EFFECT OF PHASE TRANSFER CATALYST ON CO SUBSTITUTION OF Mo(CO)₆

Hyun Soo Yang, Ha Sun Park and Young Ho Kim

Department of Chemical Engineering, Chungnam National University, Taejon 305-764, Korea

(Received 16 October 1991 • accepted 28 January 1992)

Abstract—The effect of Q^+OH^- was studied, which is formed in NaOH solution used for anion exchange with PTC, on CO substitution of molybdenum hexacarbonyl complex by strong electron donating ligand, 2,2′-bipyridine. The change of product yield was discussed according to the amount and types of solvent and PTC, their compositions, reaction temperature and time, and different cation and anion of PTC.

INTRODUCTION

Until recently, the application of phase transfer catalyst (PTC) for the substitution of metal carbonyls by other ligands is very limited in comparison with rather wide use as a catalyst for organic synthesis and polymerization [1]. The first example of PTC use to metal carbonyl chemistry was done by Abbayes and Alper [2] in 1977. Aniline was formed with excellent yields by treatment of nitro arenes with triiron dodecacarbonyl, aqueous sodium hydroxide, benzene, and benzyltriethylammonium chloride as the catalyst. In this study, the effect of phase transfer catalyst (PTC) was investigated in substitution of CO ligands of molybdenum hexacarbonyl by bidentate electron donating ligand, 2,2′-bipyridine.

In 1987, Manuta and Lees [3] prepared 2,2′-bipyridinetetracarbonyl molybdenum [Mo(CO)₄(2,2′-bpy)] by photolysis in hexane. They suggested that the overall reaction rate is controlled by the formation of Mo(CO)₅ by removing CO ligand from Mo(CO)₆. In metal carbonyls, CO is a prototypical back-bonding ligand which involves the metal d-orbitals. In reference to the group VI metal-CO bond dissociation energy (BDE), a considerable work has been carried out and reported [4], and the BDE are claimed to be dependent upon formal oxidation state of metal, coordination number, steric and electronic factors, and ancillary ligands [5]. Chatt et al. [6] substituted CO of group VI metal carbonyls by nitrogen- or phosphorous-donor ligands in boiling ethanol using inorganic catalyst of sodium borohydride. An important contribution of the study was the discovery that sodium borohydride in boiling methylated spirits catalyzed the substitution.

In 1986, Albers and Singleton [7] used cobalt (II) chloride and palladium oxide for the selective replacement of carbonyl ligands on the group VI metal carbonyls by isonitriles.

Hui and Shaw [8] examined the substitution of CO in MO(CO)₆ in the presence of PTC, tetra-n-butylammonium iodide. One of the great contributions from the study was that the rate of reaction is greatly improved by using two phase system; metal carbonyl and substituting ligand in organic phase and sodium hydroxide and PTC in aqueous phase. This result provides a valuable technique to produce many derivatives of such substituted metal carbonyls; however, it was not enough to clarify the difference of various phase transfer catalysts in CO substitution reaction.

According to the previous work, the reaction mechanism of CO substitution of Mo(CO)₆ in the presence of phase transfer catalyst was suggested as follows [9]: (1) PTC reduces the bond dissociation energy (BDE) in replacing the first CO ligand which is a rate limiting step by forming PTC-Mo(CO)₆ complex and (2) the CO substitution is facilitated by forming Mo(CO)₅COOH⁻ from the complex which is then easily reacted with ligand by nucleophilic attack.

In this study, the effect of Q^+OH^- was investigated, which is formed in NaOH solution used for anion exchange with PTC, on CO substitution of molybdenum hexacarbonyl complex by strong electron donating ligand, 2,2′-bipyridine. The change of product yields is discussed according to the amount and types of solvent and PTC, their compositions, temperature and reaction time. The effect of different cations and anions of PTC are examined as well.

