# REACTIONS OF TRANSITION METAL PEROXIDES WITH n-BUTYLLITHIUM

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SUMMARY

The ease with which lithium n-butoxide is formed on reaction of n-butyllithium with several peroxy metal compounds decreases in the order $MoO(O_2)_2 \cdot HMPA$, $CrO(O_2)_2 \cdot Py > (Ph_3P)_3PtO_2$, $(Ph_3P)_2Ir(CO)(O_2)I \gg Na_2O_2$. Isotopic labeling experiments confirm that the "peroxy" oxygen atoms are those incorporated into lithium n-butoxide from $Mo^{18}O(O_2)_2 \cdot HMPA$. Reaction of $(Ph_3P)_2PtO_2$ with n-butyllithium at low temperature yields $(Ph_3P)_2PtBu_2$; no lithium n-butoxide is formed. The peroxide ion is apparently displaced during this reaction by nucleophilic attack at the platinum atom by n-butyllithium. These observations provide further evidence indicating that the electrophilicity of the peroxy oxygen atoms of $d^8$ and $d^{10}$ transition metal–oxygen complexes is much lower than that of the peroxymolybdenum(VI) and -chromium(VI) reagents.

## INTRODUCTION

The reactions between olefins and hydrocarbons and complexes of molecular oxygen with $d^8$ and $d^{10}$ transition metals have been extensively studied, in the expectation that they might provide the basis for homogeneous, non-radical, oxidation processes. This expectation has not been realized: although a limited number of interesting oxidation reactions catalyzed by rhodium(I) and iridium(I) have been discovered, all appear to involve the generation and consumption of intermediate organic peroxides by radical chain processes[1,2]. A requirement for high reactivity of a peroxydic species toward typical olefins is an electrophilic oxygen center. While peracids[3] and molybdenum(VI)[4] and related[5] $d^0$-transition metal peroxy compounds epoxidize olefins rapidly, peroxide ion, superoxide ion, and $d^6$- and $d^8$-metal peroxides are unreactive towards olefins and similar, potentially reducing, organic species. In fact, the chemical reactivity of the oxygen moiety of these transition metal–oxygen complexes in many ways resembles that of nucleophilic peroxide ions more closely than that of electrophilic peracids[6].

In connection with a study of the mechanism of the reaction between organo-

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lithium reagents and molecular oxygen', we briefly examined the reaction of n-butyllithium with several metal peroxides. The intention of this work was to compare the reactivity of n-butyllithium, a strong organic reducing agent, toward $d^8$-, $d^6$, and $d^0$-transition metal peroxy compounds, and toward peroxide ion, in order to estimate qualitatively the susceptibility of the peroxy moiety in these complexes toward nucleophilic attack. The reaction of n-butyllithium with molecular oxygen is known to proceed rapidly at $-78°$ to form lithium n-butoxide, presumably by way of intermediate n-butyllithium hydroperoxide. The oxygen–oxygen bonds of this and many other organic derivatives of hydrogen peroxide are rapidly cleaved by organolithium reagents by nucleophilic attack at oxygen. Peroxide and superoxide ions seem relatively inert to nucleophilic cleavage. Establishing the reactivity of peroxy metal compounds toward n-butyllithium provides a qualitative test of the susceptibility of the oxygen atoms in these species to nucleophilic attack, and thus provides evidence bearing on their electrophilicity.

## RESULTS AND DISCUSSION

Reactions were carried out by allowing a solution or suspension of the metal peroxide to react with n-butyllithium for 2 h; the reaction mixture was quenched with an excess of acetic anhydride, and assayed for n-butyl acetate by GLC. Representative yields of n-butyl acetate are listed in Table 1.

At $-78°$, both peroxybis(triphenylphosphine)platinum(II) and peroxybis-(triphenylphosphine)iodocarbonyliridium(III) were inactive in transferring oxygen

TABLE 1
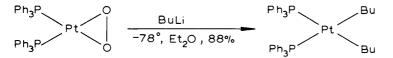
YIELDS OF n-BUTYL ACETATE OBTAINED BY REACTION OF METAL PEROXIDES WITH n-BUTYLLITHIUM

| Metal peroxide | Mol BuLi / Mol metal peroxide | Temp.[a] (°C) | Mol BuOAc / Mol metal peroxide |
|---|---|---|---|
| $(Ph_3P)_2PtO_2$ | 10 | −78 | 0 |
|  | 10 | 25 | 0.5 |
|  | 10 | 25[b] | 0.6 |
|  | 1.5 | 25 | 0.3 |
| $(Ph_3P)_2Ir(CO)(O_2)I$ | 10 | −78 | 0 |
|  | 10 | 25 | 1.0 |
|  | 1 | 25 | 0.2 |
| $OMo(O_2)_2 \cdot HMPA$ | 10 | −78 | 2.1 |
|  | 25 | 25 | 2.1 |
|  | 1 | 25 | 0.1 |
| $OCr(O_2)_2 \cdot Py$ | 8.5 | −78 | 0.8 |
|  | 25 | 25 | 2.0 |
|  | 1 | 25 | 0.6 |
| $Na_2O_2$ | 10 | −78 | 0 |
|  | 10 | 15 | 0 |

