RATE CONSTANTS AND MECHANISM OF THE REACTION OF PHOSPHITES WITH OZONE IN CARBON TETRACHLORIDE

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In the course of the reaction of ozone with trialkyl and triaryl phosphites, intermediate products are formed, which are relatively stable at –70° and break down into phosphites and oxygen when the temperature is increased [1, 2]; moreover, oxygen is partially formed in a singlet form [3]. The stoichiometry of the reaction depends on the conditions of the experiment and the nature of the phosphite used [1]; there are also indications of fulfillment of an equimolar 1:1 ratio in a broad range of temperatures and concentrations. The effective constant of the gross reaction of ozone with triphenyl phosphite has been determined [4].

In this communication we investigated the relationship between the reactivity of phosphites with respect to ozone and the nature of the substituting groups.

EXPERIMENTAL METHOD

The reactions of phosphites with O_3 were conducted in a flow-through reactor according to the method described earlier [5]. A mixture of O_3 and O_2 was bubbled through a solution of the phosphite ($\sim 10^{-5}$–10^{-4} M) in CCl_4, washed with H_2O, and conditioned with ozone. The ozone concentration at the outlet from the reactor was recorded continuously spectrophotometrically. For most of the investigated phosphites of simple structure, the stoichiometric reaction, determined graphically according to the area between curves 1 and 2 of Fig. 1 (shaded), is equal to 1:1 [compounds (I)-(X), Table 1]. In certain cases, points of inflection corresponding to the completion of the addition of one equivalent of O_3 were observed on the curve of the variation of the O_3 content at the outlet from the reactor [compounds (XI)-(XIV)], and, finally, compounds (XV)-(XX) (Table 2) interacted with 2-3 eq of O_3 without any appreciable change in the reactivity in the course of the experiment. A calculation of the rate constants of the reaction of O_3 with phosphites was performed according to the procedure of [5], measuring the O_3 concentration at the entrance and exit of the reactor as the reaction proceeded. The rate constant of the reaction was calculated according to the equation

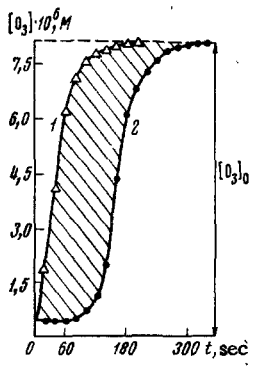
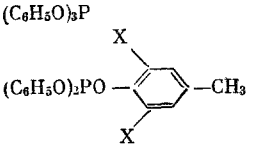
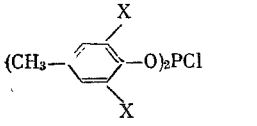
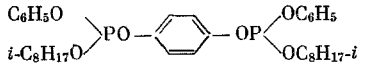
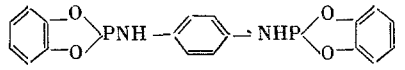
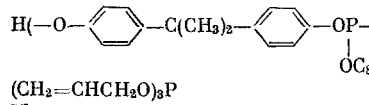


Fig. 1. Dependence of the concentration of O_3 after the reactor on the time of the reaction of ozone with triphenyl phosphite (rate of delivery of ozone 0.1 liter/min, $[O_3]_0 = 7.8 \cdot 10^{-6}$ M, $(C_6H_5O)_3P = 8 \cdot 10^{-5}$ M): 1) solubility of O_3 in the pure solvent; 2) change in the ozone concentration at the exit from the reactor.

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. S. M. Kirov Kazan' Chemicotechnological Institute. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 769-774, April, 1975. Original article submitted April 29, 1974.