Table 1. Physical properties of used PTC

PTC	Melting range	Molecular wt(g/mol)	Number of C	
BTEAC		227.78	13	
BTMAC	236-239	185.7	10	solub. in water 20 800 g/l
MTOAC		ca. 442		solub. in water 20 10 g/l
TBAHS	169-172	339.54	16	water solub.
TEAC		183.73	8	solub. in water 25 1410 g/l
ET-n-OPB	75-78	479.61	26	
TBPB		339.34	16	
TPPC	269-272	374.86	24	
TBHdPC	57-60	507.67	52	

Fig. 1. Schematic diagram of reflux reaction.
1. N_2 cylinder   2. Demoisturizer
3. O_2 removing tube (BASF R-11 cat.)
4. Cooling water   5. Reflux condenser
6. Magnetic stirring bar   7. 3-way flask
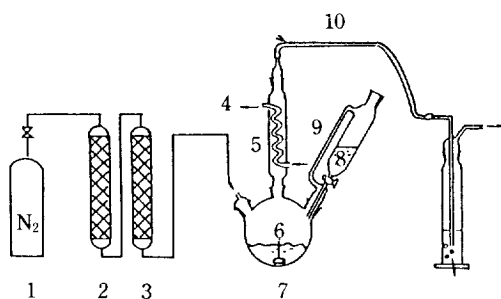8. Ligand-solvent mixture
9. Dropping funnel   10. Exit tube

EXPERIMENTAL

1. Materials

Molybdenum hexacarbonyl (Merck), ligands, and phase transfer catalysts were used without further purification. The chemicals used in this study are: (1) 2,2'-bipyridine (Aldrich) as a ligand; (2) BTEAC (benzyltrimethylammonium chloride), BTMAC (benzyltrimethylammonium chloride), MTOAC (methyltrioctylammonium chloride), TBAHS (tetrabutylammonium hydrogen sulfate), TEAC (tetraethylammonium chloride monohydrate), ET-n-OPB (ethyltri-n-octylphosphonium bromide), TBPB (tetrabutylphosphonium bromide), TPPB (tetraphenylphosphonium bromide), TPPC (tetraphenylphosphonium chloride), and TBHdPB (tributylhexadecylphosphonium bromide) (all from Merck) as phase transfer catalysts (Table 1). Reaction solvents, benzene and THF (all from Junsei), were purified by standard method under nitrogen atmosphere. The physical properties of the used PTC's are shown in Table 1.

2. Synthesis of Mo(CO)₄(2,2'-bpy)

The schematic diagram of experimental apparatus for reflux reaction is shown in Figure 1. A mixture of molybdenum hexacarbonyl, 0.3g (1.14 mmol) and solvent, mixed with 50% NaOH aq. in the presence of PTC (called as catalyst here), was placed in the reaction flask (7). Nitrogen (1) was introduced into the flask through a bluegel-packed drying tube (2) and an oxygen removing tube (3: BASF R-11 cat. packed) to avoid the oxidation of Mo(CO)₆. It was then magnetically stirred (6: 130 rpm) and heated to reflux temperature and in the course ligand dissolved in solvent (8:

1.14 mmols of 2,2'-bipyridine) was added to the mixture through dropping funnel (9). After a predetermined time of reaction, the mixture (which is constituted with product, catalyst, unconverted Mo(CO)₆ and ligand, solvent etc.) was allowed to cool to room temperature.

3. Purification and Product Identification

The reaction product was purified through use of the following procedure [10]: funnel separation, evaporation, filtration, and recrystallization. The purified product was analyzed by using UV/Vis (Kontron Unikon 860 Spectrophotometer) for the metal to ligand charge transfer transition in the 300-700 nm region [11], and IR (PU 4550 Infrared Spectrometry) for a fundamental C-O stretching vibration of produced metal carbonyl complexes, Mo(CO)₄(2,2'-bpy) [11]. In addition, EA (Yanaco CHN Corder Model MT-3 Elemental Analyzer) was used for the determination of C, H, N compositions.

