The Interaction of Phosphine Complexes of Nickel(0) with Benzoyl Peroxide, New Carboxylate Complexes of Nickel with Phosphine Ligands

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Abstract

The interaction of benzoyl peroxide with nickel(0) complexes containing different tertiary phosphines has been studied. It has been shown that under the action of the nickel(0) complexes and independent of the nature of the tertiary phosphine the cleavage of either the O–O or C–O of benzoyl peroxide occurs. In the case of the triphenylphosphine complexes of nickel(0) the main reaction products are $Ni(CO)(PPh_3)_3$ and $Ni(OCOPh)_2$. In the reaction of benzoyl peroxide with $Ni(PEt_3)_4$ the only reaction product is $Ni(OCOPh)_2(PEt_3)_2$. In the reaction of the mixture of $Ni(cod)_2$ and PCy_3 with benzoyl peroxide the formation of the carboxylate complexes $Ni(OCOPh)_2(PCy_3)_2$ or $Ni(OCOPh)_2PCy_3$ has been mainly observed. In addition, the synthesis of the carboxylate complex $Ni(OCOPh)_2(PEt_3)_2$ directly from $Ni(OCOPh)_2$ and tertiary phosphine has been carried out.

Introduction

The problem of the reaction of organometallic compounds of transition metals with organic peroxides has been repeatedly discussed in the literature [1]. Such reactions with acyl peroxides were formerly employed for the synthesis of carboxylate complexes of Fe, Ti, V, Mo, Co and Ir [2–5]. It was recently shown that the phosphine complexes of Pd(0) and Pt(0) promote the cleavage of the O–O bond of benzoyl peroxide [5, 6]. In this case the compounds of the type $M(OCOPh)_2(PPh_3)_2$ (M = Pt, Pt) formed in high yield.

The present work deals with the study of the reaction of the phosphine complexes of nickel(0) with benzoyl peroxide*. The study reported in ref. 8 briefly refers to the reaction of $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$ with benzoyl peroxide.

*For the preliminary communication see ref. 7.

Results and Discussion

The treatment of a suspension of tris(triphenylphosphine)nickel in ether with benzoyl peroxide at a reduced temperature (−50 °C) with a subsequent temperature increase up to room temperature is accompanied by a change in colour of the reaction mixture from brown to yellow and the formation of a light green precipitate. The reaction is accompanied by evolution of gaseous products which according to GLC data consist of oxygen and CO_2 traces. On the basis of the data of the elemental analysis and IR spectra it has been found that the precipitate formed represents $Ni(OCOPh)_2$, its yield being 15%. We have succeeded in isolating from the mother solution the carbonylphosphine complex $Ni(CO)(PPh_3)_3$ and triphenylphosphine, the yields being 44 and 17%, respectively.

$$Ni(PPh_3)_3 + (PhCOO)_2 \longrightarrow Ni(OCOPh)_2 + Ni(CO)(PPh_3)_3 + PPh_3 + O_2 \quad (1)$$

The chromato-mass-spectrometric analysis of the reaction mixture remaining after the isolation of $Ni(OCOPh)_2$ and $Ni(CO)(PPh_3)_3$ indicated that it contained benzoic acid (122 M^+), diphenyl (154 M^+) benzoic acid anhydride (226 M^+), triphenylphosphine (262 M^+) and triphenylphosphine oxide (278 M^+).

The increase in the time of reaction (1) results in a decrease in the yield of the carbonyl complex of nickel. Thus, if the reaction of $Ni(PPh_3)_3$ with benzoyl peroxide is carried out for 20 h, the yield of $Ni(CO)(PPh_3)_3$ decreases threefold.

The reaction of benzoyl peroxide with another complex of nickel(0), $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$, proceeds in a similar manner giving rise to $Ni(OCOPh)_2$, $Ni(CO)(PPh_3)_3$ and PPh_3 with evolution of oxygen and ethylene. It should be noted that Schott and Wilke isolated only $Ni(OCOPh)_2$ from the products of this reaction [8].

