

ACTIVATION OF CARBON DIOXIDE BY TRANSITION
METAL COMPLEXES

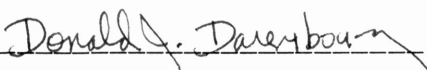
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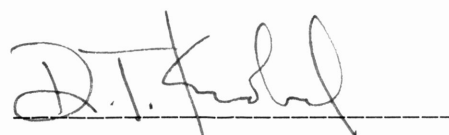

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TABLE OF CONTENTS

Abstract	1
Introduction	2
Copolymerization of CO ₂ and Epoxides	4
Experimental	
Materials and Methods	8
Preparations	9
Reaction Conditions	12
Results and Discussion	16
Conclusion	22
References	23
Tables	25
Figures	27

ABSTRACT

Group 6 metal anionic complexes, $(\text{CO})_5\text{M}(\text{O}_2\text{CR})^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}; \text{R} = \text{Me}, \text{OPh}$), were investigated for potential catalytic properties that would mediate a copolymer synthesis. Copolymers made of alternating carbon dioxide and epoxides have been activated by various reported organozinc complexes. A similar group 6 metal species was sought as a probe for the mechanistic features of a proposed catalytic cycle. At present, details about the mechanisms that facilitate carbon dioxide and epoxide copolymerization are poorly understood. In a proposed mechanistic scheme for a copolymer synthesis of CO_2 and epoxides, the activation of the CO_2 by group 6 metal complexes represents a very well-documented and important step, applicable in the chain propagation. The epoxide insertion, however, remains an elusive detail to the complete copolymer cycle. Two group 6 anionic species, $(\text{CO})_5\text{M}(\text{O}_2\text{CCH}_3)^-$, **1**, and $(\text{CO})_5\text{M}(\text{O}_2\text{COPh})^-$, **5**, represent CO_2 insertion products that were investigated for potential catalytic activity toward propylene oxide.

INTRODUCTION

Finding alternative sources for chemical feedstocks has become important as man exhausts the limited petroleum-based resources for chemical production. In the past decade attention has focused toward non-conventional sources of chemical carbon other than carbon monoxide. The result has brought about a renewed interest in the chemistry of carbon dioxide, the most abundant and inexpensive C1-molecule.(1)

Interest in carbon dioxide chemistry has also stemmed from concern over increasing concentrations of CO_2 in the atmosphere. The impact of the changed carbon dioxide content on the environment cannot be predicted with certainty. However, numerous indications suggest that an increasing concentration of atmospheric CO_2 inhibits the heat emission of surface radiation and affects the global climate on the earth.(2) An active response toward this worldwide problem is to recycle industrially produced CO_2 at its source.

Carbon dioxide is recovered as a coproduct of ammonia synthesis and in the manufacture of ethanol by fermentation. The principle applications of carbon dioxide stem largely from its physical properties. Carbon dioxide receives wide commercial usage in beverage carbonation, refrigeration, and enhanced oil recovery.(3) The chemical utility of carbon dioxide, however, comes largely from the manufacture of urea, certain carboxylic acids, and organic carbonates.(1) Urea is the primary chemical produced from carbon dioxide and is generated on the sites of ammonia plants.(2) In time, many experts predict that the chemical

industries will shift toward a greater usage of carbon dioxide in manufacturing.

In order for carbon dioxide to receive practical chemical utility, one very significant problem must be addressed. Large activation barriers must be overcome for CO₂ to react, despite the fact that CO₂ reactions are often thermodynamically favorable. In the interest of exploiting this inexpensive but inert chemical feedstock, attention has focused on the activation of CO₂ by organotransition metal complexes which mediate reactions that are energetically much less demanding.

Much of the research concerning transition metal chemistry of carbon dioxide has emphasized CO₂ coordinations to metal centers and CO₂ insertions into metal-hydrogen, -carbon, and -oxygen bonds(4b). Examples of both processes are illustrated in Fig. A and Fig. B, namely a

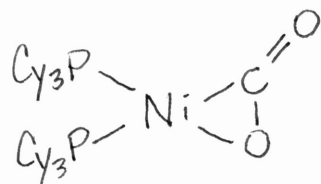


Figure A

nickel-carbon dioxide coordination compound, and a metal-formate generated by CO₂ insertion into a metal-hydride bond, respectively.

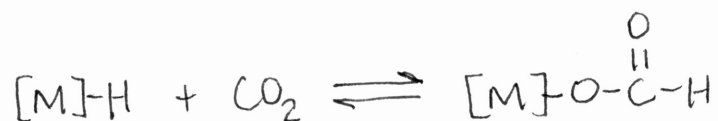
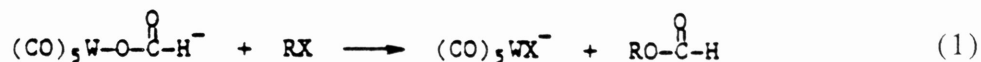


Figure B

The coupling of CO₂ with certain organic molecules, however, has not received much attention. Only a few transition metal-mediated reactions

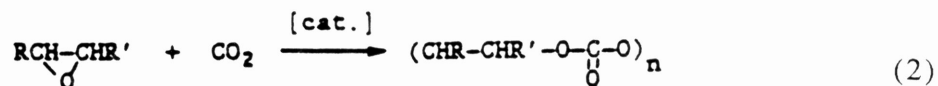
exist that directly lead to the incorporation of CO₂ into an organic product.(4c) Formate esters and copolymers of CO₂ represent two major types of CO₂ coupled products. Formate esters are readily synthesized by the reaction of a metal formate, Fig. B, with an alkyl halide, RX.