The electronic absorption spectra of purified product in dimethyl formamide or diethyl ether solvent showed the metal to 2,2'-bipyridine charge transfer in the 400-500 nm range, and charge transition transfer of 2,2'-bipyridine in the 340-400 nm range. The IR spectra of purified product showed stretching vibrations in the spectrum at 2009 cm^{-1}, 1910 cm^{-1}, 1882 cm^{-1}, and 1832 cm^{-1}. The C, H, N compositions of product were 46.12%, 2.25%, 7.72% respectively. The analytic spectra and data of the purified product measured here were in an excellent agreement with those of the pure Mo(CO)₄(2,2'-bpy).

The product yield was calculated according to the following equation.

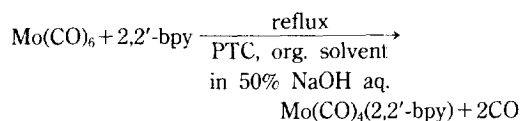**Table 2. Comparison of yields with or without phase transfer catalyst**

Without/with PTC		Solvent (org. phase)	Temp. (℃)	Time (min)	Yield (%)	Phase
without PTC		benzene	80	120	26	only in org. phase
with PTC	TBAHS	THF	66	15	66	in org. phase
	TBAHS	THF	66	30	68	and in aq. phase
	MTOAC	THF	66	120	81	(50% NaOH)

product yield (%)=

$$\frac{\text{moles of product (after reaction)}}{\text{moles of hexacarbonyls (before reaction)}} \times 100$$

RESULTS AND DISCUSSION

The reaction proceeds according to the following equation.

$$Mo(CO)_6 + 2,2'\text{-bpy} \xrightarrow[\substack{PTC, \text{ org. solvent} \\ \text{in } 50\% \text{ NaOH aq.}}]{\text{reflux}} Mo(CO)_4(2,2'\text{-bpy}) + 2CO$$

Selected experimental results and their reaction conditions are given as an example in Table 2 to compare the PTC-catalyzed reaction and the non-PTC thermal reaction. For example, 68% of product yield was measured with PTC at 15 minutes of reaction time whereas only 26% without PTC at 120 minutes. More detailed discussions with respect to the reaction variables and their effects on the product yield will be given hereafter.

1. Effect of Solvent

Benzene and THF (whose polarity is 0.0 and 5.4, respectively) were used as solvents in 50% NaOH aq. with various catalysts carrying different cations and anions with respect to quaternary phosphonium salts and quaternary ammonium salts. Product yields obtained in benzene or THF solvent are shown in Table 3.

As shown in the Figure, a substantial increase of product yield was observed in the presence of PTC. The polarity of solvents affected to a lesser extent on the change of yields. A higher yield was obtained in a more polar solvent (i.e., 75% yield in THF and 57% yield in Benzene with BTEAC). In the absence of PTC, the difference of solvents in product yield was very small. A slightly higher yield was obtained by a more polar solvent as well. A higher yield in a polar THF than in benzene results from the polar nature of intermediate in transition state, which is suggested to be Mo(CO)₅COOH⁻ in the presence of PTC by Darensbourg et al. [9]. According to Darensbourg et al., THF favors the abstraction of OH⁻ and CO ligand from Mo(CO)₅COOH⁻ by forming a temporarily

stabilized Mo(CO)₅·THF complex to substitute with electron doner of 2,2'-bpy.

2. Effect of PTC

2-1. Effect of PTC Types

Table 3 represents how the catalysts of different anion (ammonium salts, phosphonium salts) affect the product yield.

2-1-1. Quaternary Phosphonium Salts

ET-n-OPB showed a best yield among the catalysts used [ET-n-OPB(68%)>TBHdPC(61%)>TBPB(43%)>TPPC(26%)] in benzene. The variations of yield with phosphonium salts were in consistent with ammonium salts, where the CO substitution increased with longer chains and bigger sizes of attached hydrocarbons.