To explain the results obtained we have made an assumption about two possible ways of the cleavage of benzoyl peroxide under the action of triphenylphosphine nickel complexes (Scheme 1). The

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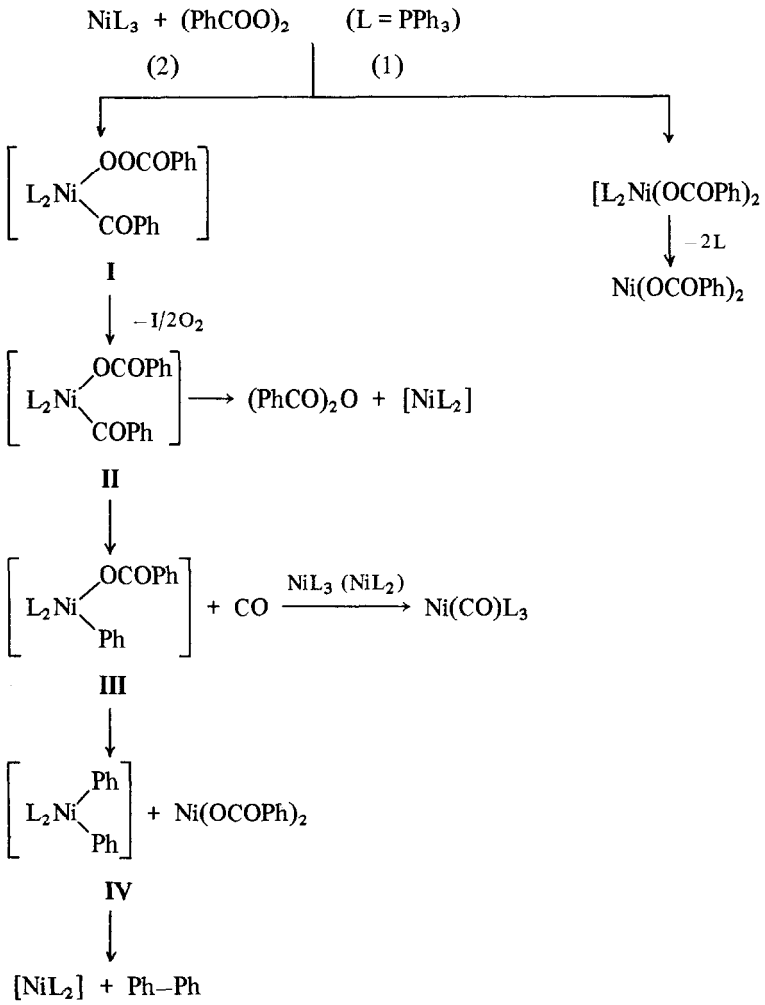

Scheme 1.

first one involves the cleavage of the peroxide O–O bond with the formation of the unstable $[L_2Ni(OCOPh)_2]$ which is then transformed into $Ni(OCOPh)_2$.

This direction of reaction is similar to the interaction of the triphenylphosphine complexes of Pd(0) and Pt(0) with benzoyl peroxide [5, 6].

The second path consists in the cleavage of the C–O bond of benzoyl peroxide with the formation of the peracyl compound (**I**) which decomposes with the evolution of O_2, producing a labile acyl derivative of nickel (**II**). This kind of behaviour is typical for the earlier described peracyl compounds of Sn, Pb, Si, Ge [9].

The likewise unstable compound **II** arising in the decomposition of **I** undergoes decarbonylation, yielding **III**, similarly to other known acyl complexes of nickel [10]. Carbon oxide evolved in this case is easily trapped, but not only by the nickel(0) complexes (NiL_2 or NiL_3). It is capable of reacting with such reactive compounds as **II** and **III**, yielding $Ni(CO)(PPh_3)_3$; besides, the compound **II** may decompose with the formation of NiL_2 and $(PhCO)_2O$. In its turn, the σ-phenyl compound **III** undergoes disproportionation yielding $Ni(OCOPh)_2$ and the diphenyl derivative of nickel (**IV**). The latter, possibly, decomposes with the formation of NiL_2 and diphenyl.

