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THE AUTOXIDATION OF DIPHENYLMETHANE CATALYZED BY CHLOROCARBONYLBIS(TRIPHENYLPHOSPHINE)RHODIUM*

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SUMMARY

Using diphenylmethane both as solvent and substrate, the catalyzed autoxidation of this hydrocarbon in the presence of chlorocarbonylbis(triphenylphosphine)-rhodium has been examined. The highly effective nature of $Rh(CO)Cl(PPh_3)_2$ in such autoxidations is demonstrated and comparisons are made to related autoxidation systems. A Haber–Weiss type of one-electron transfer involving some type of intermediate hydroperoxide complex appears to be a likely controlling mechanism.

INTRODUCTION

An examination of the recent chemical literature reveals a great deal of interest in homogeneous hydrogenation reactions catalyzed by d^8 phosphine complexes of rhodium and iridium[1] as well as in the activation of other small molecules[2] such as oxygen, carbon monoxide, sulfur dioxide, olefins and the like. Recently, oxidations of organic substrates using such complexes have been described and this prompts us to now report some of the studies conducted in these laboratories in this area.

Using diphenylmethane as both solvent and substrate, the effect of chlorocarbonylbis(triphenylphosphine)rhodium as a homogeneous catalyst for oxidation has been examined in detail. Our interest in this particular compound lay in the likelihood that it might well have the ability to reversibly form a 1/1 adduct with oxygen, $Rh(CO)Cl(PPh_3)_2 \cdot O_2$, which in turn might effect the enhanced autoxidation of an organic substrate[4]. Such molecular complexes with oxygen and their chemistry have been well documented in the case of iridium and, in at least one closely related instance[5], for rhodium; the reaction of molecular oxygen and chlorotris(triphenylphosphine)rhodium in dichloromethane has been reported to produce a complex, the oxygen then being capable of undergoing displacement by donor ligands:

$$RhCl(PPh_3)_3 + O_2 \xrightarrow{CH_2Cl_2} RhCl(PPh_3)_2 \cdot O_2 \cdot \tfrac{1}{2}CH_2Cl_2$$

Diphenylmethane offered an attractive model compound, there already being an extensive literature on its autoxidation and the mechanism involved[6]. Our data are indicated in the accompanying Table 1 and the graphs in Figures 1 through 4

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TABLE 1

HYDROPEROXIDE CONCENTRATION IN A DIPHENYLMETHANE AUTOXIDATION IN THE PRESENCE OF $Rh(CO)Cl(PPh_3)_2$

$Rh(CO)Cl(PPh_3)_2$ (moles/liter)	ROOH (%)		
	1 h	3 h	6 h
$1.45 \cdot 10^{-3}$	0.3	0.2	0.2
$2.90 \cdot 10^{-3}$	0.2	0.2	0.1
$7.25 \cdot 10^{-3}$	0.2	0.1	trace
$0.72 \cdot 10^{-3}$	0.3	0.2	0.2
$1.45 \cdot 10^{-4}$	0.6	0.8	0.6
—	0.4	1.5	1.4

of this and the sections immediately following. The highly effective catalytic nature of $Rh(CO)Cl(PPh_3)_2$ in the autoxidation of diphenylmethane has been demonstrated as shown in Figs. 1 and 2. Although the particular catalyst species [*i.e.*, an oxygen adduct such as $Rh(CO)Cl(PPh_3)_2 \cdot O_2$ or some type of hydroperoxide complex] has yet to be definitively established, significant information was obtained concerning the mode of action of the catalyst complex and the general mechanism prevailing. Further, the results allow comparisons between this homogeneous metal-ion-catalyzed autoxidation and previously reported autoxidation data.