2-1-2. Quaternary Ammonium Salts

MTOAC showed a best yield among the catalysts used [MTOAC (75%) > TEAC (62%), TBAHS (61%) > BTEAC(57%)] in benzene. As observed here, the product yield changes to a lesser extent with the chain length of hydrocarbon attached to an ammonium ion, whereas a longer chain attached to a phosphonium ion produced a higher product yield.

2-2. Effect of PTC Concentration

To obtain the effect of PTC on product yield, MTOAC and benzene were selected for catalyst and solvent, respectively, in 50% aqueous solution. The mole ratio of PTC/Mo(CO)₆ used here were 0.0, 0.05, 0.1, 0.15, 0.25, 0.35, and 0.50 at a constant temperature of 80℃ and at a constant Mo(CO)₆/2,2'-bpy mole composition of 1.0.

As shown in Figure 2, the best yield was observed at about 0.1 mole ratio where approximately 70% of product yield was obtained. This product yield is 2.5 times higher than that obtained at the same reaction condition without catalyst. At a higher PTC concentration than about 0.1 mole ratio, the product yield was shown to decrease. It may be due to the fact that OH⁻ from NaOH, Cl⁻ or Br⁻ from PTC in aqueous phase and quaternary cation in aqueous- and organic-phase form a micelle and micelle reaction tends to reduce the anion-anion exchange ability by blocking metal cation.

3. Effect of Temperature

To examine the effect of temperature on product

Table 3. Yields of Mo(CO)₄(2,2'-bpy) obtained in benzene and THF in the presence of various PTC's of quaternary ammonium and quaternary phosphonium salts

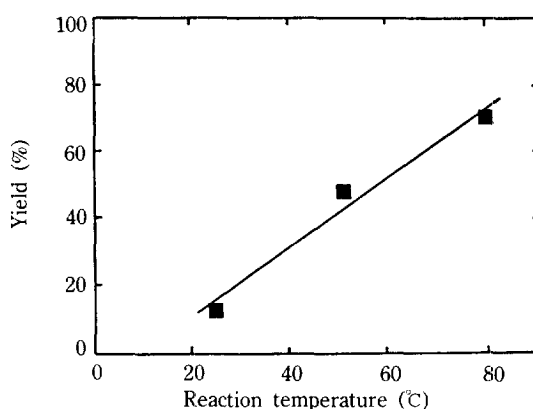| PTC/solvent	benzene	THF
without PTC		26
TEAC	62	76
BTEAC	57	75
TBAHS	61	62
MTOAC	70	81
TPPC	26	31
TBPB	43	55
TBHdPB	61	70
ET-n-OPB	68	73
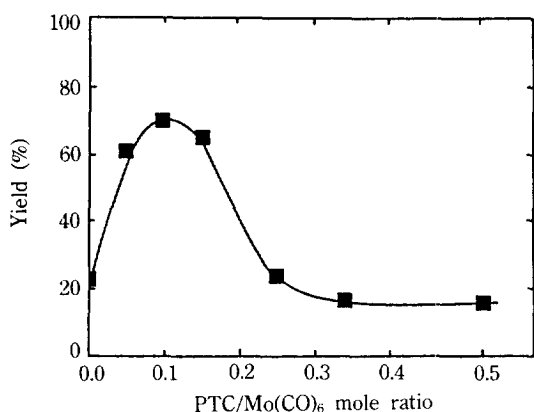
Fig. 2. Yields of Mo(CO)₄(2,2'-bpy) as a function of amount of catalyst: 2 hours of reaction at b.p.'s of MTOAC/benzene with 50% NaOH aq. and Mo-(CO)₆/2,2'-bpy=1/1 (mole/mole).

Fig. 3. Yields of Mo(CO)₄(2,2'-bpy) as a function of reaction temperature: 2 hours of reaction at b.p.'s of benzene/50% NaOH aq. and Mo(CO)₆/2,2'-bpy/ PTC (TBAHS)=1/1/0.1 (mole/mole).