Copolymers containing CO₂ cover a wide range of utility, provide some interesting chemistry, and represent the major focus of this investigation.

Copolymerization of Carbon Dioxide and Epoxides

Inoue(5) first reported that carbon dioxide undergoes an alternating copolymerization (eq. 2) with certain epoxy compounds in a reaction mediated by several organometallic catalyst systems under



mild conditions. The products are high molecular weight polycarbonates, e.g. the MW ranges from 50,000-150,000 with ethylene or propylene oxide.

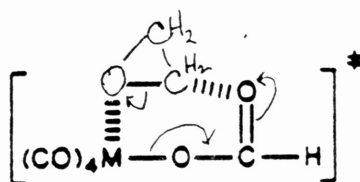
The most-studied catalysts or catalyst precursors include organozinc or organoaluminum reagents.(6) More recently, aluminum porphyrin complexes have demonstrated the catalytic activity toward these reactions,(7) but the products are non-selective and low molecular weight polycarbonates. In addition, Soga has demonstrated transition

metal systems other than zinc to be effective catalysts, such as diacetatocobalt.(8)

It is of considerable interest to note that the reaction proceeds with a variety of epoxy compounds, including ethylene, propylene, butylene, and cyclohexylene oxides, to afford the corresponding aliphatic polycarbonates.(9) However, no reaction occurs when 1,1 - disubstituted epoxy compounds are used

The generic mechanistic features of this polymerization reaction are the formation of a metal alkoxide in an initiation step, followed by chain propagation steps that involve alternating formation of metal alkylcarbonates and metal alkoxides, and a termination step such as protonation. The factors governing these reactions are at present poorly understood. The reaction scheme (Fig. D) illustrates the general reaction steps, where $[M]-OR$ and $[M]-O_2CR'$ represent the alkoxide and alkylcarbonate moieties.

Since epoxides are known to homopolymerize and form polyethers under similar reaction conditions, certain reaction kinetics must be observed in order for the copolymerization of carbon dioxide and epoxides to dominate. Carbon dioxide must react much faster with the metal alkoxides than epoxides do. Simultaneously, the reaction of epoxides and the metal alkylcarbonate species must be much faster than that of carbon dioxide and the metal alkylcarbonate. For zero-valent group 6 metal alkoxides, both of these conditions are believed to hold. Darensbourg and coworkers(10) have reported that carbon dioxide rapidly inserts into metal alkoxides at ambient temperatures and the



Since CO displacement is assisted by distal oxygen atom of the carboxylate ligand, subsequent formation of a bidentate η^2 -carboxylate moiety generates a very reactive species toward incoming ligands, L, to afford η^1 -cis-(L)(carboxylate)M(CO)₄. A similar process is anticipated for CO loss in (ROCO₂)M(CO)₅⁻ anion.

In addition, premature termination of the alkoxide derivative formed from epoxide insertion into metal carbonate species can occur via β -hydride elimination. Hence, another rate requirement is introduced, in which CO₂ must react with the epoxide insertion product faster than either β -hydride elimination or subsequent epoxide insertion can occur.

EXPERIMENTAL SECTION

Materials and Methods

Starting Materials

Glutaric acid, phenol, bis(triphenylphosphine)iminium chloride (PPNCl), and potassium acetate (KO_2CCH_3) were purchased from Aldrich Chemical and used without further purification. Propylene oxide and propylene carbonate were purchased from Aldrich Chemical and purged with a stream of dry nitrogen prior to transfer from the bottle. Tetraethylammonium hydroxide (Et_4NOH 25% in methanol, Alfa) and zinc fillings (Zn, Baker) were used as received. MCB was the source for adipic acid. Chromium, molybdenum and tungsten hexacarbonyls were purchased from Strem Chemicals and sublimed under a vacuum at 60 C. Nitrogen, argon, carbon dioxide, and carbon monoxide were purchased from AIRCO Corporation. Hydrochloric acid (aq. HCl, 37%) and sodium hydroxide pellets were obtained from Fisher Chemical and used as received.

Solvents

Tetrahydrofuran (THF, Fisher), hexane (Fisher), and dimethoxyethane (DME, Aldrich) were dried by refluxing over sodium benzophenone (Aldrich) ketyl solution under a nitrogen atmosphere and distilled prior to use. Methanol (Fisher) was dried by refluxing over magnesium turnings (Aldrich) followed by distillation. Methylene

chloride (CH_2Cl_2 , Aldrich) was dried over P_2O_5 (Aldrich) followed by distillation.