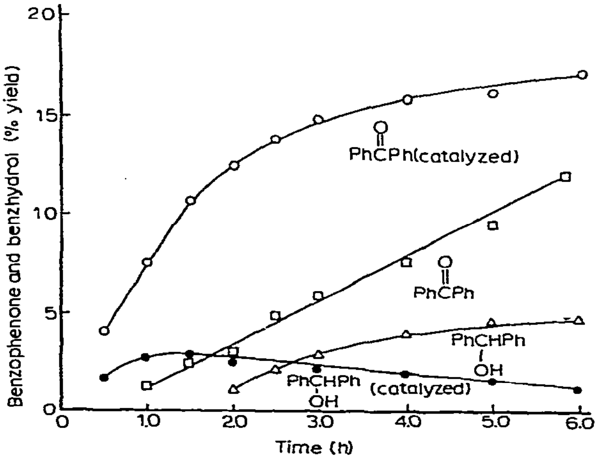

Fig. 1. Diphenylmethane autoxidation in the presence of chlorocarbonylbis(triphenylphosphine) rhodium.

RESULTS AND DISCUSSION

Background

Diphenylmethane is an unusual molecule in that it is representative of a number of benzene hydrocarbons which are subject to self-inhibiting or autoretardation reactions[6]. Such retardations have been shown to be due to the *in situ* formation of phenolic inhibitors as oxidation side-products. This phenomenon introduces into any

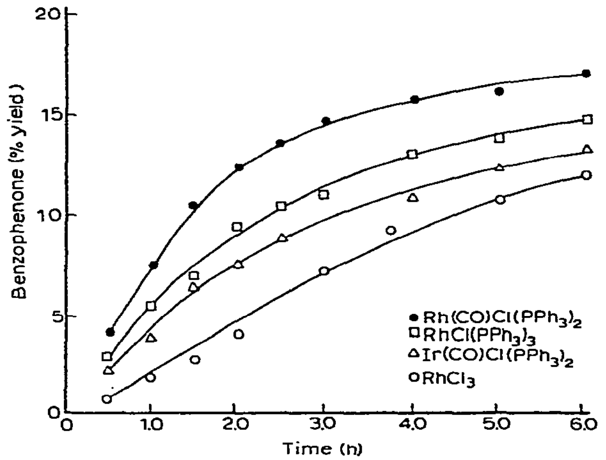

Fig. 2. Diphenylmethane autoxidation in the presence of some compounds of iridium and rhodium.

autoxidation study the complicating factor that the observed rate may in fact be determined by the rate of formation and the efficiency of the inhibitor itself rather than by the stability of the hydrocarbon. However, it has been shown that such retardation reactions do not generally occur until a considerable amount of oxidation has taken place.

In this investigation (Fig. 1), we chose to determine product formation as a means of following the course of the reaction; *i.e.*, the apparent rate of formation of benzophenone and benzhydrol. It was felt that there would be no difficulty in interpreting these data since prior work based on oxygen uptake measurements (a measure of initial reaction rate) showed nearly identical reaction rate profiles for similar autoxidations. For example, the autoxidation of diphenylmethane at 110°, followed by oxygen absorption, has been shown to have a characteristic oxygen absorption *versus* time curve almost identical to that obtained by following the formation of the carbonyl product *versus* time. Fluorene has shown similar results as have other related benzene hydrocarbons[6,7].

Catalysis of diphenylmethane autoxidations

Recent communications[3] have reported the autoxidation of ethylbenzene, tetralin, cyclohexene and cyclopentene using different d^8 complexes as homogeneous catalysts. Although hydrocarbon reactivites in autoxidation reactions are vastly different[6] (tetralin will autoxidize to form hydroperoxides at a much faster rate than will ethylbenzene), the differences are most likely due to the nature of the possible inhibitors or retardants and their rates of formation. All these catalyzed reactions parallel diphenylmethane with regard to the major products formed. For example, ethylbenzene has produced phenylethanol and acetophenone as reaction products as well as small amounts of peroxidic materials.