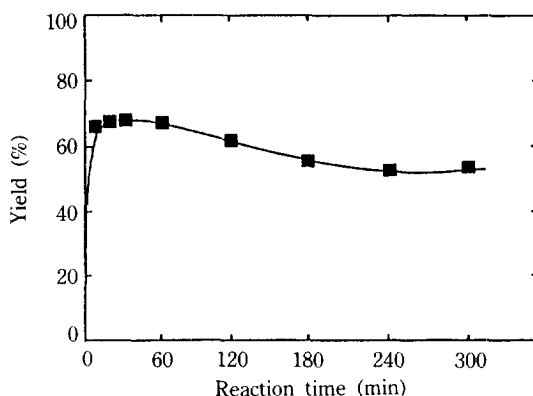Fig. 4. Yields of Mo(CO)₄(2,2-bpy) as a function of reaction time: at b.p.'s of TBAHS/THF with 50% NaOH aq.

yield, three different temperatures of 25, 50 and 80℃ were applied in benzene and 50% NaOH aq. with TBAHS as catalyst. The results are shown in Figure 3. According to the Figure, the product yield increased by increasing temperature up to the boiling point of solvent (80℃ for benzene). The reason for such a high yield at an elevated temperature appears to be due to the lowering of the barrier of activation energy and thermodynamic tendency toward the formation of intermediate (the rate determining step). In addition, the NaOH aq. solution, which is used for initiating cation exchange between Mo(CO)₆ and PTC catalyst, appears to provide more OH⁻ ions by increasing temperature, and to activate anion exchange of PTC catalyst.

4. Effect of Reaction Time

To examine the effect of reaction time on product yield, various reaction times were taken in THF (at

boiling point, 66℃) and 50% NaOH aq. with PTC of TBAHS and the results are shown in Figure 4.

Firstly, the product yield comes to a maximum around 30 minutes, where approximately 68% yield is achieved, after which it decreases. Such a maximum yield can be distinctively compared with the yield of about 26% at 120 minutes of thermal reaction without catalyst.

Secondly, the product yield of Mo(CO)₄(2,2'-bpy) decreased by increasing reaction time because of its thermal degradation. Such a thermal instability of molybdenum carbonyl derivatives was also observed by Kolthammer et al. [12] in CO substitution of Mo(CO)₆ by piperidine ligand in the absence of catalyst. They reported the compounds carrying Mo-N linkage is nor-
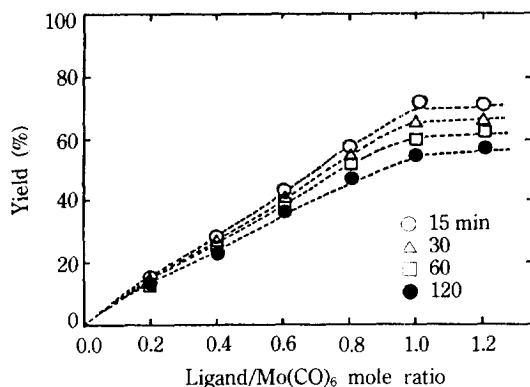
Fig. 5. Yields of Mo(CO)₄(2,2′-bpy) as a function of mole ratio of 2,2′-bpy/Mo(CO)₆ at different reaction time: at b.p.'s of THF/50% NaOH aq. with PTC (TBPB).

mally very reactive and, tends to be unstable at a higher temperature due to its poor ability of receiving π-electrons. It is also reported that the thermal dissociation of Group VI metal carbonyl is in the order of Mo>W>Cr and undergoes at a relatively high rate even at a lower temperature.

5. Effect of 2,2-bpy/Mo(CO)₆ Mole Ratio

To examine how product yield varies with the change of concentration of 2,2′-bpy, various mole ratios of 2,2′-bpy/Mo(CO)₆ were used with TBPB as catalyst and in THF/50% NaOH aqueous solution. Figure 5 shows the variation of product yield as a function of mole ratio at different reaction time. In the Figure, the product yields were shown on the basis of initial moles of Mo(CO)₆.