Methods

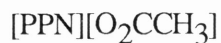
All reactions were carried out under a dry nitrogen atmosphere on a double-manifold Schlenk vacuum line, unless specified otherwise. Solid transfers were performed under a stream of nitrogen or in an argon-filled drybox. Routine infrared spectra were recorded in a 0.10mm NaCl sealed cell on a IBM FT-IR model 32 spectrometer. The spectra were calibrated against water-vapor below 2000 cm^{-1} . ^{13}C NMR measurements were carried out on a Varian model XL-200 spectrometer.

Preparations

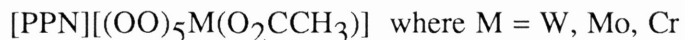
$\text{Zn}[\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2]$ where $n = 3$ (glutaric acid), 4 (adipic acid)

Zinc fillings were first dissolved in hydrochloric acid to generate a zinc chloride solution. Zinc hydroxide was precipitated by the addition of a conc. solution of sodium hydroxide solution to the zinc chloride solution, followed by copious washings of cold water. The white solid was filtered and dried under vacuum overnight. 5.0 g of zinc hydroxide and 7.3 g of adipic acid (or 6.6 g of glutaric acid) were transferred into a 500 ml Schlenk flask and degassed. After the addition of 150 ml of dry ethanol, the reaction mixture was stirred at 55 C for 24 hours under nitrogen. The white solid was filtered, washed with cold ethanol (3x5 ml), and

dried under vacuum overnight. The infrared spectral data are given in Table 1



This reagent was synthesized according to the procedure first reported by Martinsen and Songstang (13) with minor modifications. In general, 11.64 g of PPnCl were dissolved by heating in 120 ml of distilled water in a 250 ml erlenmeyer flask. 40 g of potassium acetate in 50 ml of water were added to the hot PPnCl solution. The reaction mixture was stirred for ca. 2 hours and then placed in an ice-water bath for another hour. After filtration, the white solid was washed with cold water (3x1 ml) and with cold diethyl ether (3x1 ml). The solid was dried under vacuum overnight and 10.45 g of product was isolated (86.2% yield based on PPnCl) with a melting point of 168-170 C.



The procedure followed was first reported by Darensbourg and co-workers (14). 1 g of PPNO₂CCH₃ (mp = 168-170 C) and 0.71 g of W(CO)₆ (0.53 g of Mo(CO)₆ or 0.44 g of Cr(CO)₆, respectively) were placed in a 100 ml Schlenk flask fitted with a condenser. After evacuating and back-filling the flask three times, 35 ml of degassed DME (1,2 dimethoxyethane) were added. The reaction mixture was then stirred under nitrogen and refluxed for 30 min. The resulting orange solution was cooled to room temperature and half of the solution was removed under vacuum. After the addition of 30 ml of degassed hexane, the

solution was stored in a freezer overnight. The resultant solid was collected by filtration under nitrogen and dried under vacuum overnight. For the molybdenum or chromium derivatives, the procedure was exactly the same with the exception that the reflux time was only 12 and 25 minutes, respectively. The infrared spectral data for the group 6 acetates appear in Table 2.

[Et₄N][OPh]

This reagent was prepared according to the procedure reported by McNeese and co-workers (15). 6.67 g of phenol was dissolved in 50 ml of dry methanol in a 200 ml round-bottom flask, and 43.8 g of Et₄NOH in methanol (25% w/w) was added to the solution. The flask was fitted with a reflux condenser and heated to 65 C for 2 hours. After the solution cooled, the methanol was removed under vacuum. The product was extracted from the resultant residue with THF/CH₃CN (6:1 v/v) and filtered. Cooling below -11 C caused the precipitation of white crystals of Et₄NOPh (13.6 g, 85% yield).

[Et₄N][Cr(CO)₅OPh]

This complex was prepared according to the method reported by Darensbourg et al. (10) 0.452 g of Cr(CO)₆ dissolved in 55 ml of THF was irradiated with a 450-W mercury vapor lamp under a nitrogen purge in a water-cooled photocell for 60 minutes. The resultant red-orange solution contained Cr(CO)₅(THF) and was analyzed vide infra for reaction completion. The solution contained mostly Cr(CO)₅(THF) (IR ν(CO): 2074

(w), 1939 (s) 1895 (m) cm^{-1}) and the relative concentration of $\text{Cr}(\text{CO})_6$ (IR $\nu(\text{CO})$: 1978 cm^{-1}) was very small.

The $\text{Cr}(\text{CO})_5\text{THF}$ solution was transferred by cannula to a degassed flask containing 0.472 g of $[\text{Et}_4\text{N}][\text{OPh}]$. The desired product formed upon stirring the solution for 5-10 minutes at 0 C, where it was maintained under a carbon monoxide purge in order to avoid decomposition. The primary component of the reaction mixture was $[\text{Et}_4\text{N}][\text{Cr}(\text{CO})_5\text{OPh}]$ (IR $\nu(\text{CO})$: 2056 (w), 1915 (s), 1856 (m) cm^{-1}).