TABLE 1. Rate Constants of the Elementary Steps and Stoichiometric Coefficient of Ozone β in the Reaction of Phosphites with Ozone [22°, CCl_4. Here and henceforth X = $C(CH_3)_3$]

Phosphite	Formula	$k_0 \cdot 10^{-4}$, $M^{-1} \cdot sec^{-1}$	$k_1/k_2 \cdot 10^{-4}$	β	Method of synthesis
(I)	$(CH_3O)_3P$	42,5	108,0	1,1	[6]
(II)	$(C_2H_5O)_3P$	45,0	36,8	1,0	[6]
(III)	$(i\text{-}C_8H_{17}O)_3P$	28,6	19,7	1,0	[6]
(IV)	$(i\text{-}C_8H_{17}O)_2POC_6H_5$	23,8	17,0	1,3	[6]
(V)	$(C_6H_5O)_2POC_8H_{17}\text{-}i$	10,0	18,5	1,2	[6]
(VI)	$(C_6H_5O)_2POC_8H_{17}\text{-}n$	15,8	14,2	1,2	[6]
(VII)	$(C_6H_5O)_3P$	5,6	4,1	1,0	[7]
(VIII)		14,7	39,0	1,1	—
(IX)	$(C_6H_5O)_2PC_6H_5$	31,3	35,3	1,1	[8]
(X)		1,5	3,9	0,9	[9]
(XI)		2,4	0,8	0,9	[10]
(XII)		1,3	9,7	0,9	[11]
(XIII)*		25,6	99,0	0,9	[12]
(XIV) †	$(CH_2{=}CHCH_2O)_3P$	13,3	0,24	1,1	[7]
	The same	2,0	0,0017	4,1	

* The constants were related to a monomer unit of the polyphosphite.

† The total stoichiometry of the consumption of ozone is close to 4 (see Table 2); to determine the constants, the dependence of k_{obs} on [P] in the first and fourth stages was correspondingly analyzed.

$$k = \frac{W([O_3]_0 - [O_3]_{gas})}{\alpha [P] [O_3]_{gas}} \quad (1)$$

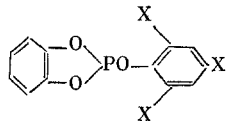
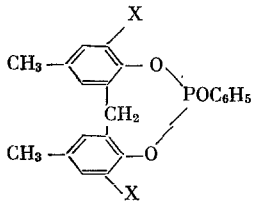
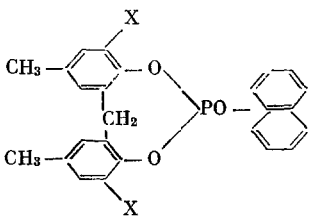
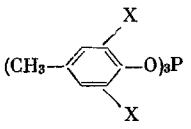
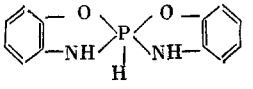
where W is the rate of delivery of O_3, related to a unit volume of the solution, sec^{-1}; α is the solubility coefficient; $[O_3]$ and $[O_3]_{gas}$ are the concentrations of ozone and exit of the reactor ($[O_3]_0 \sim 10^{-6}$-10^{-5} M), while [P] is the phosphite concentration at each given moment of time.

The phosphites used at this time (see Tables 1 and 2), with the exception of (VIII) and (XVIII), were synthesized and purified according to the well-known procedures (see the last columns of Tables 1 and 2).

Synthesis of Diphenylionyl Phosphite (VIII). To a solution of phenol in a fourfold excess (relative to the liberated HCl) of triethylamine (TEA) an equivalent amount of the dichloride of ionylphosphorous acid was added dropwise over a period of 0.5 h. The reaction mixture was heated for 6 h at 100°, after which it was cooled, TEA hydrochloride was filtered off, and the excess TEA was distilled off. The residue was distilled off under vacuum, isolating the fraction with bp 215-217° (2 mm), dense yellowish liquid. Found: C 74.34; H 7.50; P^{3+} 7.22%. $C_{33}H_{33}O_3P$. Calculated: C 74.30; H 7.57; P^{3+} 7.10%.