Firstly, the product yield increased at a linear rate by increasing the concentration of 2,2′-bpy until the mole ratio of 2,2′-bpy/Mo(CO)₆ reaches near unity, and similar trend was observed regardless of different reaction time. However, the product yield was relatively constant with 2,2′-bpy concentration after unit mole ratio.

Secondly, the product yield decreased with increasing reaction time. The reason for a lower product yield at a longer reaction time is due to the thermal degradation of Mo(CO)₄(2,2′-bpy) by its thermal instability, as explained in the above.

Thirdly, product Mo(CO)₂(2,2′-bpy)₂ was expected to be formed by adding excess of 2,2′-bpy. Nevertheless it was not identified. This experimental fact is in consistent with the result of Stiddard [13]. It was proposed that the substitution of CO in Mo(CO)₆ by one mole of 2,2′-bpy ligand increases the bond strength of CO of product by back bonding and addi-

tional CO substitution does not take place even by adding excess moles of ligand.

CONCLUSION

The effect of PTC on substituting CO of Mo(CO)₆ by 2,2′-bipyridine was examined and the following experimental results are obtained.

1. Effect of Solvent and PTC

In the presence of PTC, a slightly higher product yield was obtained in a more polar solvent. In case of phosphonium salt PTC, a longer hydrocarbon chain attached to phosphonium ion produced a higher product yield, whereas product yield was very similar with ammonium salts PTC regardless of length of hydrocarbon chains.

2. Effect of PTC Concentration

A best product yield of 70% was obtained at about 0.1 mole ratio of PTC(MTOAC)/Mo(CO)₆, which is 2.5 times higher than that obtained at the same reaction condition in the absence of catalyst.

3. Effect of Temperature and Time

A higher product yield was obtained at a higher temperature and at a shorter reaction time. In this study, the maximum yield was obtained at a boiling point of solvent and in approximately 30 minutes of reaction time.

4. Effect of 2,2′-bpy/Mo(CO)₆ Mole Ratio

A best product yield was obtained at Mo(CO)₆/2,2′-bpy=1/1 where about 70% of yield based on Mo(CO)₆ was measured at 15 minutes of reaction time.

ACKNOWLEDGEMENT

REFERENCES

1. Starks, C. M. and Liotta, C.: "Phase Transfer Catalyst", Academic press, (1987).
2. Abbayes, H. and Alper, H.: *J. Am. Chem. Soc.*, **99**, 98 (1977).
3. Manuta, D. M. and Lees, A. J.: *J. Chem. Ed.*, **64**, 637 (1987).
4. Lewis, K. E., Golden, D. M. and Smith, G. P.: *J. Am. Chem. Soc.*, **106**, 3905 (1984).
5. Collman, J. P., Hegedus, L. S., Norton, J. R. and Finke, R. G.: "Principles and Applications of Organotransition Metal Chemistry", Mill Valley, California (1987).

6. Chatt, J., Leigh, C. J. and Thankarajan, N.: *J. Orga-nomet. Chem.,* **29**, 105 (1971).

7. Alber, M. O. and Singleton, E.: *J. Chem. Ed.,* **63**, 444 (1986).

8. Hui, K. Y. and Shaw, B. L.: *J. Organomet. Chem.,* **124**, 262 (1977).

9. Darensbourg, D. J., Bellus, P. A. and Froelich, J. A.: *J. Am. Chem. Soc.,* **102**, 4688 (1980).

10. Stiddard, M. H. B.: *J. Chem. Soc.,* 756 (1963).

11. Manuta, D. M. and Lees, A. J.: *J. Chem. Ed.,* 7 (1987).

12. Kolthammer, B. W. S., Legzdins, P. and Malito, J. T.: *Inorg. Synth.,* **19**, 208 (1979).

13. Stiddard, M. H. B.: *J. Chem. Soc.,* 4712 (1962).