Kurkov, Pasky and Lavigne[3] have recently established the radical nature of catalyzed autoxidations of both ethylbenzene and cyclohexene using chlorotris(triphenylphosphine)rhodium. They proposed a mechanism involving Rh^{II} and Rh^{III} species in a sequence of reactions similar to the well-known Co^{II} ion catalyzed radical oxidation of hydrocarbons (a Haber–Weiss mechanism). We have looked at both the initiation and the inhibition of the $Rh(CO)Cl(PPh_3)_2$ catalyzed autoxidation of diphenylmethane (Fig. 3). Phenolics such as 2,6-di-tert-butyl-*p*-cresol completely inhibit the reaction as would be expected if free radical processes were involved. A prolonged and enhanced initiation has been demonstrated with di-tert-butyl peroxide in the presence of this rhodium metal complex catalyst. It is well known that most autoxidation reactions involve free radical chain processes*. The data pertaining to the radical nature of the homogeneous metal-ion-catalyzed ethylbenzene autoxidation is compelling and our own experiments with diphenylmethane undeniably point toward similar conclusions.

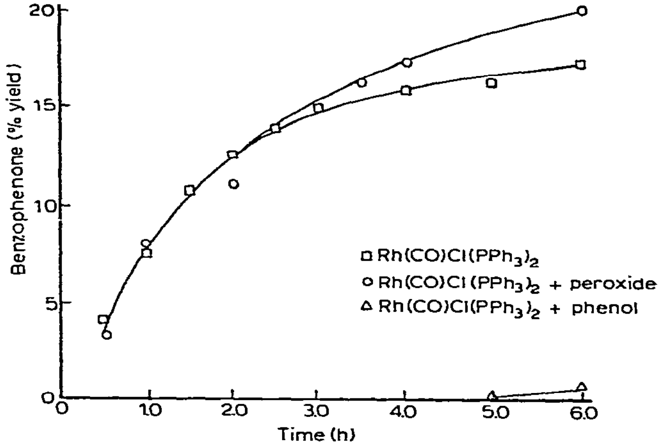

Fig. 3. Diphenylmethane autoxidation in the presence of $Rh(CO)Cl(PPh_3)_2$ with added initiator and inhibitor.

Effect of cyanocarbon compounds

In addition to these inhibitor and activator studies described, several experiments of a different nature have been performed to help shed some light on the role that the metal species plays in these apparently free radical processes. Three cyanocarbon adducts of chlorocarbonylbis(triphenylphosphine)rhodium were prepared according to the general procedures outlined by Baddley[9]. Only two of the compounds were sufficiently stable to isolate readily. The strongly electrophilic olefin, tetracyanoethylene, formed an extremely stable complex through bonding of the metal to the cyanoolefin. This complex proved to be essentially inactive as a diphenylmethane autoxidation catalyst (Fig. 4). Fumaronitrile is capable of forming a moderately stable complex through similar bonding and demonstrated a degree of reactivity intermediate in level between the tetracyanoethylene adduct and the uncomplexed chlorocarbonylbis(triphenylphosphine)rhodium. An acrylonitrile complex was so unstable it could not be readily isolated although there was qualitative evidence for its existence in solution. Reactivity in this instance was no different than that of the uncomplexed rhodium compound.

Inasmuch as it might be expected that cyanoolefins could add to four-coordinate d^8 complexes to form a five-coordinate species with the olefin occupying a coordination site by π-bonding[10], one might also expect such an electrophilic olefin to

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* For a recent comprehensive review of the subject, see ref. 8.

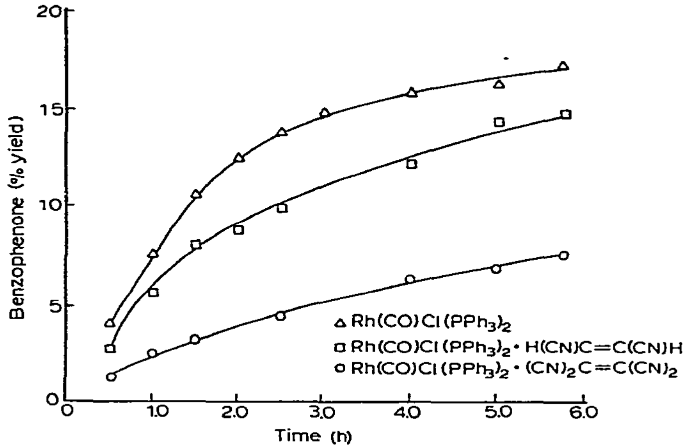
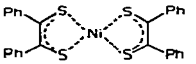


