

Oxidation of triphenylphosphine and norbornene by nitrous oxide in the presence of Co^{II}LCl₂ [L = 3-phenyl-5-(2-pyridylmethylidene)-2-thiohydantoin]: the first example of Co^{II}-catalyzed alkene oxidation by N₂O

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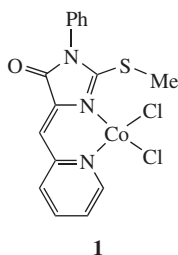
New catalytic oxidation reactions using N₂O as an oxidant and a CoCl₂ complex with 3-phenyl-5-(2-pyridylmethylidene)-2-thiohydantoin as a catalyst are described.

Nitrous oxide (N₂O) is a by-product of chemical processes involving nitric acid. The attractive option for N₂O is its use as an oxidant for organic compounds from the point of view of green chemistry, nitrous oxide would be preferable to many other oxidants because the only by-product is N₂. While nitrous oxide has to be a thermodynamically powerful oxidant, the oxidizing processes are surprisingly slow and well developed only under elevated temperatures.^{1,2} Thus, being in principle attractive either as an oxidant² or as potential 1,3-dipolarophile,² the scope and limitation of N₂O as the reagent in organic chemistry should be developed.

Obviously, the success of N₂O application depends on finding a proper catalyst, and we just will mention some of the attempts in this direction. Firstly, some small secondary alcohols and primary amines were oxidized by N₂O at room temperature in the presence of platinum black,³ which indicates the possibility of heterogeneous catalysis. Secondly, we point out the heterogeneous catalytic oxidation of benzene into phenol by N₂O.⁴

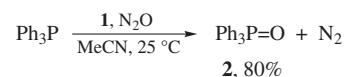
Third, although N₂O does react with several metal complexes, it is generally regarded as kinetically inert toward reduction and a 'poor' ligand.⁵ Despite the intense current interest in transition metal-mediated N₂O activation, a little metal complexes containing the N₂O ligand with Ru⁶ and Fe⁷ have been identified. Catalytic metal-mediated reactions of N₂O have been found.^{8–11}

Recently, we have reported the syntheses of a Co^{II} complex with 3-phenyl-5-(2-pyridylmethylidene)-2-thiohydantoin **1** ligand.¹² This complex demonstrated a capability to react reversibly with molecular oxygen¹³ and to catalyze alkene epoxidation by PhIO and H₂O₂.¹⁴

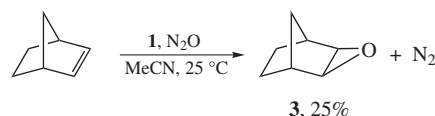


Here, we describe the use of complex **1** for activation of nitrous oxide in oxidation reactions with triphenylphosphine and norbornene.[†]

We have found that, if N₂O is bubbled to a solution of **1** and Ph₃P at room temperature, catalytic oxidation to O=PPh₃ **2** takes place.



Norbornene reacts with nitrous oxide in the presence of complex **1** at room temperature to form 3-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene **3** in 25% yield.



Almost equal yields of **3** were obtained at room temperature in an autoclave or by bubbling N₂O. The N₂ by-product is assumed but not experimentally confirmed.

The interaction of complex **1** with N₂O was studied by cyclic voltammetry.[‡] The electrochemical behaviour of **1** in water (Figure 1) and as a **1**/hexadecyltrimethylammonium bromide (hdab) film (Figure 2) in the absence and presence of N₂O was studied.

† Oxidation reactions.

1. Bubbling. In the two-necked flask equipped with the gas supply pipe and condenser either triphenylphosphine (0.55 g, 2.1 mmol) or norbornene (0.2 g, 2.1 mmol) and 0.01 g (0.023 mmol) of the catalyst were placed. Freshly distilled acetonitrile (10 ml) was added to the mixture and N₂O (medical quality; from Criogen, <http://criogen-firma.ru/>) was bubbled during 10 h. The mixture was passed through the SiO₂ column using methylene chloride as an eluent. After the evaporation of the solvent, the mixture was analyzed by ¹H and ³¹P NMR spectroscopy. The reaction with norbornene was also realized at 80 °C, but only trace amount of **2** was obtained.

2. Autoclave. A stir bar, substrate, catalyst and 10 ml of acetonitrile were placed in a 150 ml stainless steel vessel under argon. The vessel was putted in to the cooling bath (–100 °C, liquid nitrogen–sand) and ~ 5 ml of nitrous oxide was condensed. The vessel was closed and heated to the room temperature. After 3 h of shaking, it was opened and the mixture was passed through the SiO₂ column using methylene chloride as an eluent. After the evaporation of the solvent, the mixture was analyzed by ¹H and ³¹P NMR spectroscopy. Triphenylphosphine oxide **2** and 3-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene **3** were identified based on ¹H, ³¹P NMR and GLC data.

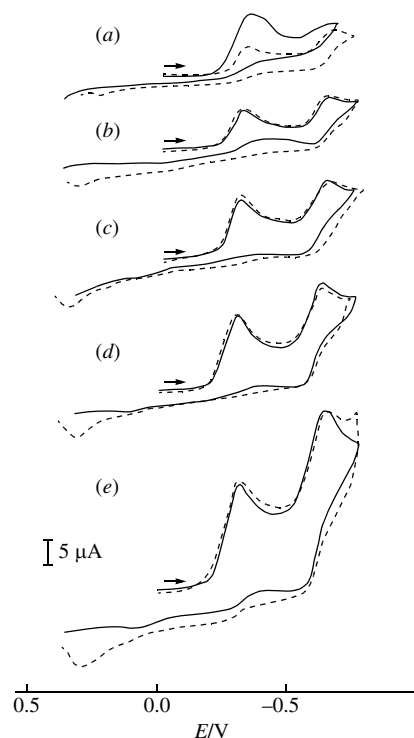


Figure 1 Cyclic voltammograms of complex **1** in MeCN solution (GC electrode, Bu_4NBF_4): in the presence of N_2O (solid line) or without N_2O (dotted line). Scan rate: (a) 20; (b) 50; (c) 100; (d) 200 and (e) 500 mV s^{-1} .