$[\text{Et}_4\text{N}][\text{Cr}(\text{CO})_5\text{O}_2\text{COPh}]$

A freshly prepared THF solution of $[\text{Et}_4\text{N}][\text{Cr}(\text{CO})_5\text{OPh}]$, **4**, was purged with carbon dioxide at 0 C. An infrared spectrum recorded immediately after the addition of CO_2 revealed the presence of the insertion product, $\text{Cr}(\text{CO})_5\text{O}_2\text{COPh}^-$, **5**. The product was used in situ for subsequent studies of catalytic activity toward propylene oxide. The major component in solution was **5** (IR $\nu(\text{CO})$: 2060 (w), 1923 (s), 1859 (m) cm^{-1}).

Reaction Conditions

Polymer Synthesis

I. Zinc adipate, zinc glutarate. The procedure followed that reported by Soga and coworkers(8a) with slight modification. A 300 ml Parr autoclave was charged with 2.0 g of zinc adipate (or zinc glutarate) and 40 ml of propylene oxide (PO). Next, 500 psi of CO_2 was transferred

to the reactor through a port. The reaction mixture was stirred rapidly and heated at 60 C for 40 hours. After the reactor returned to room temperature, the zinc species was removed by filtration. The solution was diluted with methanol and washed with dilute hydrochloric acid. The resulting copolymer was precipitated by adding copious amounts of water and was dried under vacuum overnight. The infrared $\nu(\text{CO})$ absorbances for the group 6 acetates appear in Table 1.

II. Group 6 acetates. The above techniques were followed for the catalytic investigation of group 6 acetates, **1**. A solution of 30 ml of PO and 1.4 g of $(\text{CO})_5\text{M}(\text{OAc})$, **1**, prepared in a Schlenk flask was transferred to the autoclave via cannula. The reaction mixture was heated at 60 C for 40 hours, upon which time an undiluted sample was studied *vide infra*. The major components of the solution (where $\text{M} = \text{W}$) were $\text{W}(\text{CO})_6$ (IR $\nu(\text{CO}) = 1976 \text{ cm}^{-1}$) and $\text{W}(\text{CO})_5(\text{OAc})^-$ (IR $\nu(\text{CO}) = 2059 \text{ (w)}, 1955 \text{ (w)}, 1906 \text{ (s)}, 1843 \text{ (m)} \text{ cm}^{-1}$). The IR band at 1976 cm^{-1} had grown in over time, whereas the other IR bands exhibited a decrease in relative intensity.

Control Reactions

I. CO₂ and PO. In the first experiment, 20 ml of PO and 500 psi of CO₂ were charged into a 300 ml Parr autoclave and sealed. The reagents were heated at 60 C for 24 hours, at which time a sample was drawn and analyzed *vide infra*. An undiluted sample revealed that no IR $\nu(\text{CO})$ frequencies had appeared under the given reaction conditions.

II. Group 6 hexacarbonyl. In the next experiment, 100 ml of $M(CO)_6$ (where $M = Cr, W$), 2 ml of PO, and 500 psi were charged into a 25 ml Parr "microbomb." The reaction mixture was heated at 60 C for 21 hours. An infrared spectrum was obtained for an undiluted sample drawn at this time. An IR spectrum of the sample (neat) revealed that no new $\nu(CO)$ bands had appeared, and the intensity of one band (IR $\nu(CO)$: 1976 cm^{-1}) had decreased.

III. Copolymer decomposition. In this experiment, 150 ml of $M(CO)_5(OAc)$, **1**, (where $M = Cr, W$; and OAc = acetate) and 890 mg of polypropylene carbonate (prepared from zinc adipate synthesis) were transferred to a 100 ml Schlenk flask and dissolved in 20 ml of THF. The reaction mixture was heated at 60 C and infrared spectra were obtained for undiluted samples drawn at $t = 1, 4, 24$ hours. No appreciable change was observed in the IR spectra of the samples (neat).

Epoxide Activation

I. Group 6 acetates. In a 25 ml Schlenk tube, 35 mg of **1** and 1 ml of PO were dissolved in 2 ml THF. The reaction mixture was heated at 60 C and infrared spectra were obtained for undiluted samples drawn at $t = 1, 4$ hours. In addition, a similar experiment was performed with 30 mg of **1** and 8 ml of PO charged into the "microbomb." Identical studies were also made *vide infra* for the latter. In both experiments, the major component exhibited a decreased intensity of its $\nu(CO)$ peaks.

II. Metal CO_2 -insertion product. In another experiment, 3 ml of PO were introduced to a Schlenk flask at -78 C that contained a group 6

CO₂-insertion product, (CO)₅Cr(O₂COPh), confirmed *vide infra*. An infrared spectrum was obtained for an undiluted sample drawn at t = 30 minutes. Shortly thereafter, the flask was allowed to return to room temperature, but it developed a fracture in the bottom. The experiment was discontinued due to difficulties in experimental technique after another attempt. The major components were observed *vide infra* to be **4** and **5**, although no change was displayed in the IR spectra for the ν(CO) region.