Fig. 4. Diphenylmethane autoxidation in the presence of cyanocarbon complexes of $Rh(CO)Cl(PPh_3)_2$.

exert a substantial effect on the electron density about the central metal atom which in turn should affect its role in a Haber–Weiss type of free radical mechanism. One can actually observe this effect by noting changes in the carbonyl stretching frequency in the infrared. On the other hand, the remarkable affinity of such olefins to form metal complexes of this type may indicate a highly unfavorable competition in the formation of the real catalyst complex in this autoxidation reaction. The catalytic effect of chlorocarbonylbis(triphenylphosphine)rhodium in the autoxidation of diphenylmethane becomes more and more inhibited with increased degree of complexing to the more strongly electrophilic olefin.

Effect of an inhibitor

In another group of experiments, small amounts of the highly effective hydroperoxide decomposition agent, nickel tetraphenylbis(dithiene)



was introduced into a diphenylmethane autoxidation in the presence of $Rh(CO)Cl(PPh_3)_2$. This served to destroy any hydroperoxides formed and resulted in the complete inhibition of any reaction for long periods of time. In addition to being an efficient peroxide decomposition agent, the compound is also very effective as a free radical acceptor. In our hands, the uncatalyzed autoxidation was completely inhibited, well beyond the expected induction period observed in the presence of such free radical acceptors as 2,6-di-tert-butyl-*p*-cresol.

Discussion

The original basis for these studies was our interest in the Vaska compounds and their ability to bind oxygen reversibly. This manifested itself specifically in rhodium compounds, rather than their iridium analogs, in which it could be assumed that the complex with molecular oxygen would be less tightly held together and thus the oxygen might be more available for entry into an autoxidation process in some activated form. All the information accumulated to date supports a basic free radical mechanism involving a metal-ion-catalyzed hydroperoxide decomposition as the radical source. The autoxidation was significantly inhibited by phenolic free-radical inhibitors such as 2,6-di-tert-butyl-*p*-cresol and completely inhibited by neutral nickel tetraphenylbis(dithiene) which has been independently shown to be both a formidable hydroperoxide decomposition agent and free radical acceptor while di-tert-butyl peroxide augmented the role of the catalyst. The catalyzed reactions showed much smaller hydroperoxide concentrations during the active portion of the reaction than did similar uncatalyzed reactions (Table 1) demonstrating the likely participation of hydroperoxide decomposition products in the chain propagation steps leading to products. Finally, by introducing what is probably a competitive complexing reaction with the strongly delocalizing cyanocarbon olefins, the role of complex formation in such reactions has been demonstrated for the case of a catalyzed diphenylmethane autoxidation.

The Haber–Weiss mechanism as originally proposed[11] was written for a hydrogen peroxide decomposition in the presence of Fe^{II} species. It has been subsequently found by many investigators that organic hydroperoxides similarly decompose due to the action of a number of transition metal ions. One of the most extensively studied has been the cobalt ion system which has been discussed and interpreted by Russell[12], Uri[13] and others. In proposing such a mechanism modeled after a Haber–Weiss type metal ion catalyzed chain initiation leading to free radical formation and subsequent initiation of autoxidation, two schemes must be considered. The first involves Rh^{I} species and a Rh^{II} intermediate in a one-electron transfer:

$$Rh^{I} + ROOH \rightarrow Rh^{II} + RO^{\bullet} + OH^{-}$$
$$Rh^{II} + ROOH \rightarrow Rh^{I} + ROO^{\bullet} + H^{+}$$