Benzoic acid detected in the reaction mixture appears to be formed as a result of the splitting of the hydrogen atom from the solvent by the $PhCOO^{\bullet}$ radical [11].

A certain similarity with such an unusual nonsymmetric cleavage of the C–O bond in benzoyl peroxide can be also found in the reactions of the nickel(0) complexes with carboxylic acid esters involving the cleavage of the $R'C(O)\text{-}OR$ bond ($R' = Et$, $R = Ph$, C_6H_4Me-*p*, C_6H_4OMe-*p*; $R' = Me$, $R = Ph$) and formation of $Ni(CO)(PPh_3)_3$ [12].

Different results were obtained in studying the reaction of benzoyl peroxide with the nickel(0) complexes stabilized by triethyl- and tricyclohexyl-

phosphines possessing stronger electron-donor properties as compared to triphenylphosphine.

It has been established that the reaction between $Ni(PEt_3)_4$ and benzoyl peroxide occurs intensively already at −65 °C and leads to the formation of $Ni(OCOPh)_2(PEt_3)_2$ (yield 78%).

$$Ni(PEt_3)_4 + PhCOO\text{–}OOCPh \longrightarrow Ni(OCOPh)_2(PEt_3)_2 + 2PEt_3 \quad (2)$$

The structure of the carboxylate complex $Ni(OCOPh)_2(PEt_3)_2$ obtained for the first time has been considered on the basis of the data of the elemental analysis and IR spectrum, the latter containing absorption bands typical for the carboxylate group [13] in the region 1600–1570 cm^{-1} (ν_{as}) and 1365 cm^{-1} (ν_s).

It is noteworthy that in reaction (2) the carbonylphosphine complexes of nickel are not formed and $Ni(OCOPh)_2(PEt_3)_2$ is the only reaction product. This is evidenced by the IR spectrum of the reaction mixture, which shows no absorption bands in the metal-carbonyl region. Consequently, $Ni(PEt_3)_4$ in contrast to $Ni(PPh_3)_3$ promotes only the cleavage of the O–O bond, but not of the C–O bond of benzoyl peroxide.

The complex $Ni(OCOPh)_2(PEt_3)_2$ is very sensitive towards the action of atmospheric oxygen, and also to that of organic solvents. In this case it loses one PEt_3 molecule and is irreversibly transformed into a green-coloured complex practically insoluble in organic solvents and corresponding, according to elemental analysis data, to the formula $Ni(OCOPh)_2PEt_3$. The presence of carboxylate groups in this compound has been established on the basis of data of the IR spectrum containing absorption bands ν_{as}(OCO) in the 1630–1575 cm^{-1} region and ν_s(OCO) at 1400 cm^{-1}.

When studying the interaction of benzoyl peroxide with the nickel(0) complexes containing PCy_3 it was found that the reaction of the mixture of bis(cyclooctadiene-1,5)nickel and PCy_3 (1:3) with benzoyl peroxide takes place only at room temperature. In this case the carboxylate complex $Ni(OCOPh)_2(PCy_3)_2$ is formed in a 65% yield.

$$Ni(cod)_2 + 2PCy_3 + (PhCOO)_2 \longrightarrow Ni(OCOPh)_2(PCy_3)_2 + 2cod \quad (3)$$

cod = cyclooctadiene-1,5

The use of rigorously stoichiometric quantities of reagents in reaction (3) leads to a decrease of the yield of $Ni(OCOPh)_2(PCy_3)_2$ down to 23% and to the formation of $Ni(OCOPh)_2$ in a 36% yield.

In both cases we have detected in the reaction mixture and characterized by IR spectral data, ν(CO) 1980 and 1920 cm^{-1} [14], the carbonyl phosphine complex $Ni(CO)_2(PCy_3)_2$ which could not be isolated in an individual state.