Results and Discussion

Prior to the investigation of potential copolymer catalysts derived from group 6 metals, the copolymer synthesis of polypropylene carbonate was performed according to the method reported by Soga.(8a) Familiarization with the experimental techniques and the reaction vessel, a Parr autoclave, were achieved for the given reaction conditions. The autoclave was charged with the catalyst, comonomer, and 500 psi of carbon dioxide and heated to 80 C. A product was isolated and resembled a tacky, white elastomer that was soluble in THF, chloroform, and methylene chloride. The copolymer was then characterized by FT (Fourier transform) infrared spectroscopy and FT-NMR techniques, and the spectral data appear in Table 1. Detail of infrared bands However, little has been reported about spectral data of polypropylene carbonate (Table 1), other than the infrared active carbonyl region.(8) Nonetheless, the acquired spectra provide useful references for monitoring subsequent reactions.

Under similar reaction conditions, group 6 metal pentacarbonyl acetates (M = Cr, Mo, W) were investigated as potential catalysts in the copolymer synthesis. None of these metal acetate complexes, however, exhibited catalytic activation of carbon dioxide (CO₂) and propylene oxide (PO) to produce the desired copolymer. The reaction was monitored *vide infra* of the undiluted THF solution for the appearance of the three active bands in the aforementioned $\nu(\text{CO})$ region. Although two bands appeared at (s)1814 cm⁻¹ and (m)1460 cm⁻¹ that were characteristic of two of the three bands observed in the reference

active stretch at $(m)1752\text{ cm}^{-1}$ was not observed. The relative intensities of the observed infrared active stretches increased between $t = 1$ and 24 hours, and no significant difference in intensity level between 24 and 40 hours. Since the sample spectra did not correlate to the reference spectrum according to band patterns and intensities, the formation of another product from the reaction became probable.

The literature has reported that the copolymer reactions were often accompanied by the formation of both the cyclic oligomer and the homopolymer of PO. An infrared reference spectrum confirmed the identity of the unknown product to be cyclic propylene carbonate. From the two reference spectra that appear in Fig. the unique band at 1752 cm^{-1} becomes the "fingerprint" for the copolymer. The cyclic oligomer does not possess such a distinguishable infrared active band, since its presence or absence in a sample can be hidden by two of the active $\nu(\text{CO})$ bands of the copolymer that occur at the same frequencies.

Control experiments were then carried out in order to test the dependence of the cyclic oligomer formation on the presence (or absence) of various species other than the initial metal acetate in the reaction mixture. In separate experiments, the group 6 metal acetate species was either removed entirely or substituted with its corresponding hexacarbonyl complex for the same reaction conditions. In the first experiment, both PO and CO_2 (500 psi) were charged into the autoclave and it was determined *vide infra* that no product had formed in the absence of the metal acetate species. In another experiment, the presence of only metal hexacarbonyl, a decomposition product of the

metal pentacarbonyl acetate, also did not mediate the formation of the cyclic oligomer from CO_2 and PO. Thus the acetate species is either the active catalyst or catalyst precursor for an active species other than the metal hexacarbonyl, upon which the formation of the cyclic oligomer is dependent.

However, it has also been reported that the polycarbonate of CO_2 and PO will decompose in an inert atmosphere at temperatures above 180 C to generate its respective cyclic carbonate.(8) Therefore, another experiment was designed to determine whether the cyclic carbonate resulted from the decomposition of its respective polycarbonate in the presence of the acetate complex. A sample of polypropylene carbonate, acquired from a prior synthesis, and a group 6 acetate were dissolved into THF and were heated at 55-60 C under a nitrogen atmosphere. The results from infrared studies of samples drawn at various times were rather inconclusive, since the intensity of the unique band at 1752 cm^{-1} attributed to the copolymer did not exhibit a measurable decrease. This experiment would be more conclusive had the band at 1752 cm^{-1} disappeared altogether or almost entirely. In addition, the reaction temperature is well below the reported value required in order to overcome the activation barrier. It is likely that, under these conditions, the metal acetate species is not an active catalyst toward polycarbonate decomposition.

The generation of the cyclic carbonate is considered to be a single unit-long polymer that has collapsed to form a ring. Referring to the overall proposed reaction Scheme for the desired copolymer, the cyclic

oligomer most probably results from a termination step that occurs after the insertion of the first PO but before a subsequent CO₂ insertion. The oligomer reacts with itself to produce its cyclic form and to liberate a metal species.

Under similar reaction conditions, experiments were performed to detect the possible formation of the cis-epoxide substitution complex and/ or the epoxide insertion product. It is expected that the formation of cis-(epoxy)M(CO)₄(OAc), **2**, generated from the coordination of PO to the CO-labile M(CO)₅(OAc), **1**, can be distinguished *vide infra* from **1** (where OAc = acetate) due to changes in band patterns, associated with different geometries. A monosubstituted six-coordinate species like **1** exhibits 3 infrared active ν(CO) bands characteristic of C_{4v} geometry.

C_{4v}

C_{2v}

Whereas a cis-disubstituted six-coordinated species like **2** exhibits 4 infrared active ν(CO) bands that are characteristic of C_{2v} geometry.

Hence, both **1** and **2** should be distinguishable in the event that **2** is formed during the experiment.

