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STUDY OF THERMAL STABILITY OF OZONIDES OF PHOSPHOROUS ACID ESTERS

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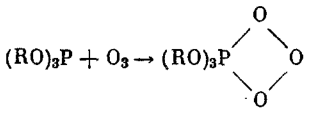
The reaction of phosphorous acid esters $(RO)_3P$ with ozone at low temperatures lead to the corresponding ozonides $(RO)_3P \cdot O_3$ [1], which are used as oxidizing agents [1, 2] and sources of singlet oxygen [3, 4]. To use $(RO)_3P \cdot O_3$ in oxidation reactions, we must know their thermal stability. In the present article the results are reported of a study on the thermal stability of the ozonides of trialkyl and triaryl phosphites.

EXPERIMENTAL

Trimethyl (I), triethyl (II), tributyl (III), tricyclohexyl (IV), trioctyl (V), triphenyl (VI), tri-(2-methylphenyl) (VII), tri-(2-chlorophenyl) (VIII), tri-(3-chlorophenyl) (IX), tri-(4-chlorophenyl) (X), tri-(2,4-dichlorophenyl) (XI), tri-(2,4,6-trichlorophenyl) phosphites (XII) were synthesized and purified according to [5, 6]. The solvent, methylene chloride, was purified and thoroughly dried [7]. The ozonides of phosphites (Ia)-(XIIa) were obtained by the ozonization of the corresponding phosphites (I)-(XII) at ~−90°C to −80°C [1]



(I)—(XII) (Ia)—(XIIa)

The kinetics of the thermal decomposition of ozonides (Ia)-(XIIa) was studied in analogy to the method in [3, 8].

RESULTS AND DISCUSSION

It was found that the decomposition of the ozonides (Ia)-(XIIa) is described by a first-order equation (we should note that the thermolysis of ozonides of cyclic and mixed alkyl aryl phosphites proceeds according to a similar kinetic order [3, 9-13])

$$-d\,[(RO)_3P \cdot O_3]/dt = k_0\,[(RO)_3P \cdot O_3]$$

where k_0 is the decomposition rate constant. The values of k_0, E_0, $\log A_0$ for the thermolysis of (Ia)-(XIIa) are listed in Tables 1 and 2. With respect to their thermal stability, compounds (Ia)-(XIIa) can be arranged into the following series (−65°C): (IIa) < (IIIa) < (Va) < (IVa) < (Ia) < (VIIa) < (XIa) ≈ (Xa) ≈ (VIa) < (IXa) < (XIIa) < (VIIIa).

An analysis of the change in k_0 depending on the structure of $(RO)_3P \cdot O_3$ according to the Taft equation (Fig. 1)

$$\lg k_0/k_0' = \rho \Sigma \sigma^*$$

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TABLE 1. Rate Constants of Overall Thermal Decomposition k_0 (cm^{-1}) of Phosphite Ozonides $(RO)_3P \cdot O_3$ in CH_2Cl_2

R	Compound	T, °C	$k_0 \cdot 10^2$	R	Compound	T, °C	$k_0 \cdot 10^3$	R	Compound	T, °C	$k_0 \cdot 10^3$
CH_3	(Ia)	−65	0,38			0	54,3	$4\text{-}ClC_6H_4$	(Xa)	−10	1,54
C_2H_5	(IIa)	−65	11,00			10	138,0			0	4,48
C_4H_9	(IIIa)	−65	8,22			20	197,0			10	7,20
C_6H_{11}	(IVa)	−65	1,80	$2\text{-}ClC_6H_4$	(VIIIa)	−7,5	0,67			20	24,00
C_8H_{17}	(Va)	−65	2,00								
C_6H_5	(VIa)	−41	0,0079			1,5	2,51	$2,4\text{-}Cl_2C_6H_3$	(XIa)	−12	0,65
		−25	0,12			10	5,48			0	1,32
		−17	0,12			20	17,30			5	2,09
		0	0,86	$3\text{-}ClC_6H_4$	(IXa)	−20	0,30			20	5,48
		10	4,86			−10	1,54	$2,4,6\text{-}Cl_3C_6H_2$	(XIIa)	−10	0,36
		20	11,00			0	3,10			0	1,28
$2\text{-}CH_3C_6H_4$	(VIIa)	−30	2,06			20	21,90			8	2,87
		−20	2,56							22	11,70

