

STRUCTURE, AND KINETICS OF THE THERMAL DECOMPOSITION OF ORGANIC PHOSPHITE OZONIDES[†]

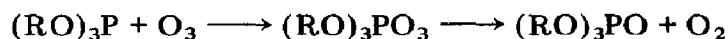
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Summary

Activation parameters for uncatalyzed loss of oxygen from phosphite ozonide solutions ($R \equiv$ alkyl or aryl)



were measured for a number of different phosphites in several solvents. Triphenyl phosphite ozonide in toluene, chlorobenzene and acetonitrile showed E_a (kcal mol⁻¹) = 19.4 - 20.1 and $\log A = 13.5 - 13.6$, where A is in reciprocal seconds, whereas in dichloromethane the rate constants were not very reproducible and depended on the precautions followed to exclude moisture from the ozonide preparations. Activation parameters for triphenyl phosphite ozonide in dichloromethane reported in the literature or derived from reported rate constants vary from $\log A = 8.1$ to $\log A = 11.9$ and from E_a (kcal mol⁻¹) = 14.4 to $E_a = 17.2$. Other phosphite ozonides show activation parameters which range approximately between the extremes given above for triphenyl phosphite ozonide, even in solvents other than dichloromethane. Possible reasons for these differences are discussed together with earlier theories to account for them. A molecular weight determination and the ³¹P nuclear magnetic resonance spectrum of trimethylolpropane phosphite ozonide are consistent with a monomeric non-equilibrating structure.

1. Introduction

The labile adducts of ozone and certain phosphites [1] are of interest (a) as sources for singlet (¹Δ_g) oxygen [2], (b) as singlet oxygenoid reagents capable of donating two oxygen atoms to substrates and (c) because of an unusual structure-stability relationship toward loss of oxygen in the absence of other reactants [3 - 6]. The catalyzed decomposition of phosphite

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ozonides can be induced with olefins [3, 5] or controlled with pyridine-methanol to give singlet oxygen at any desired temperature [4]. The uncatalyzed thermal decomposition, by contrast, shows puzzling features, as illustrated by the enormous difference between the two rather similar molecules, $(\text{CH}_3\text{CH}_2\text{O})_3\text{PO}_3$ (which decomposes above -100°C) and $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{O})_3\text{PO}_3$ (which decomposes above 0°C).

In this paper we present some kinetic and other evidence concerning this subject.

2. Experimental details

The phosphites were purchased or synthesized according to conventional literature procedures, and were distilled, crystallized or sublimed before use. Reagent grade solvents were redistilled from drying agents. The ozonides were prepared as described [3 - 6] and transferred with a cold dry syringe, or with reduced pressure through ground glass connections, to a nitrogen-flushed flask for measurement of oxygen evolution by manometry. The solutions were stirred magnetically and held to $\pm 0.1^\circ\text{C}$ in a cold bath or with a jacket containing circulating liquid. The rates of oxygen evolution generally showed first-order kinetics over 3 - 5 half-lives as long as the half-life was greater than about 3 min.

Freezing point depression (FPD) studies were carried out with around 60 ml of ozonide solution in redistilled 2,5-hexanedione (Aldrich), with a Beckmann thermometer purchased from Sargent-Welch (catalog number S-81155). Air was prevented from entering the solution with a slow stream of nitrogen delivered through a small copper tube which hung over the lip of the Dewar.

Two determinations on trimethylolpropane phosphite ozonide gave the data listed in Table 1. The nuclear magnetic resonance (NMR) spectra were recorded with a Bruker model WP-360 instrument.

TABLE 1

Results of two determinations on trimethylolpropane phosphite ozonide

Amount of phosphite (g)	0.8450	0.8381
Amount of solvent (g)	59.5	58.2
Freezing point (ozonide) ^a ($^\circ\text{C}$)	-2.51	-3.60
Freezing point (phosphate) ^a ($^\circ\text{C}$)	-2.53	-3.61
Freezing point (solvent) ^a ($^\circ\text{C}$)	-1.98	-3.11
Volume of O_2 at 21°C ^b (cm^3)	84 ± 1	75.5 ± 1.0

^a Relative readings in degrees Celsius $\pm 0.02^\circ\text{C}$ (two or three determinations). The freezing point of the pure solvent is about -5°C .