The new complex $Ni(OCOPh)_2(PCy_3)_2$ is oxidatively stable in the solid state and decomposes in solution. The $^{31}P\{^1H\}$ NMR spectrum of this compound, recorded in toluene, contains one singlet signal at 11.58 ppm indicating the equivalence of the phosphorus atoms. The IR spectrum of $Ni(OCOPh)_2(PCy_3)_2$ shows absorption bands ν_{as}(OCO) in the 1625–1575 cm^{-1} range and ν_s(OCO) at 1360 cm^{-1}, similar to the absorption bands of $Ni(OCOPh)_2(PEt_3)_2$.

With a further decrease in the quantity of PCy_3 in reaction (3) and the equimolar ratio of the reagents $Ni(cod)_2$ to PCy_3 the formation of a new carboxylate complex $Ni(OCOPh)_2PCy_3$ (yield 49%) occurs

$$Ni(cod)_2 + PCy_3 + (PhCOO)_2 \longrightarrow Ni(OCOPh)_2PCy_3 + 2cod \quad (4)$$

According to the data of the IR and ^{31}P NMR spectra the reaction mixture contains neither $Ni(OCOPh)_2(PCy_3)_2$ nor $Ni(CO)_2(PCy_3)_2$.

$Ni(OCOPh)_2PCy_3$ obtained, similarly to $Ni(OCOPh)_2(PCy_3)_2$, is stable to atmospheric oxygen. When dissolved in ether, benzene and acetone, it produces green solutions which soon form jelly-like precipitates. The IR spectrum of $Ni(OCOPh)_2PCy_3$ shows the bands ν_{as}(OCO) in the 1630–1580 cm^{-1} range and ν_s(OCO) at 1410 cm^{-1} which do not coincide with the corresponding bands in the spectrum of $Ni(OCOPh)_2(PCy_3)_2$.

In contrast to $Ni(OCOPh)_2$, in the spectrum of $Ni(OCOPh)_2PCy_3$ there are observed the bands ν(CH) 2970 and 2870 cm^{-1} related to the vibrations of the PCy_3 ligand. Thus, the study of the reaction of benzoyl peroxide with the nickel(0) complexes containing different tertiary phosphines indicates that in the case of PEt_3 and PCy_3 the main direction of these reactions involves the cleavage of the O–O bond of benzoyl peroxide with the formation of carboxylate nickel complexes. At the same time, in the case of the nickel complexes with PCy_3 there is also observed, although to a significantly smaller degree, the cleavage of the C–O bond of the peroxide reagent and the formation of the carbonyl compound $Ni(CO)_2(PCy_3)_2$. This second reaction path becomes the main one in the interaction of the triphenylphosphine complexes of nickel with benzoyl peroxide.

We have also studied the possibility of the synthesis of the carboxylate complexes $Ni(OCOPh)_2(PR_3)_n$ (n = 1,2) directly from nickel benzoate and tertiary phosphine. In this case it was found that the reaction of $Ni(OCOPh)_2$ with an excess of PEt_3 in benzene at room temperature gives rise to $Ni(OCOPh)_2(PEt_3)_2$ (43% yield)

$$Ni(OCOPh)_2 + 2PEt_3 \longrightarrow Ni(OCOPh)_2(PEt_3)_2 \quad (5)$$

If PCy_3 is used in place of PEt_3 for reaction (5), the complex $Ni(OCOPh)_2(PCy_3)_2$ is not formed.

The variation of the reaction conditions: a temperature increase, a substitution of ether for benzene does not lead to the formation of $Ni(OCOPh)_2(PCy_3)_2$. A similar negative result was obtained in using triphenylphosphine in the reaction with $Ni(OCOPh)_2$.

Experimental

The $^{31}P\{^1H\}$ NMR spectra were recorded with a Bruker WP-200 SY spectrometer (81.01 MHz), with the external standard 85% H_3PO_4.

The IR spectra were recorded on a UR-20 spectrometer as KBr tablets.

