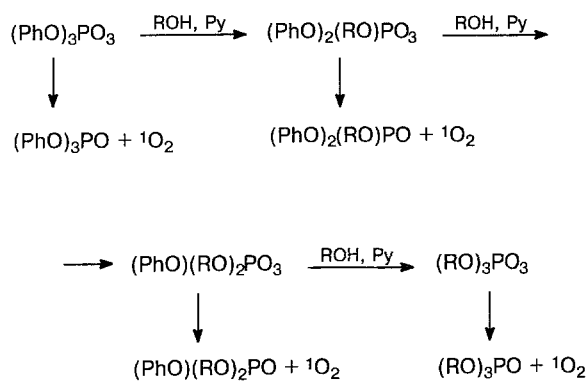
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Pyridine accelerates the decomposition of triphenylphosphite ozonide in  $\text{CH}_2\text{Cl}_2$ . The addition of ethanol to the  $(\text{PhO})_3\text{PO}_3\text{-C}_5\text{H}_5\text{N-CH}_2\text{Cl}_2$  system increases the rate of the process. The kinetic regularities of the decomposition of  $(\text{PhO})_3\text{PO}_3$  in the presence of pyridine, ethanol-pyridine, and propan-2-ol-pyridine mixtures in  $\text{CH}_2\text{Cl}_2$  are studied.

**Key words:** trioxides, phosphite ozonides; decomposition of peroxides, catalysis by amines.

It is known that a binary methanol-pyridine (2 : 1, v/v) mixture exerts a catalytic effect on the decomposition of triphenylphosphite ozonide.<sup>1</sup> A mechanism of this process involving the exchange of the ligands at the P atom followed by the rapid decomposition of mixed alkylarylphosphite ozonide has previously<sup>2</sup> been suggested.



(Py — pyridine)

However, the kinetics of this process have been studied insufficiently. In this work, the kinetic regularities of the decomposition of  $(\text{PhO})_3\text{PO}_3$  in the presence of pyridine and pyridine-alcohol binary mixtures (ethanol and propan-2-ol) are studied.

## Experimental

Triphenylphosphite ozonide was prepared by the ozonization of  $(\text{PhO})_3\text{P}$  at  $-80^\circ\text{C}$  similarly to the procedure described previously.<sup>3</sup> Methylene chloride was used as the solvent. When the ozonization was completed, the ozonide solution was blown through with argon and stored at  $-80^\circ\text{C}$ . Methylene chloride, pyridine, isopropanol, and ethanol were

dried and purified according to the known procedures.<sup>4,5</sup> An ozonator, whose construction has been described previously,<sup>6</sup> was used for the preparation of ozone.

Phosphite ozonides and the products of their decomposition were identified by  $^{31}\text{P}$  NMR on a Bruker AM300 spectrometer by their characteristic signals.<sup>7</sup>

The kinetics of the decomposition of  $(\text{PhO})_3\text{PO}_3$  were studied by chemiluminescence by the decay of singlet oxygen irradiation in the IR spectral range.<sup>8</sup>

An  $\sim 2.5 \cdot 10^{-4}$  M solution of  $(\text{PhO})_3\text{PO}_3$  was used. The concentration of pyridine ([Py]) was varied from 0.01 to 0.1 mol L<sup>-1</sup>. The temperature was varied from  $-50^\circ\text{C}$  to  $6^\circ\text{C}$ .