^b Corrected with a blank run under the same conditions.

3. Results and discussion

In Table 2 we summarize some activation parameters for oxygen evolution from phosphite ozonides from this study and previous studies. In five cases the pre-exponential factors are within an order of magnitude of the value from transition state theory with no entropy contribution, *i.e.* $\log(ekT/h) = 13.1$ at -10°C . (If the two O—O bonds in the ozonide are kinetically equivalent, then $\log A$ is calculated to be 13.4, where A is in reciprocal seconds.) The other cases show lower and variable values of both $\log A$ and E_a . This division also occurs with triphenyl phosphite ozonide and is associated specifically with the use of CH_2Cl_2 as the reaction medium. In our experience the rate constants with this solvent depended on the mode of preparation. (With special care ($(\text{PhO})_3\text{P}$ distilled from sodium at a pressure of less than 1 mmHg; solvents distilled from drying agents; MgClO_4 -dried reagent gases), transparent ozonide solutions in PhCH_3 or CH_2Cl_2 could be obtained at -78°C . Subsequent exposure of the solutions to moist air reduced the rates of O_2 evolution as much as sixfold in CH_2Cl_2 , but had no effect when PhCH_3 was the solvent.)

TABLE 2

Activation parameters for phosphite ozonide decompositions

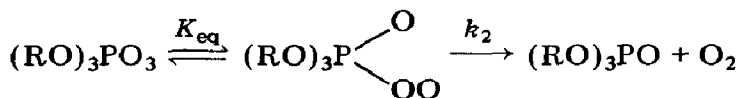
Phosphite ^a	Solvent	$\log A$	E_a (kcal mol ⁻¹)	Reference
1 $(\text{PhO})_3\text{P}$	PhCH_3	13.6 ± 0.7	20.1 ± 0.8	— ^b
2 $(\text{PhO})_3\text{P}$	PhCl	13.5 ± 0.4	19.6 ± 0.4	— ^b
3 $(\text{PhO})_3\text{P}$	CH_3CN	13.5 ± 0.4	19.4 ± 0.4	— ^b
4 $(\text{PhO})_3\text{P}$	CH_2Cl_2	9.4 ± 0.4	14.4 ± 0.5	[2]
5 $(\text{PhO})_3\text{P}$	CH_2Cl_2	$8.8 - 10.4$	12.9 ± 16	[7]
6 $(\text{PhO})_3\text{P}$	CH_2Cl_2	(11.9)	(17.15)	[8] ^c
7 $(\text{PhO})_3\text{P}$	CH_2Cl_2	8.1 ± 0.7	12.4 ± 0.8	[3]
8 $(\text{PhO})_2\text{POCH}_3$	CH_2Cl_2	12.3 ± 0.1	15.4 ± 0.1	[8]
9 $(o\text{-C}_6\text{H}_4\text{O}_2)\text{POPh}$	Acetone	5.0 ± 1.4	10.3 ± 1.8	— ^b
10 $(\text{CH}_2\text{O})_2\text{POPh}$	Acetone	13.5 ± 0.4	21.6 ± 0.5	— ^b
11 $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{O})_3\text{P}$	Acetone	(3.1)	(8.5)	— ^{b, c}

^a $(\text{PhO})_3\text{P}$, triphenyl phosphite; $(\text{PhO})_2\text{POCH}_3$, methyldiphenyl phosphite; $(o\text{-C}_6\text{H}_4\text{O}_2)\text{POPh}$, catechol phenyl phosphite; $(\text{CH}_2\text{O})_2\text{POPh}$, phenyl ethylene phosphite; $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{O})_3\text{P}$, trimethylolpropane phosphite.

^bThis work (for uniformity, activation parameters and errors were recalculated from others' data with our own computer program).

^cCalculated from rate constants at two temperatures.