The GLC analysis of the gases was performed on a LHM-80 chromatograph equipped with a catarometer, using a 300 X 0.3 cm column filled with molecular sieves 5 Å at 20 °C, and helium as carrier gas.

The reaction mixture of reaction (1) was analysed on a Varian MAT-311A chromato-mass-spectrometer at the ionizing voltage 70 eV (a 2500 X 0.02 cm column with 5% SE-30; 150–250 °C; helium as carrier gas). The compounds $Ni(OCOPh)_2$, $Ni(cod)_2$, $Ni(PEt_3)_4$, $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$, $Ni(PPh_3)_3$ were synthesized as described in refs. 15–19; PEt_3 and PCy_3 were obtained according to refs. 20 and 21.

All experiments in the synthesis and isolation of nickel complexes were carried out under an argon atmosphere in absolute solvents distilled under argon directly prior to use.

Reactions of the Triphenylphosphine Complexes of Nickel(0) with Benzoyl Peroxide

(a) A solution of $(PhCOO)_2$ (2.87 g, 11.83 mmol) in 50 ml of ether was added to the suspension of $Ni(PPh_3)_3$ (7.53 g, 8.90 mmol) in 100 ml of ether at −50 °C. The reaction was stirred for 1 h at 22 °C. In this case there were observed the dissolution of the initial substances, the formation of a light green precipitate and the evolution of gaseous products. According to GLC data 15 ml of oxygen and trace amounts of CO_2 were evolved. The precipitate was filtered, washed with benzene and ether and dried in vacuum at 110 °C. On account of hydroscopicity the substance was isolated in the form of the crystallohydrate, 0.43 g (15%) of $Ni(OCOPh)_2 \cdot H_2O$ was obtained. IR spectrum: $\nu_{as}(OCO)$ in the 1600–1560 cm^{-1} range and $\nu_s(OCO)$ at 1400 cm^{-1} [15].

The mother solution was evaporated to minimal volume, 15 ml of CH_3OH was added, the resulting precipitate was filtered and dried in vacuum; 3.42 g (44%) of $Ni(CO)(PPh_3)_3$ was obtained, melting point (m.p.) 179–180 °C (acetone). IR spectrum: $\nu(C{\equiv}O)$ 1928 cm^{-1} [22]. $^{31}P\{^1H\}$ NMR spectrum (toluene, δ ppm): 31.76. After the evaporation of the methanol solution the resinous residue was recrystallized from ethanol; 1.21 g (17%) of PPh_3 was obtained, m.p. 76–78 °C [23].

(b) Following method (a), from $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$ (3.29 g, 5.40 mmol) and $(PhCOO)_2$ (1.74 g, 7.18 mmol), 0.36 g (21%) of $Ni(OCOPh)_2 \cdot H_2O$, 1.50 g (32%) of $Ni(CO)(PPh_3)_3$ and 0.47 g (33%) of PPh_3 were obtained.

(c) Following method (a), from $Ni(cod)_2$ (0.85 g, 3.10 mmol), PPh_3 (1.60 g, 6.20 mmol) and $(PhCOO)_2$ (0.82 g, 4.12 mmol), 0.19 g (19%) of $Ni(OCOPh)_2 \cdot H_2O$, 0.60 g (22%) of $Ni(CO)(PPh_3)_3$ and 0.56 g (34%) of PPh_3 were obtained.

$Ni(OCOPh)_2(PEt_3)_2$

(a) A suspension of $(PhCOO)_2$ (1.00 g, 1.10 mmol) in 10 ml of ether was added to the suspension of $Ni(PEt_3)_4$ (1.67 g, 3.15 mmol) in 5 ml of ether at −78 °C. The reaction mixture was stirred for 0.5 h at −65 °C and for 20 min at 22 °C. The orange precipitate was filtered and dried in vacuum; 1.30 g (78%) of $Ni(OCOPh)_2(PEt_3)_2$ was obtained, m.p. 83–85 °C (dec.). *Anal.* Found: C, 58.21; H, 7.53; P, 11.70. Calc. for $C_{26}H_{40}NiO_4P_2$: C, 58.15; H, 7.51; P, 11.53%.