A second possibility is a process involving a two-electron transfer:

$$Rh^{I} + 2\,ROOH \rightarrow Rh^{III} + 2\,RO^{\bullet} + 2\,OH^{-}$$
$$Rh^{III} + 2\,ROOH \rightarrow Rh^{I} + 2\,ROO^{\bullet} + 2\,H^{+}$$

The two-electron transfer process might well be the favored one based on the relative ease with which Rh^{III} species can be reduced to Rh^{I} species and the fact that Rh^{II} species are indeed very unusual[4,14]. However, it has been shown in several cases that the most effective metal catalysts in autoxidation processes have been those oxidized through one-electron transfers such as $Fe^{II} \rightarrow Fe^{III}$ and $Co^{II} \rightarrow Co^{III}$, whereas metals oxidized by two-electron transfers as $Sn^{II} \rightarrow Sn^{IV}$ and $Tl^{I} \rightarrow Tl^{III}$ are far less successful. We have also found Rh^{III}, as the trichloride, to be considerably less reactive as a diphenylmethane autoxidation catalyst in these reactions. Although one is forced to assume a Rh^{II} intermediate, the former mechanism involving the one-electron transfer seems generally easier to rationalize at the present time.

In summary

The results of the nickel experiments and those experiments using the olefin complexes were most interesting to us. They definitively established the mechanism for these diphenylmethane autoxidations as involving a metal-ion-catalyzed hydroperoxide decomposition. But further, they pointed up the existence of some type of intermediate complex involving the catalytic agent, $Rh(CO)Cl(PPh_3)_2$, or some transformation product thereof. The selective and efficient destruction of any diphenylmethane hydroperoxide by the nickel tetraphenylbis(dithiene) complex served to inhibit any autoxidation at all. Copping and Uri[15] have shown these complexes to be 'unprecedented' in their reactivity toward the characteristic sulfide decomposition of peroxides which do not involve any free radical intermediates. It can therefore be tacitly assumed that a primary process in the overall mechanism is hydroperoxide decomposition by a Haber–Weiss route leading to free radicals. On the other hand, the role of some type of intermediate complex involving the rhodium species is implicitly indicated by the apparent blocking of an available bonding site on the d^8 complex by the cyanocarbon olefins with a resulting diminution in the rates of formation of products. A number of workers[16] have suggested that in a hydrocarbon medium, metal-ion catalysts tend to form intermediate hydroperoxide complexes and this may well be the competing agent.

EXPERIMENTAL

Diphenylmethane was obtained from Eastman Organic Chemicals, distilled once through a two-foot spinning band column and then passed through silica gel to remove traces of benzophenone and moisture. Purity was greater than 99.9% by GLC. The apparatus and experimental conditions involved the use of a 125-ml Morton flask fitted with a special side-arm designed to take a small serum cap, condenser, thermometer, stirrer and a gas inlet tube terminating in a course fritted disk extending to the bottom. Exactly 50 g of diphenylmethane and 50 mg of analytically pure catalyst (obtained commercially or synthesized according to the literature procedures of Chatt or Wilkinson) were used and oxygen bubbled through at the rate of 225 ml/min during the various time intervals noted. Fifty mg of the inhibitors and activators mentioned were used. A temperature of 130° was maintained throughout. The analytical technique consisted in removing samples with a microsyringe at various prescribed time intervals directly through the serum cap with subsequent GLC determinations on a Versamid resin column using flame and TC detection systems.

Hydroperoxide determinations were made by a modified iodometric procedure in which an aliquot of the reaction mixture was introduced into a flask containing potassium iodide and acetic acid in water. The resulting mixture was heated on a steam bath for ten minutes and then cooled to ice bath temperatures after which a measured excess of standard thiosulfate was added. The mixture was immediately extracted with cold ether, the ether extract then washed with water and the combined water layers titrated with standard iodine solution to a starch-iodine endpoint. Reproducibility was excellent and in good agreement with known standards run in parallel experiments.

The nickel tetraphenylbis(dithiene) was obtained from Professor Schrauzer's laboratory and used as received.

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