Synthesis of Tri-(2-tert-butyl-4-methylphenyl)phosphite (XVIII). To a solution of 2-tert-butyl-4-methylphenol in a fourfold excess of TEA we added dropwise an equivalent amount of PCl_3 at 75° over a period of 0.5 h; the mixture was exposed for 10 h at 120°, then cooled and, by adding petroleum ether, TEA hydrochloride precipitated and filtered off. The petroleum ether, excess TEA, and unreacted phenol were distilled off. The residue was recrystallized from petroleum ether, mp 109-110°. Found: P_{tot} 6.00; P^{3+} 5.82%. $C_{39}H_{45}O_3P$. Calculated: P^{3+} 5.96%.

TABLE 2. Effective Rate Constants and Stoichiometric Coefficient β of the Consumption of O_3 in the Reaction with Phosphites (CCl_4, 22°)

Phosphite	Formula	$k_{obs} \cdot 10^{-4}$ $M^{-1} \cdot sec^{-1}$*	β	Method of synthesis
(XIV)	$(CH_2=CHCH_2O)_3P$	5,30 (1,0) 2,28 (2,0) 2,26 (2,9)	4,1	[6]
(XV)		0,74 (0,7) 0,86 (1,0) 0,93 (1,3)	2,6	[13]
(XVI)		1,01 (1,0) 1,60 (1,40) 3,85 (1,6)	1,6	[14]
(XVII)		1,14 (1,2) 1,24 (1,4) 3,65 (1,6)	1,9	[14]
(XVIII)		0,31 (0,5) 0,41 (0,9) 0,57 (1,4)	1,9	—
(XIX)	$(C_6H_5NH)_3P$	0,16 (0,4) 0,11 (1,3) 0,07 (2,5)	2,9	[15]
(XX)		0,03 (1,0) 0,05 (3,9) 0,08 (4,8)	5,0	[16]

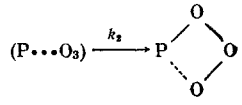
*In parentheses: the stoichiometric coefficient of the consumption of ozone by the moment of time at which the value of k_{obs} was measured.

DISCUSSION OF RESULTS

The second-order rate constants, calculated according to Eq. (1), decrease with increasing phosphite concentration. This permits us to assume that the rate constants found are effective values. An analysis of the possible kinetic schemes, explaining this phenomenon, showed that the only scheme corresponding to the aggregate of the experimental data and the literature material [17], is the scheme with the formation of an intermediate complex

$$P + O_3 \xrightarrow{k_0} (P \ldots O_3)$$

$$(P \ldots O_3) + P \xrightarrow{k_1} 2P + O_3$$

$$(P \ldots O_3) \xrightarrow{k_2} \text{  }$$

A consideration of this scheme under the condition of equilibrium with respect to the intermediate complex leads to the following expression for the reaction rate:

$$-\frac{d[O_3]}{dt} = \frac{k_0 k_2}{k_1[P] + k_2}[P][O_3]$$

Consequently, the effective rate constant k_{obs} depends on the concentration [P]

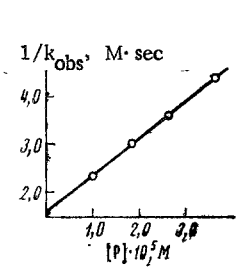


Fig. 2

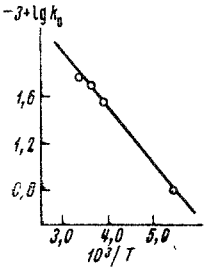


Fig. 3

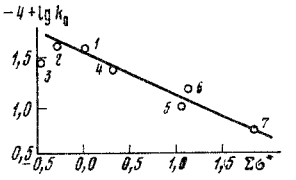


Fig. 4

Fig. 2. Dependence of the reciprocal of the effective constant of the reaction of triphenyl phosphite with O_3 on the current concentration of phosphite (CCl_4, 22°).

Fig. 3. Temperature dependence of the true rate constant of the reaction of triphenyl phosphite with O_3 in CCl_4 (at the temperature −90°, the solvent 2,4-dimethylhexane was used).