TABLE 2. Activation Parameters for the Thermal Decomposition Reaction of $(RO)_3P\cdot O_3$

R	k_0 (—65°)	lg A_0	$\Delta S_0^{\neq}$ (0°C) cal/(mole·degree)	E_0	$\Delta H_0^{\neq}$ (0°)
	cm^{-1}			kcal/mole	
C_6H_5	$1,71\cdot10^{-6}$ a $1.86\cdot10^{-6}$ b $0,76\cdot10^{-6}$ c $11,70\cdot10^{-6}$ d	10,50±0,61	−12,4	15,48±0,71	14,94
2-$CH_3C_6H_4$	$1,66\cdot10^{-3}$	4,18±0,74	−41,3	6,62±0,90	6,08
2-ClC_6H_4	$5,89\cdot10^{-8}$	11,62±0,71	−7,2	17,94±0,90	17,40
3-ClC_6H_4	$4,80\cdot10^{-7}$	9,77±1,03	−15,7	15,31±1,27	14,77
4-ClC_6H_4	$1,78\cdot10^{-6}$	8,26±1,23	−22,6	13,33±1,56	14,79
2,4-$Cl_2C_6H_3$	$1,79\cdot10^{-6}$	6,57±1,10	−30.3	11,72±1,40	11,18
2,4,6-$Cl_3C_6H_2$	$8,00\cdot10^{-8}$	10,42±0,21	−12,7	16,66±0,33	16,12

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a) The present work.
b) [3].
c) [9].
d) [11] [the values of k_0 (−65°C) were calculated from the Arrhenius equation].

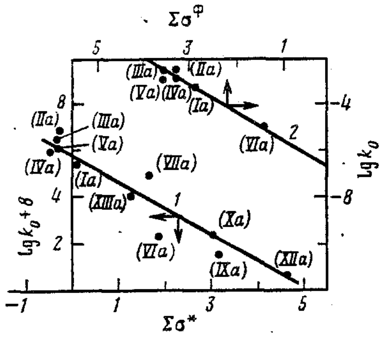

Fig. 1

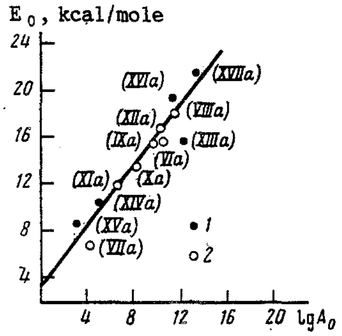

Fig. 2

Fig. 1. Dependence of $\log k_0$ on the sum of Taft constants Σσ* (1) and the sum of Kabachnik constants (2) for the thermal decomposition of $(RO)_3P\cdot O_3$ (CH_2Cl_2, −65°C). The numeration of points of (Ia)-(VIIa), (IXa), (Xa), (XIIa) corresponds to that given in Table 1; (XIIIa) refers to the methyl diphenyl phosphite ozonide [9].

Fig. 2. Dependence of E_0 on $\log A_0$ for the thermal decomposition reaction of $(RO)_3P\cdot O_3$ [the numeration of points of (VIa)-(XIIa) corresponds to that in Table 1]; (XIIIa)-(XVIIIa) — data for thermolysis of ozonides of methyl diphenyl phosphite [9], phenyl O-phenylene phosphite [13], trimethylolpropane phosphite [13], the ozonide of 1-phospha-2,8,9-trioxaadamantane [10], ethylenedioxyphenyl phosphite [13]). Literature data (1), the present work (2).