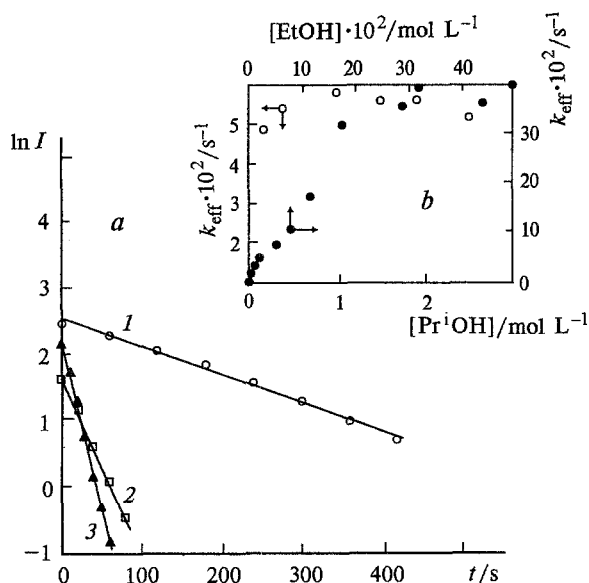
## Results and Discussion

The addition of pyridine increases the rate of triphenylphosphite ozonide decomposition. When the concentration of Py is constant, the decomposition of  $(\text{PhO})_3\text{PO}_3$  is first-order (Fig. 1). The effective rate constants ( $k_{\text{eff}}$ ) found from the semilogarithmic anamorphoses of the kinetic curves of the luminescence decay are presented in Table 1.

**Table 1.** Effective rate constants for the consumption of  $(\text{PhO})_3\text{PO}_3$  in  $\text{CH}_2\text{Cl}_2$  at  $-15^\circ\text{C}$

$[\text{Py}] \cdot 10^2/\text{mol L}^{-1}$	$k_{\text{eff}} \cdot 10^2/\text{s}^{-1}$
0	0.45
1	1.35
2	2.50
3	4.4
4	4.49
5	6.67
7.5	9.03
10	12.27

Note. The error in the determination of  $k_{\text{eff}}$  does not exceed 20 %.



**Fig. 1** *a.* Semilogarithmic anamorphoses of the kinetic curves of the chemiluminescence decay upon the decomposition of triphenylphosphite ozonide in  $\text{CH}_2\text{Cl}_2$  at  $-15^\circ\text{C}$  in the absence of pyridine (1), in the presence of pyridine (2) ( $[\text{Py}]_0 = 2 \cdot 10^{-2} \text{ mol L}^{-1}$ ), in the presence of pyridine and alcohol (3) ( $[\text{Py}]_0 = 2 \cdot 10^{-2} \text{ mol L}^{-1}$ ,  $[\text{EtOH}] = 9 \cdot 10^{-3} \text{ mol L}^{-1}$ ).  $I$  is the intensity of chemiluminescence.

*b.* Dependence of  $k_{\text{eff}}$  for the decomposition of  $(\text{PhO})_3\text{PO}_3$  on the concentration of alcohol in the pyridine–ethanol and pyridine–propan-2-ol systems ( $\text{CH}_2\text{Cl}_2$ ,  $-15^\circ\text{C}$ ,  $[\text{Py}]_0 = 2 \cdot 10^{-2} \text{ mol L}^{-1}$ ).

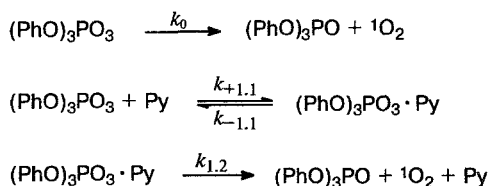
The analysis of the data in Table 1 shows that  $k_{\text{eff}}$  depends linearly on  $[\text{Py}]$ :

$$k_{\text{eff}} = a + b[\text{Py}], \quad (1)$$

where  $a/\text{s}^{-1}$ ,  $b/\text{L mol}^{-1} \text{ s}^{-1}$  are the constant rates at a given temperature. Therefore, an empirical expression can be written for the reaction rate ( $w$ ):

$$w = a[(\text{PhO})_3\text{PO}_3] + b[(\text{PhO})_3\text{PO}_3][\text{Py}]. \quad (2)$$

The form of Eq. (2) testifies that there are two channels for the consumption of ozonide according to first- and second-order kinetic laws. Since pyridine is virtually not consumed in the reaction, the second process can be considered as the catalytic process, which occurs *via* the formation of the donor-acceptor complex:



At  $a = k_0$  and  $b = k_{1.2}k_{+1.1}/(k_{-1.1} + k_{1.2})$  the empirical Eq. (2) for the rate of ozonide consumption coincides

**Table 2.** Temperature dependence of  $k_{\text{eff}}$  in  $\text{CH}_2\text{Cl}_2$  ( $[\text{Py}]_0 = 2 \cdot 10^{-2} \text{ mol L}^{-1}$ )

$T/^\circ\text{C}$	$k_{\text{eff}} \cdot 10^2/\text{s}^{-1}$
-1.5	1.9
-10	2.1
-20.5	3.3
-31	5.3
-41	8.1
-50	7.1