The other species, (CO)₅M(epoxyacetate), **3**, can result from PO insertion into the metal-acetate bond of **1**. The formation of **3** under the reaction conditions should also be distinguishable *vide infra* from **1**, since both species have inherently different metal-oxygen bonds. The two

strong $\nu(\text{CO})$ bands differ sufficiently (by at least 10 cm^{-1}) for infrared spectral resolution between group 6 acetates and simple group 6 alkoxides. Thus, the generation of **3** under the given conditions should also be distinguishable *vide infra* from **1**.

However, the formation of neither **2** or **3** were observed *vide infra* under various reaction conditions. Both **1** and PO were charged into a 25 ml Parr "microbomb" and heated to 60 C under a nitrogen in a closed system. A sample drawn after 1 hour exhibited *vide infra* no change or shift in the infrared active $\nu(\text{CO})$ band spectrum of **1**, although a decrease in peak intensity were observed. Another sample drawn after 4 hours showed the disappearance of the infrared active $\nu(\text{CO})$ bands. Upon further inspection of the sample, from the reaction where $M = \text{Cr}$, a green product was observed that is often characteristic of chromium oxide. It is possible that PO serves as an oxygen-donor to convert **1** to its metal oxide. Also, under similar conditions that employed THF solvent and a 25 ml Schlenk tube, the formation of **2** or **3** were not observed. Hence, the results did not observe a solvent dependence. In short, the group 6 acetates do not permit PO insertion nor coordination under the given conditions.

The reactivity of another group 6 metal species was also investigated for activity toward PO insertion / coordination. Darensbourg and coworkers(10) have demonstrated that certain group 6 aryloxides, $(\text{CO})_5\text{M}(\text{OPh})$, **4**, are very reactive toward CO_2 insertion under mild conditions. This CO_2 insertion also represents the first step in the proposed Scheme for copolymer synthesis.

An experiment was performed to investigate whether the CO₂ insertion product, (CO)₅M(O₂COPh), **5**, would undergo a subsequent PO insertion. The formation of the PO insertion product, (CO)₅M(OC₃H₆O₂COPh), **6**, represents in turn the next step in the proposed copolymer cycle. After addition of CO₂ to the freshly prepared aryloxy moiety, **4**, a sample was drawn at 20 m and the undiluted form exhibited *vide infra* the characteristic $\nu(\text{CO})$ spectrum of **5**. Without isolating the CO₂ insertion product, **5**, an excess (3 ml) of PO was added to the reaction mixture at -78 C under a carbon dioxide atmosphere. After 30 m under the given conditions, a sample was drawn and the undiluted reaction mixture did not exhibit *vide infra* a change in the active $\nu(\text{CO})$ spectrum of **5**. The investigation at higher temperatures, however, was not accomplished due to difficulties in experimental technique. Hence, the results of PO insertion are rather inconclusive. Further experimentation at higher temperatures will afford more conclusive results. The investigation, at best, did give evidence for the inactivity of the phenoxycarbonate moiety, **5**, toward PO under the low temperature conditions.

CONCLUSIONS

The group 6 metal anionic complexes, $(\text{CO})_5\text{M}(\text{O}_2\text{CR})^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}; \text{R} = \text{Me}, \text{OPh}$), that were investigated did not activate the formation of polypropylene carbonate in the presence of carbon dioxide and propylene oxide. A cyclic side-product, however, was formed under the given reaction conditions. This cyclic carbonate may offer new insight into this chemistry, since it is essentially a unit-long polycarbonate. A better understanding of the conditions or process, by which the cyclic carbonate forms, could lead to a more effective catalyst system. The formation of the cyclic carbonate may also provide a means to determine the termination step, to be avoided, and its mechanism.

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TABLE 1

Infrared Active $\nu(\text{CO})$ Modes for Propylene Carbonates, in cm^{-1}

Sample (THF)	$\nu(\text{CO})$		
polymeric PC	m 1814	m 1752	s 1458
cyclic PC ¹	s 1814	s 1809	m 1460

¹ Often accompanies copolymer reaction

² Group VI metal pentacarbonyl acetates as PPN salts

TABLE 2

Infrared Active $\nu(\text{CO})$ Modes for $(\text{CO})_5\text{M}(\text{O}_2\text{CCH}_3)$ for $\text{M} = \text{Cr}, \text{W}, \text{Mo}$

Sample (THF)	$\nu(\text{CO})$			
Tungsten ²	s 1906	m 1843	w 2059	w 1955
Molybdenum ²	s 1917	m 1845	w 2060	w 1967
Chromium ²	s 1915	m 1845	w 2053	w 1964