(b) Three ml of PEt_3 (2.40 g, 19.80 mmol) were added to the suspension of $Ni(OCOPh)_2$ (2.00 g, 6.60 mmol) in 30 ml of benzene. The reaction mixture was stirred for 2 h at 22 °C. Then it was filtered through a paper filter and evaporated to minimal volume. The resulting orange substance was filtered, washed with a small amount of benzene and dried in vacuum; 1.52 g (43%) of $Ni(OCOPh)_2(PEt_3)_2$ was obtained, m.p. 86–88 °C (dec.).

$Ni(OCOPh)_2PEt_3$

The complex $Ni(OCOPh)_2(PEt_3)_2$ (0.54 g, 1.00 mmol) was treated with 10 ml of benzene. After an hour the isolated green precipitate was filtered, washed with benzene and dried in vacuum; 0.47 g (87%) $Ni(OCOPh)_2PEt_3$ was obtained, m.p. 194–198 °C. *Anal.* Found: C, 57.48; H, 6.02; P, 7.07. Calc. for $C_{20}H_{25}NiO_4P$: C, 57.32; H, 6.01; P, 7.39%.

Reactions of $Ni(cod)_2$ with Benzoyl Peroxide in the Presence of PCy_3

(a) With a 1:3 ratio of $Ni(cod)_2$ to PCy_3

A suspension of $(PhCOO)_2$ (1.36 g, 4.88 mmol) in 20 ml of ether was added to a suspension of $Ni(cod)_2$ (1.01 g, 3.68 mmol) and PCy_3 (3.08 g, 11.03 mmol) in 20 ml of ether at −78 °C. The reaction mixture was stirred for 2 h at 22 °C. The yellow range precipitate was filtered, washed with ether and dried in vacuum; 2.0 g (65.3%) of $Ni(OCOPh)_2(PCy_3)_2$ was obtained, m.p. 125–128 °C (dec.). *Anal.* Found: C, 70.11; H, 9.19; P, 7.17. Calc. for $C_{50}H_{71}NiO_4P_2$: C, 70.25; H, 8.90; P, 7.19%.

(b) With a 1:2 ratio $Ni(cod)_2$ to PCy_3

In a similar way to (a), using $Ni(cod)_2$ (1.63 g, 5.93 mmol), PCy_3 (3.33 g, 11.86 mmol) and (Ph-

$COO)_2$ (1.85 g, 7.65 mmol), 1.16 g (23%) of Ni-$(OCOPh)_2(PCy_3)_2$, m.p. 126–128 °C (ether) was obtained. After the evaporation of the reaction mother solution and treatment of the residue with 10 ml of CH_3OH a green crystalline substance precipitated which was filtered, washed with CH_3OH and dried in vacuum; 0.64 g (36%) of $Ni(OCOPh)_2$ was obtained. IR spectrum: $\nu_{as}(OCO)$ in the 1600–1560 cm^{-1} range and $\nu_s(OCO)$ at 1400 cm^{-1} [15].

(c) With a 1:1 ratio of $Ni(cod)_2$ to PCy_3

A suspension of $(PhCOO)_2$ (1.41 g, 5.80 mmol) in 20 ml of ether was added to a suspension of $Ni(cod)_2$ (1.23 g, 4.50 mmol) and PCy_3 (1.25 g, 4.50 mmol) in 30 ml of ether at −78 °C. After stirring for 2 h at 22 °C the resulting yellow–green precipitate was filtered, washed many times with ether and dried in vacuum, 1.28 g (49%) of Ni-$(OCOPh)_2PCy_3$ was obtained, m.p. 225–227 °C (dec.). *Anal.* Found: C, 63.92; H, 7.33; P, 5.19. Calc. for $C_{32}H_{43}NiO_4P$: C, 66.20; H, 7.46; P. 5.33%.

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