*Note.* The error in the determination of  $k_{\text{eff}}$  does not exceed 20 %.

with the equation resulting from the reaction scheme

$$w = k_0[(\text{PhO})_3\text{PO}_3] + \frac{k_{1.2}k_{+1.1}}{k_{-1.1} + k_{1.2}} [(\text{PhO})_3\text{PO}_3][\text{Py}]$$

and makes it possible to determine the rates of the catalytic and non-catalytic processes separately. According to the data presented in Table 1,  $k_0 = (3.3 \pm 0.5) \cdot 10^{-3} \text{ s}^{-1}$  and  $k_{1.2}k_{+1.1}/(k_{-1.1} + k_{1.2}) = 1.2 \pm 0.1 \text{ L mol}^{-1} \text{ s}^{-1}$ . At  $-15^\circ\text{C}$  and  $[\text{Py}] > 2.8 \cdot 10^{-3} \text{ mol L}^{-1}$  the catalytic decomposition makes the major contribution to the rate of the process.

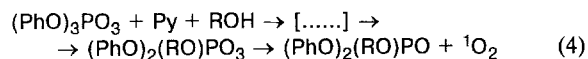
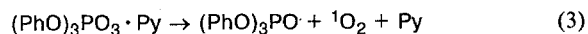
A break is characteristic of the temperature dependence of  $k_{\text{eff}}$  (Table 2). In the range from  $-41^\circ\text{C}$  to  $-1.5^\circ\text{C}$ , the activation energy of the process is negative:  $\log k_{\text{eff}} = -(5.56 \pm 0.02) - (-4.8 \pm 0.2)/\theta$ , where  $\theta = 2.3RT \text{ kcal mol}^{-1}$ . The negative activation energy is probably related to the complicated reaction mechanism *via* the formation of the  $[(\text{PhO})_3\text{PO}_3 \cdot \text{Py}]$  complex (see scheme presented above).

Addition of ethanol or propan-2-ol to the  $(\text{PhO})_3\text{PO}_3\text{—Py—CH}_2\text{Cl}_2$  system increase the rate of ozonide decomposition still more (see Fig. 1). In special experiments it was established that the addition of ethanol (0.1 to 0.7 mol  $\text{L}^{-1}$ ) to the  $(\text{PhO})_3\text{PO}_3\text{—CH}_2\text{Cl}_2$  system in the absence of pyridine exerts no effect on the rate constant of the decomposition of triphenylphosphite ozonide. The decomposition of  $(\text{PhO})_3\text{PO}_3$  in the presence of both pyridine and alcohol occurs according to the first-order law with the rate constant  $k_{\text{eff}}$ . When  $[\text{Py}] = \text{const} = 2 \cdot 10^{-2} \text{ mol L}^{-1}$ , the dependence of  $k_{\text{eff}}$  on the concentration of alcohol has a limiting character (see Fig. 1). A break is also typical of the temperature dependence of  $k_{\text{eff}}$ .

In the interval from  $-35.5^\circ\text{C}$  to  $6^\circ\text{C}$   $E_{\text{eff}}$  is equal to  $(-4.4 \pm 0.1) \text{ kcal mol}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ .

The catalytic effect of the alcohol additives is related to the replacement of the ligands at the P atom in the ozonide molecule, as it was assumed in the work by Bartlett.<sup>2</sup> The replacement of the phenoxy group by the ethoxy group is confirmed by  $^{31}\text{P}$  NMR spectroscopy: the signal of diphenylethyl phosphate  $(\text{PhO})_2(\text{EtO})\text{PO}$  ( $-11 \text{ ppm}$ ) is recorded in the reaction mixture. It was

established in special experiments that no transesterification of diphenyl phosphate by ethanol occurs under our experimental conditions. Therefore, there are two channels of the catalytic decomposition of ozonide in the  $(\text{PhO})_3\text{PO}_3\text{---ROH---Py---CH}_2\text{Cl}_2$  system: the decomposition of ozonide bound in the complex (Eq. (3)) and the exchange of the ligands at the P atom followed by the rapid decomposition of mixed alkylarylphosphite ozonide (Eq. (4)).



This work was financially supported by the Russian Foundation for Basic Research (Project No. 93-03-5231).

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Received September 6, 1994