Previous workers [8] invoked pseudorotation of an open-chain intermediate (II) in equilibrium with the parent ozonide (I) as a way to explain the structural dependence of the ozonide stabilities (in CH_2Cl_2) ($\text{R} \equiv$ alkyl or aryl):

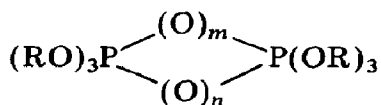


I II

It is difficult to reconcile this intermediate with kinetic evidence in related systems. For instance, if $\Delta H(\text{I} - \text{II})$ is as low as 2 kcal mol⁻¹ [9], then the equilibrium concentration of II will be large enough that the predominant mode of decay of II should be through bimolecular self-reaction, if radicals of the type (RO)₄POO· serve as a model [10]. (If intermediate II is a zwitterion [8], electrostatic attraction should also lead to rapid self-reaction in non-polar media.) It can be estimated that $\Delta H(\text{I} - \text{II})$ must be 5 kcal mol⁻¹ or more for this reaction not to be significant. Since $E_{\text{obs}} = \Delta H(\text{I} - \text{II}) + E_2$, the values of E_2 must then be less than about $E_{\text{obs}} - 5$, which is between 3 kcal mol⁻¹ (Table 2, case 11) and 17 kcal mol⁻¹ (Table 2, case 10).

Among first row elements the β -scission reaction of 1,4-biradicals is usually competitive with rotation and ring closure [11], also implying a very low value of E_2 . Similarly, the β -scission of 2-phenylethoxyl, which is *endothermic* by about 4 kcal mol⁻¹, has $E_a = 4.8$ kcal mol⁻¹ [12]. Since ΔH_2 is roughly 55 kcal mol⁻¹ *exothermic* [13], it is difficult to believe that E_2 is much higher than in these model systems, which then demands that $\Delta H(\text{I} - \text{II})$ is in the range of $E_{\text{obs}} - 4.8$, or 3 - 15 kcal mol⁻¹. In a two-step mechanism it is apparent that the relative energetics of scission of the open-chain intermediates cannot be the most significant contribution to the kinetic differences between phosphite ozonides.

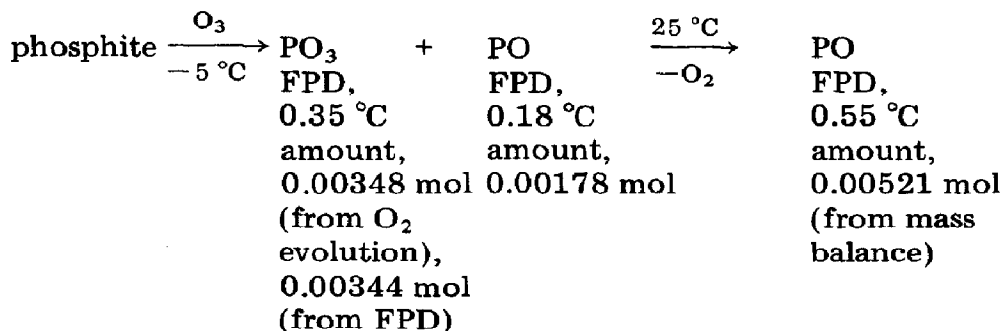
Since E_{obs} for the ozonides is comparable with or less than the estimated bond strength in alkyl trioxides [9], one of us proposed [3] that dimerization of II did occur, and the observed kinetics reflected loss of oxygen from a relatively strain-free oligomer (III):



III

Bartlett and Chu [3] concluded that triphenyl phosphite ozonide was monomeric from FPD measurements on concentrated solutions in CHCl₃. A possible explanation for the enormously different kinetic stabilities of the ozonides is then that the more stable ozonides, including the bicyclic phosphite ozonides, are dimeric (III; $m + n = 6$) and that the less stable ozonides, such as triphenyl phosphite ozonide, are monomeric. This explanation would be consistent with a more stable intermediate II derived from cyclic phosphites [8], which might dimerize at low temperature prior to giving phosphate and singlet oxygen on warming.

