

LETTERS
TO THE EDITOR

Catalytic Oxidation of Triphenylphosphine
with Nitrogen(I) Oxide in the Presence
of Tetrakis(*tert*-butyl)phthalocyanine Complexes

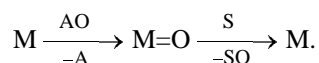
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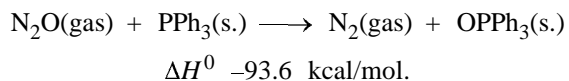
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It is known that the molecule of nitrogen(I) oxide is thermodynamically unstable with respect to its constituent elements (ΔG_f^0 24.9 kcal/mol, ΔH_f^0 19.6 kcal/mol). At the same time, the key reaction for the thermal decomposition of N_2O : $N_2O(\text{gas}) \rightarrow N_2(\text{gas}) + O(\text{gas})$ (3P) (ΔH^0 (39.7 kcal/mol), is highly endothermic and has a high activation energy. As a result, nitrogen(I) oxide demonstrates a significant kinetic inertness to decomposition up to 500°C [1].

Nevertheless, nitrogen(I) oxide attracts considerable interest as an ecologically pure and a potentially strong oxidative agent. Therefore, it seemed promising to make use of the ability of metal complexes to catalyze oxygen transfer from a donor, i.e., oxidant AO, to an acceptor, i.e., substrate S.



From thermodynamic calculations it follows that the oxidation of PPh_3 with nitrogen(I) oxide is highly exothermic [2].



However, only three works are available in the literature, where this reaction was performed under mild conditions: with low-valent nickel complexes [3], $[H_3Co(PPh_3)_3]$ [4], and pentacyanooxomolybdate $[PPh_4][Mo(CN)_5(O)]$ [5] as catalysts. According to our unpublished data, the reaction of N_2O with triphenylphosphine in the presence of 10 mol% of $[RhCl(PPh_3)_3]$, too, gives Ph_3PO . Atlay *et al.* [6] found that the peroxo complex $[RhCl(PPh_3)_3(O_2)]$ is responsible for the formation of triphenylphosphine oxide, when the starting rhodium compound reacts

with oxygen in benzene solution in the presence of excess Ph_3P . The mechanism of this process for N_2O is unknown. Finally, Groves and Roman [7] reported that in a nitrogen(I) oxide atmosphere $Ru(II)TMP \cdot (THF)_2$ rapidly converts to *trans*- $Ru(VI)TMP(O)_2$ (TMP is tetramesitylporphyrin) capable of oxidating dimethyl sulfide to sulfoxide and styrene to oxirane.

We chose as catalysts a series of 2,9,16,23-tetrakis(*tert*-butyl)phthalocyanine (**I**) complexes, including those with aluminum $\{I[Al(III)Cl]\}$, cobalt $\{I[Co(II)]\}$, copper $\{I[Cu(II)]\}$, magnesium $I[Mg(II)]$, and $AlCl$ applied on a basic alumina $\{I[AlCl/Al_2O_3]\}$. Triphenylphosphine was used as a model substrate.

Metal phthalocyanines **I** exhibit a considerable catalytic activity in various chemical processes, including oxidation [8]. Molecular oxygen, alkyl and acyl peroxides, amine *N*-oxides, hypochlorites, and iodosoarenes are most frequently used as oxo donors in the latter reactions.

All experiments were carried out by the following scheme: A solution of 0.02 mmol of phthalocyanine **I** and 2 mmol of a substrate in 10 ml of benzene was placed in a 80-ml autoclave filled with nitrogen(I) oxide. The bottom was cooled to condense about 5 ml of N_2O , after which the autoclave was hermetically closed and heated at 85°C for 6 h. The postreaction mixture, if necessary, was separated chromatographically (neutral Al_2O_3 , activity grade II).

With $I[Al(III)Cl]$ and $I[Cu(II)]$, the contents of triphenylphosphine were 8 and 15%, while those of triphenylphosphine oxide, 81 and 80%, respectively. With the other catalysts and with no catalysts, the contents of PPh_3 and $OPPh_3$ were near 40 and 50%, respectively. At 130°C, the only oxidation product was triphenylphosphine oxide (94% yield), even in the absence of phthalocyanine complexes.

Similar oxidative properties was reported by Saegura *et al.* [9], who under the similar conditions prepared cyclohexyl isocyanate from the corresponding isocyanide (130°C, 16 h, 20%) and triethyl phosphate from triethyl phosphite (80%). Poh *et al.* [10] oxidized a series of tertiary phosphines, using supercritical nitrogen(I) oxide (60–100°C, 100–140 atm) both as a reagent and as a solvent. Since with styrene instead of PPh₃ we found no oxygenated products, a conclusion was drawn that the basicity and (or) nucleophilicity of PPh₃ plays a noticeable role in the stage of oxo transfer from metal complex to substrate. Analogous dependence was, for example, noted by Reynolds *et al.* [11] in their kinetic study on the reduction of Mo(O)₂(S₂CNEt₂) in the series of tertiary phosphines Et_nPH_{n-3}P, where in going from $n = 0$ to $n = 3$ the reaction rate constant changed 7 times [9].

The studies on utility of N₂O as an oxidant in the presence of metal phthalocyanine complexes will be continued.

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