Figure D

Reaction Scheme for Copolymerization of CO₂ and PO

where R = H, Me, OPh

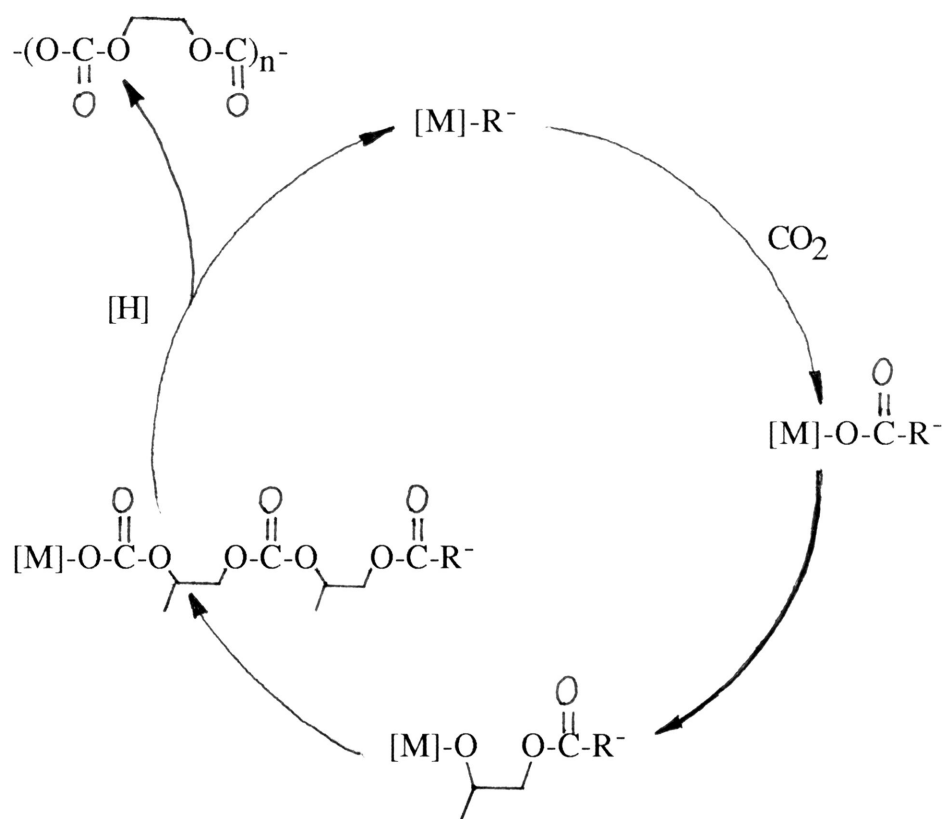
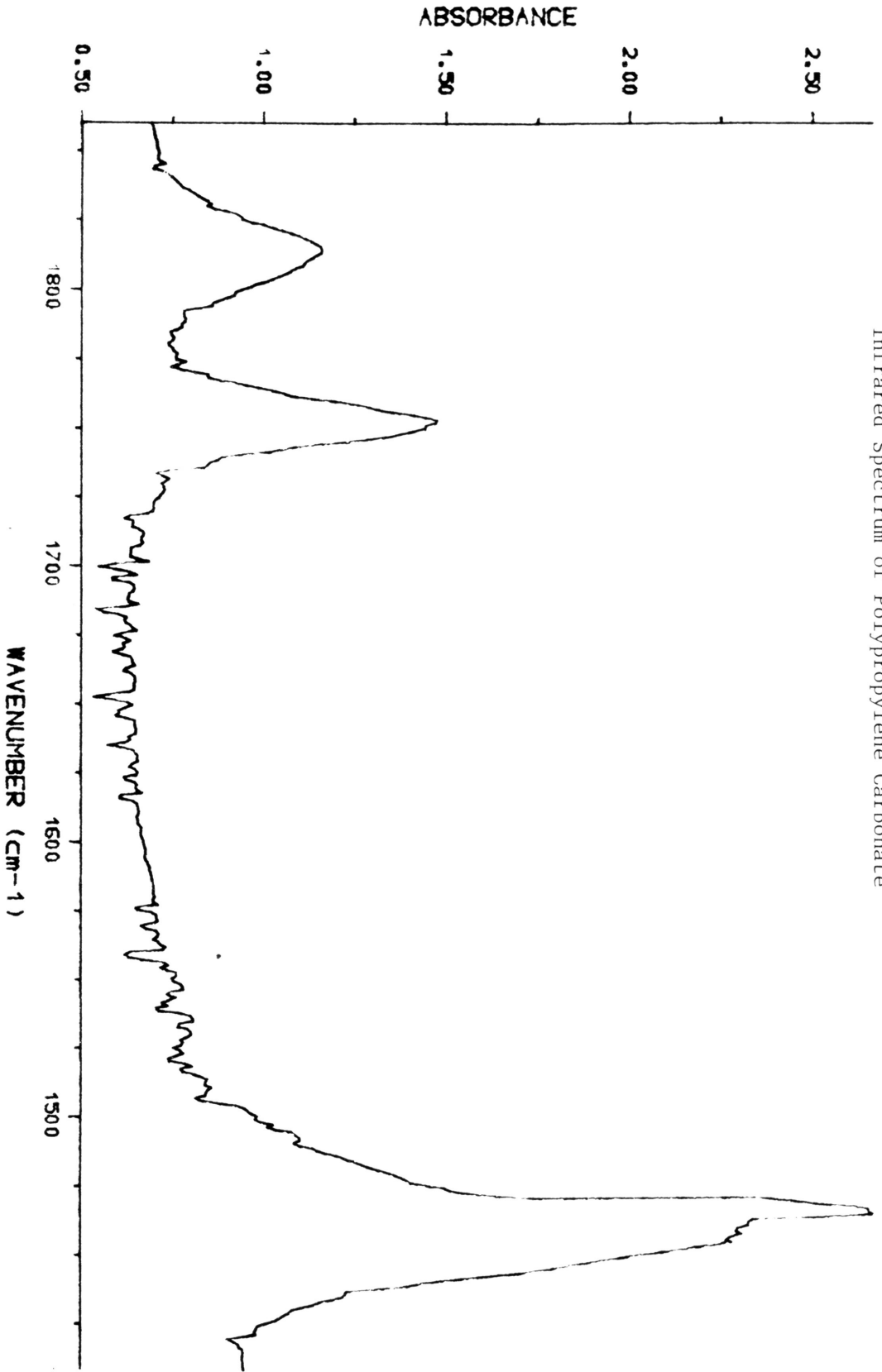