To test this hypothesis we prepared an ozonide solution from trimethylolpropane phosphite in hexane-2,5-dione, which showed an FPD of 0.55 °C. On standing at 25 °C, this relatively stable ozonide evolved 0.00348 mol of oxygen, and the resulting phosphate solution showed an FPD of 0.53 °C, corresponding to $K_f = 6.3$. The deficit of oxygen from the theoretical 0.00521 mol is assumed to be associated with the presence of alkyl phosphate together with ozonide in the original reaction mixture. From our K_f we estimate that 0.18 °C of the FPD of the ozonide solution was due to this phosphate. The remaining FPD (0.35 °C) must be due to 0.00344 mol of bicyclic phosphite ozonide:



This is in good agreement with the concentration calculated from the oxygen evolution under the assumption of a monomeric ozonide. Alternatively, the FPD and the mass of solute lead to a calculated molecular weight of 221 ± 23 , compared with an expected value of 210. The same conclusion resulted when the molalities were calculated from a K_f based on the FPD of a solution of naphthalene in 2,5-hexanedione.

Thus the ozonides from triphenyl phosphite and from the bicyclic phosphite are both monomeric, and the enormous differences in kinetic stability between them are not due to a difference in the size of the phosphite-ozone aggregate.

We were also unable to find evidence for open-chain or oligomeric structures with NMR techniques. A solution of triphenyl phosphite ozonide in CD₂Cl₂ was prepared and the ³¹P NMR spectrum recorded at -30 °C with a 360 MHz instrument. We observed only narrow singlets at -17.13 ppm and -62.16 ppm, corresponding to triphenyl phosphate and triphenyl phosphite ozonide respectively. The sample was removed from the spectrometer, cooled at -78 °C, and one equivalent of triphenyl phosphite was added. The sample was replaced in the NMR spectrometer and the spectrum recorded. The ozonide and phosphate were again observed at -17.20 and -62.21 ppm, and a new minor signal was observed at +126.5 ppm, corresponding to some unreacted triphenyl phosphite. In neither spectrum were other signals observed near -60 ppm. (The presence of III ($m = n = 2$) with a ³¹P resonance signal 1 ppm shifted from that of compound I has been suggested [1].)

The ^{31}P and ^{13}C spectra of the ozonide from trimethylolpropane phosphite ozonide were also recorded. The ^{31}P signal of the phosphite ozonide and phosphate decomposition product in CDCl_3 were centered at -42.39 ppm and -7.54 ppm respectively, and each showed splitting into septets by the six methylene hydrogen atoms (Fig. 1). The ozonide signals were only slightly broader than those of the phosphate, which can be ascribed to a slight non-equivalence of the protons due to the presence of the ozonide ring.