[a] Reactions carried out at 25° were run in benzene and those at −78° in diethyl ether unless otherwise noted. [b] Diethyl ether solvent.

to n-butyllithium. The latter compound appeared to be unreactive in any sense toward n-butyllithium at this temperature; the former reacted smoothly, but generated only di-n-butylbis(triphenylphosphine)platinum(II) in 88% yield. Thus, in neither compound is the peroxide moiety cleaved nucleophilically by n-butyllithium at low

$$\underset{Ph_3P}{\overset{Ph_3P}{>}}Pt\overset{O}{\underset{O}{<}}\mid \quad \xrightarrow[-78°, \; Et_2O \, , \; 88\%]{BuLi} \quad \underset{Ph_3P}{\overset{Ph_3P}{>}}Pt\underset{Bu}{\overset{Bu}{<}}$$

temperature, although it is displaced during nucleophilic attack on platinum. At 25°, oxygen atoms from both the peroxyplatinum and -iridium complexes are transferred to the n-butyl moiety of n-butyllithium. Since, in principle, one $MO_2$ moiety might give rise to two equivalents of lithium n-butoxide, the observed yields of n-butyl acetate never exceed 50% of that theoretically possible in these or the other reactions summarized in Table 1.

As expected, the peroxymolybdenum(VI) and -chromium(VI) species are more reactive than the peroxy complexes of platinum and iridium: both react readily with n-butyllithium at $-78°$ to form lithium n-butoxide. In order to confirm that this reactivity is due to the peroxy moieties rather than to the isolated "oxo" oxygen atom, n-butyllithium was allowed to react with 30% isotopically enriched $^{18}OMo(O_2)_2 \cdot$ HMPA*. None of the $^{18}O$ label was incorporated into the n-butyl acetate. Sharpless, Townsend, and Williams have established that the "peroxy" oxygen atoms are those that are active in epoxidation of olefins[8].

$$\underset{HMPA}{\overset{\overset{^{18}O}{\|}}{\underset{O}{\overset{O}{>}}Mo\underset{O}{\overset{O}{<}}}} \quad \xrightarrow[2) \; Ac_2O]{1) \; BuLi \, , \; 25° , \; C_6H_6} \quad Bu^{16}O\overset{O}{\overset{\|}{C}}CH_3$$

Sodium peroxide is unreactive toward n-butyllithium both at $-78°$ and at 25°.

The conclusion from these studies is that the peroxy moieties of the platinum and iridium metal–oxygen complexes are relatively unreactive toward n-butyllithium, and is in accord with the low electrophilicity inferred for these groups from studies of their low reactivity toward olefins and hydrocarbons. Although the experiments outlined here permit their reactivity to be defined qualitatively only as intermediate between that of the peroxy moieties of the peroxymolybdenum(VI) and -chromium-(VI) compounds and that of sodium peroxide, the observation that nucleophilic attack at the platinum atom of peroxybis(triphenylphosphine)platinum(II) at $-78°$ occurs more rapidly than nucleophilic attack at the oxygen atoms of this complex indicates that the electrophilic reactivity of this peroxy moiety is low. This conclusion is in accord with the observations made by others that the reactivity of peroxybis-(triphenylphosphine)platinum(II) seems to be highest in reactions in which the peroxy moiety acts formally as a nucleophile rather than as an electrophile[6].

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EXPERIMENTAL

*General methods*

All vapor phase chromatographic analyses were carried out using a 6 ft, 0.125 in. stainless steel 10% UC-W98 Silicon Rubber on 80–100 mesh Chromosorb P column with an F & M Model 810 instrument equipped with a flame ionization detector and Disc integrator. Absolute yields of n-butyl acetate were calculated from peak areas using n-nonane as an internal standard. Melting points were determined using a Thomas–Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded either as potassium bromide pellets or as solutions using a Perkin–Elmer Model 237 or 237B grating spectrophotometer. Band positions are reported in wave numbers. The mass spectra were obtained using a Hitachi–Perkin–Elmer RMU-6D mass spectrometer. Benzene was distilled from a blue suspension of sodium benzophenone ketyl. Ethyl ether was distilled from a suspension of calcium hydride under a nitrogen atmosphere.