Fig. 4. Dependence of $\log k_0$ on the sum of the Taft σ^* constants of the substituents in the reaction series $P(OX')(OX'')(OX''')$ (the numbers of the points correspond to the numbers of the compounds in Table 1).

$$k_{obs} = \frac{k_0 k_2}{k_1 [P] + k_2} \tag{2}$$

Equation (2) can be transformed to the following form:

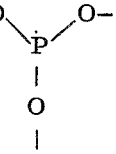
$$\frac{1}{k_{obs}} = \frac{1}{k_0} + \frac{k_1}{k_0 k_2} [P] \tag{3}$$

On the basis of Eq. (3), from the experimental dependence of the effective constant k_{obs} on the phosphite concentration, we can determine the true rate constant k_0 of the reaction of ozone with phosphite, and also calculate k_1/k_2.

The dependence of $1/k_{obs}$ on the phosphite concentration (Fig. 2) satisfies Eq. (3) well. From Table 1 it is evident that the values of the true rate constant k_0 for phosphites are rather high ($2 \cdot 10^4$-$5 \cdot 10^5$ liters/mole). Assuming that the mechanism of the reaction is unchanged from solutions in CCl_4 to 2,4-dimethylhexane, we investigated the temperature dependence of the constants k_0, as well as the ratio k_1/k_2, for triphenyl phosphite in the interval 22 to −90°. For k_0 we obtained the equation (Fig. 3):

$$k_0 = 2.3 \cdot 10^6 \exp(-2100 \pm 500/RT) M^{-1} \cdot sec^{-1}$$

The ratio k_1/k_2 is practically independent of the temperature. Consequently, the activation energies of the two steps of decomposition of the complex differ by no more than 1 kcal/mole and are evidently small in absolute value.

Then a comparison of the true rate constants k_0 of the reaction of O_3 with phosphates with the Taft σ^* constants of the substituents in the fragment  shows that with increasing electron-donor capacity of the substituent, the values of k_0 increase (Fig. 4).

From the slope of the straight line in a plot of $\log k_0$ vs $\Sigma\sigma^*$ for the investigated phosphites [the coefficient of correlation (without consideration of the point 3) $r = 0.98$], we found the coefficient $\rho = -0.44$. This pattern reflects not only the tendency in the variation of the reactivity of phosphites, but also shows that in the formation of the intermediate complex (P . . . O_3) there is probably a displacement of electron density from the phosphorus atom to the ozone molecule. The influence of polar factors is evidently also substantially manifested in the series of values of k_1/k_2 (see Table 1): the higher the electron density on

the phosphorus atom in the complex, the larger this ratio becomes, i.e., the more readily the complex is "broken up" by phosphite molecules.

It has already been mentioned that the stoichiometry of the reaction of some of the investigated phosphites differs from 1:1 (see Table 2). It can be assumed that in these cases stable products are formed, capable of reacting again with ozone. As was shown by special experiments for the conversion products of phosphite (XVI), neither phosphate nor the acid $>P(H)=O$, which practically do not react with ozone under the conditions of the experiment, can be such products. For such compounds it was impossible to construct the dependence $1/k_{obs} = f([P])$ and calculate k_0, and therefore Table 2 cites the value of k_{obs}, which are evidently three to four times lower than k_0.

Usually the introduction of nitrogen atoms into the molecule of the organic compound increases its tendency to participate in electrophilic reactions as a result of the presence of an unshared pair of electrons on the nitrogen. For phosphites it was found that the introduction of a nitrogen atom into the molecule (XIX) appreciably lowers the effective rate constant of its interaction with ozone.

CONCLUSIONS

1. An analysis of the kinetics of the reaction of ozone with phosphites shows that the steps of formation of a relatively stable product $(RO)_3PO_3$ is preceded by the formation of an intermediate unstable complex.

2. A method was developed for determining the rate constants of the primary step of the reactions of phosphites with ozone, and the rate constants were determined for 14 phosphites.

3. An empirical equation relating the induction constant of the substituents to the reactivity of phosphites with respect to ozone was found.

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