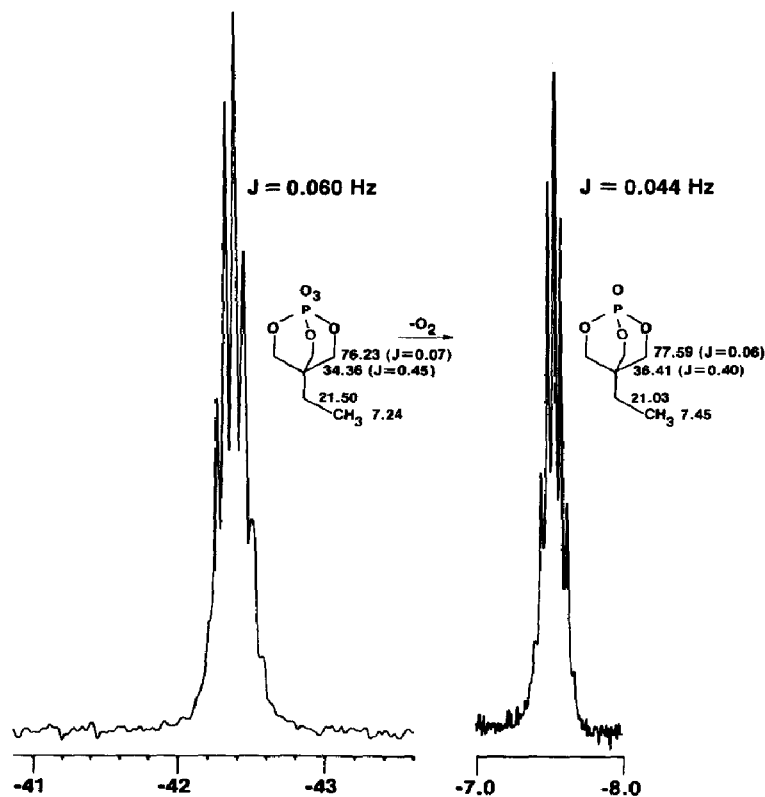


Fig. 1. ^{31}P NMR spectra relative to external H_3PO_4 , showing P-H splittings J . The ^{13}C NMR positions, relative to tetramethylsilane, were measured from a single CDCl_3 solution showing both species at -15°C .

The ^{13}C spectrum of the bicyclic phosphite ozonide in CDCl_3 displayed a triplet from solvent, and very narrow lines at the positions indicated on the structures in Fig. 1. The initial spectrum showed signals due to both phosphite ozonide and phosphate. The assignments were made by warming and re-recording the spectrum under the original conditions, in which the phosphate signals increased and the ozonide signals decreased. No unassigned signals were present in the spectrum. The resonances ascribed to the ring carbon are split into doublets by the ^{31}P , and the larger splitting appears in the more remote bridgehead atom. It is also noteworthy that the terminal

methyl carbon shows an easily resolved chemical shift between phosphite ozonide and phosphate, even though it is five atoms removed from the phosphorus atom!

The NMR and molecular weight determinations do not suggest the presence of any relatively stable ozone-phosphite compounds other than I at low temperature. On the basis of the foregoing evidence, we propose that in the five cases in Table 2 with high values of $\log A$, the ozonide decomposes by irreversible O—O bond scission to give a singlet biradical, which undergoes immediate β -scission to phosphate and singlet oxygen. This simple mechanism is consistent with production of singlet oxygen, the absence of solvent effect (cases 1 - 3) and consistent with only a small degree of reorganization of the molecule in the transition state as suggested by the values of $\log A$.

In the other cases, and particularly when the ozonide is expected to be inherently stable, we suggest that the above mechanism is overtaken or masked by a second, possibly induced, mode of decomposition. The participation of side reactions was particularly evident in the case of catechol phenyl phosphite ozonide (Table 2, case 9), since the ozonide solutions darkened during oxygen evolution and gave variable rate constants, even though apparent first-order kinetics always obtained. In most cases, however, the reaction mixtures remained colorless and gave reproducible results except in CH_2Cl_2 . Our experience with the latter solvent suggests a role of water or acid, although we have not investigated this point further.

The greater stability of ozonides from cyclic and bicyclic phosphites and the instability of ozonides from simple alkyl phosphites do correspond to the order of the relative base strengths of the phosphite precursors (e.g. trimethyl > methyl ethylene > $\text{P}(\text{OCH}_2)_3\text{CCH}_2\text{Br}$ [14]). The more electro-positive phosphorus in the cyclic case apparently results in a strengthening of the O—O bond of the ozonide, and in an elevated E_a for the simple scission reaction. (Consistent with this is a threefold decrease in the rate constant for O_2 evolution from tris(*p*-cyanophenyl) phosphite ozonide compared with the parent compound (acetone, -14°C .)

Analogous effects are present in bis(trifluoromethyl)trioxide, whose O—O bond strength is increased to an estimated 29 - 30 kcal mol^{-1} [15]. Another similarity is provided by a series of cyclic and bicyclic hydroxylamines with the structure $\text{R}_2\text{NO—H}$, in which the O—H bond strengths increase by 7 kcal mol^{-1} in progressing from a cyclic to a more constrained bicyclic compound with the nitrogen as the bridging atom [16].

4. Conclusions

The NMR spectra and molecular weights of two phosphite ozonides do not support dimerization or equilibrating structures as ways to account for differences in their thermal stabilities. The kinetic parameters for oxygen evolution from a series of ozonides suggest that at least two decomposition

mechanisms are operating. This feature makes it difficult to design a phosphite ozonide that would be stable to storage at ambient temperatures, since the effect of structural features of a particular phosphite on the rate of one pathway for ozonide decomposition may not be the same as for another.

Acknowledgments

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