Pergamon

Tetrahedron Letters, Vol. 38, No. 10, pp. 1711-1712, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00177-9

Catalysis of the Oxidation of Triphenylphosphine and of Trimethyl Phosphite by Hydrogen Peroxide in the Presence of Fe^{III} Compounds

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Abstract: The oxidation of triphenylphosphine to the corresponding oxide in pyridine is faster in the presence of Fe^{III} compounds, especially $FeCl_3$. Even greater effects are seen for the oxidation of trimethyl phosphite. © 1997 Elsevier Science Ltd. All rights reserved.

In the Fe^{III}-Fe^{V} manifold of Gif Chemistry, illustrated (without ligands) in Scheme 1, we have always proposed that the reaction of the Fe^{III} species with H_2O_2 is fast.[1,2] When simple ligands are used, as in $FeCl_3$, the catalase reaction is indeed very fast.[3] For this reaction we have presented evidence that H_2O_2 reacts with the Fe^{V}=O to furnish $Fe^{V}—O—O—H$ which collapses as indicated to Fe^{III} and O_2. The enzyme catalase also reacts very rapidly with H_2O_2.[3]

Scheme 1

In a recent paper, Talsi and his collaborators have shown by EPR and ^{1}H-NMR spectroscopy that similar reactions, with picolinic acid ligands, are also very fast.[4] We now wish to report another way in which the speed of the reaction of H_2O_2 with an Fe^{III} species can be evaluated.

It is well known that P^{III} species react rapidly with H_2O_2 to furnish the corresponding oxo-compounds and water. If one could demonstrate that Fe^{III} had a powerful catalytic effect on this reaction then it would be clear that the H_2O_2 had reacted with Fe^{III} to make an iron species which was a much faster oxidant of P^{III} than the hydrogen peroxide originally used.

In the Table we have summarized data on the rates of reaction of PPh_3 and $(MeO)_3P$ with H_2O_2 and the effect of 10% of an Fe^{III} catalyst. In the case of $(MeO)_3P$ there is very large rate difference using $FeCl_3$ and a number of other ligands including picolinic acid. In the case of PPh_3 there is a major rate difference also using $FeCl_3$. The other differences are also significant since only 0.1 mmol of catalyst was used.

We conclude that the rate of reaction of H_2O_2 with Fe^{III} using various ligands is 40 times or more faster than the reaction of H_2O_2 and PPh_3 without the catalyst. Hence, the rate of reaction of H_2O_2 with Fe^{III} in Gif-type Chemistry using the same ligands is not the rate limiting step. The effects are even greater with $(MeO)_3P$.

Table 1. Oxidation of PPh_3 and $(MeO)_3P$ with H_2O_2 in the presence or absence of Fe^{III} salts [a]

Entry	Reagents	Conditions	Half-life
1	$PPh_3 + H_2O_2$	---	4 min
2	$PPh_3 + H_2O_2$	$FeCl_3{\bullet}6H_2O$	< 10 sec
3	$PPh_3 + H_2O_2$	$Fe(acac)_3$	30 sec
4	$PPh_3 + H_2O_2$	$Fe(PA)_3$ [b]	50 sec
5	$PPh_3 + H_2O_2$	$Fe(NO_3)_3{\bullet}9H_2O$	1 min
6	$(MeO)_3P + H_2O_2$	---	75 min
7	$(MeO)_3P + H_2O_2$	$FeCl_3{\bullet}6H_2O$	< 10 sec
8	$(MeO)_3P + H_2O_2$	$Fe(acac)_3$	5 ~ 6 min
9	$(MeO)_3P + H_2O_2$	$Fe(PA)_3$ [b]	1 min
10	$(MeO)_3P + H_2O_2$	$Fe(NO_3)_3{\bullet}9H_2O$	9 min

a) All the experiments were carried out with Fe^{III} (0.1 mmol), PPh_3 or $(MeO)_3P$ (1 mmol) and H_2O_2 (1 mmol) in pyridine (3 mL) at -20 °C. b) PA = Picolinate.

EXPERIMENTAL

The experiments were carried out on a Varian 200 MHz NMR with a broadband probe. Typical instrumental parameters: Spectral width: 26000 Hz; Acquisition time: 0.58 sec; Pulse width: 10.0 μsec; Frequency: 81 MHz; Delay: 0 sec; Number of transients: 16.

In a typical experiment, triphenylphosphine (1 mmol, 262 mg) or trimethyl phosphite (1 mmol, 124 mg) and the Fe^{III} salts (0.1 mmol) were dissolved in pyridine (3 mL) in a 10 mm NMR tube. The NMR tube contained a sealed tube with $CD_3C_6D_5$ which was used to lock the NMR. The resulting solution was cooled to -20 °C and 30% H_2O_2 (1 mmol, 100 μL) was added. The tube was then immediately transferred to the NMR probe. The variation of $PPh_3/O{=}PPh_3$ or $(MeO)_3P/(MeO)_3P{=}O$ (ratio of peak intensities) was then plotted as a function of time and the half-lives of the reactions were thus determined.

ACKNOWLEDGMENTS

We thank Quest International, the Welch Foundation, the N.S.F. and the Schering-Plough Corporation for the support of this work.

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(*Received in USA* 2 *December* 1996; *accepted* 23 *January* 1997)