Figure E
Infrared Spectrum of Polypropylene Carbonate



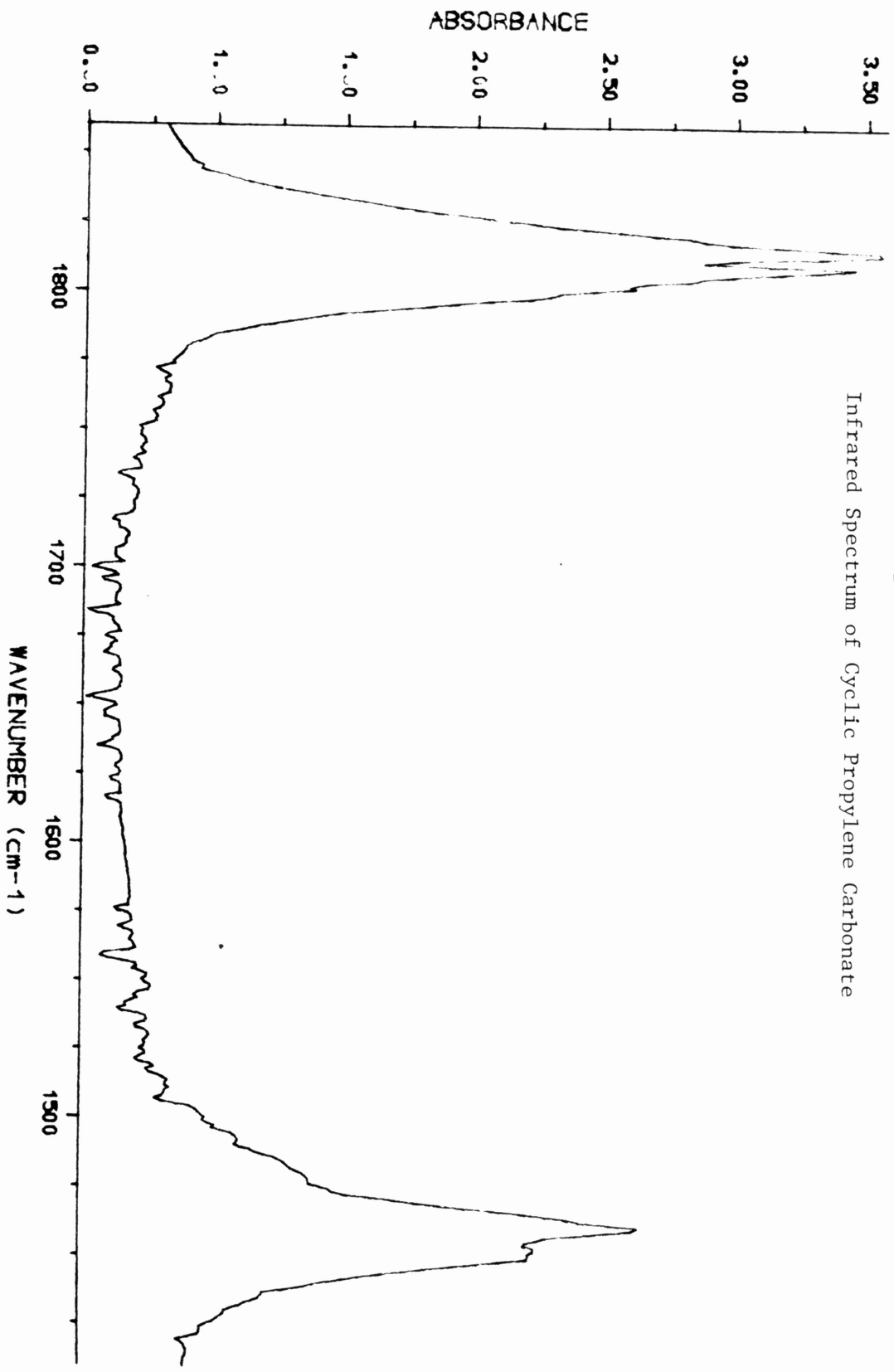


Figure F
Infrared Spectrum of Cyclic Propylene Carbonate