It is known that electrochemical reduction of N_2O occurs only at very negative potentials.¹⁵ In both experiments (in the solution and in the layer of hdab), the voltammetric response of **1**/hdab in the presence of N_2O and without it was the same at scan rates of 500, 200, 100 and 50 mV s^{-1} . But at slow scan rate (20 mV s^{-1}) the potential of first oxidation peak in the presence of N_2O shifts by 0.07 mV to less negative potential, whereas the potential of second oxidation peak shifts by 0.05 mV to more negative potential [Figure 1(a)]. These facts confirm the interaction of both initial and reduced forms of complex **1** with N_2O .

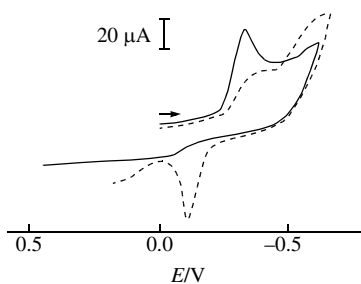


Figure 2 Cyclic voltammogram of complex **1** in hdab film (GC electrode, H_2O , LiClO_4): in the presence of N_2O (solid line) or without N_2O (dotted line). Scan rate, 20 mV s^{-1} .

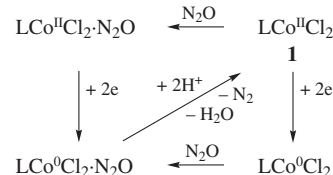
‡ *Electrochemical studies* were carried out on a PI-50-1.1 potentiostat in MeCN or H_2O . Glassy-carbon (2 mm in diameter in MeCN; 4 mm in diameter in H_2O) disks polished by Al_2O_3 (< 10 μm) were used as working electrodes; a 0.05 M Bu_4NClO_4 solution in MeCN or 0.1 M LiClO_4 solution in H_2O served as the supporting electrolyte; $\text{Ag}/\text{AgCl}/\text{KCl}$ (sat.) was used as the reference electrode. All measurements were carried out under argon; the samples were dissolved in the pre-deaerated solvent. N_2O was bubbled through the aqueous solution, and the positive pressure of N_2O was maintained in an electrochemical cell during experiment.

1/hdab film preparation. The solutions of hdab (0.1 mol dm^{-3} , 10 μl) and **1** (10^{-4} mol dm^{-3} , 10 μl) in MeCN were cast onto the surface of basal-plane-oriented GC electrode. The **1**/hdab-modified electrode was allowed to stand overnight in a close vessel and then dried in open air for at least 12 h, then in the Ar stream for 10 min.

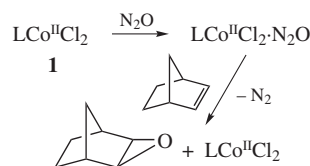
At one time the increasing of the first wave current and the decreasing of next waves currents were observed. The current increasing is consistent with an electrocatalytic process at the potential of the $\text{Co}^{\text{II}}/\text{Co}^0$ redox couple. Apparently, the dependence of voltammetric response on the scan rate is determined by the ratio of the rates of two processes: (1) coordination of the reduced form of **1** (Co^0 intermediate complex) with N_2O , and (2) further reduction of this Co^0 intermediate complex to metal Co^0 . Obviously, an intermediate complex formed at the first stage of the reduction is not 'caught' by a coordination with N_2O when the scan rates are too high (> 20 mV s^{-1}) and undergoes further reduction [Figure 1(a)]. But if the scan rate is relatively low (≤ 20 mV s^{-1}), the intermediate coordinates with N_2O yielding new complex $\text{LCo}^0\text{Cl}_2\cdot\text{N}_2\text{O}$, which further forms Co^{II} complex as a result of intramolecular redox process with a deliberation of N_2 thus finishing a catalytic cycle. Only a small part of primarily formed Co^0 intermediate undergoes further reduction resulting in decrease of posterior peaks intensity [Figure 1(b)–(e)].

The presumable mechanisms of the N_2O interactions with **1** in an electrochemical cell both in the presence and absence of alkene are shown in Scheme 1. Two parallel processes take place in the electrochemical cell: (a) the initial reduction of complex **1** followed by complexation with N_2O to 1^{2-} and regeneration of **1** accompanying by N_2 deliberation and (b) complexation of **1** with N_2O at first followed by reduction of N_2O -containing complex with N_2 evolution. The source of H^+ for the formation of H_2O probably is the solvent (water); so, the whole reaction is electrochemically catalyzed reduction of N_2O . In the case of chemical reactions, norbornene (Scheme 1) or PPh_3 acts as the electron donor and the reaction products are oxygen-containing compounds (**2** or **3**) and N_2O .

In electrochemical cell:



In the reaction (on norbornene example):



Scheme 1

In conclusion, complex **1** is capable of catalyzing norbornene and Ph_3P oxidation by nitrous oxide under ambient conditions. To our knowledge, it is the first example of such catalyzed alkene oxidation by N_2O .

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