Bis(triphenylphosphine)iodocarbonyliridium(I) was purchased from Strem Chemicals and was used without further purification. A solution of n-butyllithium in hexane used in this study was purchased from the Foote Mineral Company.

*Peroxybis(triphenylphosphine)platinum(II)*

Peroxybis(triphenylphosphine)platinum(II) was prepared from tetrakis(triphenylphosphine)platinum(0)[9] by published procedures[10].

*Peroxybis(triphenylphosphine)iodocarbonyliridium(III)[11]*

The procedure employed was similar to that for the preparation of peroxybis-(triphenylphosphine)platinum(II) except that bis(triphenylphosphine)iodocarbonyliridium(I) was used in place of tetrakis(triphenylphosphine)platinum(0).

*Chromium pentoxide–pyridine, $OCr(O_2)_2 \cdot Py$*

Following the published procedure[12], to a solution of 2.0 g of chromium trioxide in 75 ml of water at 0° was added a solution of 4.5 g of pyridine, 2 ml of 30% hydrogen peroxide, and 20 ml of water. The solid chromium pentoxide–pyridine complex formed immediately and was isolated by filtration. The complex was washed with ice water, alcohol, and ether, and was recrystallized from ether, yielding 1 g of a purple solid (38%); IR (KBr pellet), 880 (O–O stretch) cm$^{-1}$.

*General procedure for the reaction of n-butyllithium with metal peroxides*

A carefully weighed amount of the metal peroxide (typically, 1 mmol) was placed in a 40 ml centrifuge tube equipped with a Teflon-coated magnetic stirring bar and a No-Air stopper. The tube was flushed with nitrogen and 20 ml of solvent was introduced via cannula. Reactions carried out at 25° were normally performed in benzene as the solvent, while those run at −78° were done in ethyl ether. A solution of n-butyllithium in hexane was added to the solution of peroxymetal compound stirring at the desired temperature via syringe. The mixture was stirred for two hours and was quenched with 1 ml of thoroughly degassed acetic anhydride. A known quantity of n-nonane was added as an internal standard, and the n-butyl acetate produced was analyzed by GLC.

*Reaction of peroxybis(triphenylphosphine)platinum(II) with n-butyllithium at −78°*

Peroxybis(triphenylphosphine)platinum(II) (0.5 g, 0.67 mmol) was placed in a

40 ml centrifuge tube equipped with a No-Air stopper and a Teflon-coated magnetic stirring bar. The tube was flushed with nitrogen and 10 ml of ethyl ether was added via cannula. The suspension was cooled to $-78°$ and 8.4 ml of 1.6 $N$ n-butyllithium in hexane (13.4 mmol) was added by syringe. The mixture was allowed to stir for two hours at $-78°$, brought to $0°$ for fifteen minutes, and the tube was centrifuged. The liquid phase was removed through a cannula leaving behind 0.4 g (88 %) of colorless di-n-butylbis(triphenylphosphine)platinum(II). This complex was recrystallized from methylene chloride, and had m.p. (dec) 125–130°, (lit.[13] m.p. 132–134°). The IR spectrum and $R_f$ values of this substance using either silica gel or alumina with methylene chloride were indistinguishable from those of an authentic sample[14].

### Reaction of $^{18}OMo(O_2)_2 \cdot HMPA$ with n-butyllithium

A weighed sample of $^{18}OMo(O_2)_2 \cdot HMPA$ (40 mg) was placed in a 40 ml centrifuge tube equipped with a No-Air stopper and a magnetic stirring bar. The tube was degassed with a stream of nitrogen, and freshly distilled benzene (4 ml) was added by cannula. The solution was stirred at room temperature, while n-butyllithium (0.75 ml of 1.6 $N$ butyllithium in hexane) was added by syringe. The resulting reaction mixture was stirred at room temperature for 1 h and was quenched with 0.5 ml of degassed acetic anhydride. The product mixture was subjected to GLC–mass spectral analysis*, indicating the presence of n-butyl acetate, with no detectable $^{18}O$ incorporation (less than 2 %).

In a control experiment the above procedure was duplicated except that the $^{18}OMo(O_2)_2 \cdot HMPA$ complex was not included in the reaction. Analysis of the product mixture showed no detectable n-butyl acetate formed.

### ACKNOWLEDGEMENT

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