(σ* is the polar constant for substituents R) gives $\log k_0^{\prime} = -2.08 \pm 0.31$, $\rho = -1.20 \pm 0.15$, $r = 0.937$ (r is correlation coefficient) at −65°C [compounds (VIIIa) and (XIa) were not taken into consideration in the analysis because of the absence of the corresponding σ* constants]. Exclusion of triphenyl phosphite ozonide (VIa) from the correlation increases r to 0.959; in this case $\log k_0^{\prime} = -1.96 \pm 0.26$, $\rho = -1.17 \pm 0.12$. To plot the correlational dependence, the following values of σ* were used [14, 15]: 0 (CH_3), −0.1 (C_2H_5), −0.13 (C_4H_9), −0.17 (cyclo-C_6H_{11}), 0.60 (C_6H_5), 1.0 (4-ClC_6H_4), 1.04 (3-ClC_6H_4), 1.54 (2,4,6-$Cl_3C_6H_2$); σ* of (C_8H_{17}) was assumed to be equal to σ* of ($C_5H_{11}{}_2$) = −0.162. The correlation between $\log k_0$ and the sum of the Kabachnik constant for substituents R $\Sigma\sigma^{\Phi}$, (Fig. 1) leads to $\log k_0 = (-8.59 \pm 0.83) - (2.08 \pm 0.26)\Sigma\sigma^{\Phi}$, $r = 0.969$ (σ^{Φ}: −0.96 (CH_3), −1.10 (C_2H_5), −1.22 (C_4H_9), −1.11 (C_8H_{17}), −1.19 (C_6H_{11}), −0.472 (C_6H_5) [14]).

The negative value of ρ in the correlation relationships obtained indicates that in the transition state a positive charge accumulates on the reaction center, while the introduction of electron-acceptor substituents retards the decomposition of $(RO)_3P\cdot O_3$.

There is a linear dependence between the values of E_0 and $\log A_0$ (Fig. 2); $E_0 = (3.43 \pm 1.18) + (1.22 \pm 0.13)\log A_0$, $r = 0.947$ (Fig. 2). The exclusion of tricresyl phosphite ozonide (VIIa) and methyl diphenyl phosphite ozonide (XIIIa) [13] from this dependence gives: $E_0 = (3.82 \pm 0.86) + (1.23 \pm 0.09)\log A_0$, $r = 0.976$.

The presence of compensational effect possibly indicates one single mechanism of the thermolysis of (VIa)-(XIVa) (the data for (XIIIa)-(XVIIIa) were taken from [13, 9, 10]). The isokinetic temperature, calculated according to the slope of the $-\Delta H_0^{\neq} - \Delta S_0^{\neq}$ graph, is equal to 58 ± 20°C, which is much higher than the experimental temperature (Table 1). Calculation of the isokinetic temperature according to [16] showed that for the ozonides studied the lines of the $\log k_0$ vs $(1/T)$ dependence intersect at the same point 77 ± 5°C [compounds (VIa) and (XIa) do not fit this dependence]. Thus, with increase in temperature, the stability of the different $(RO)_3P\cdot O_3$ reach the same level.

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CONCLUSIONS

1. Rate constants and activation parameters were measured for the thermal decomposition of ozonides of trimethyl, triethyl, tributyl, tricyclohexyl, trioctyl, triphenyl, tri-(2-methylphenyl), tri-(2-chlorophenyl), tri-(3-chlorophenyl), tri-(4-chlorophenyl), tri-(2,4-dichlorophenyl), tri-(2,4,6-trichlorophenyl) phosphites.

2. The dependence of the rate constant of the thermolysis of the phosphite ozonides on the structure is satisfactorily described by the Taft and Kabachnik correlation equations. A compensational effect is observed between the energy of activation and the preexponential factor.

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