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## Genesis of a Supported-Metal Catalyst. Aggregation of Polymer-Bound Rhodium Clusters

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**Abstract:** Poly(styrene-divinylbenzene) functionalized with  $\text{PPh}_2$  groups was allowed to react with a solution of  $\text{Rh}_6(\text{CO})_{16}$  in benzene at 25 °C. The product was a polymer containing small Rh clusters, which after reaction with CO exhibited carbonyl spectra like that of  $\text{Rh}_6(\text{CO})_{13}(\text{PPh}_3)_3$ . The polymer was an active, stable catalyst for the hydrogenation of ethylene and cyclohexene at 1 atm and 80 °C. When traces of oxygen were present in the reactants flowing over the catalyst, the phosphine groups were oxidized and the Rh agglomerated, slowly forming a supported-metal catalyst having Rh entities about 20 Å in diameter. The metal entities of various sizes were distinguished by kinetics of the olefin hydrogenation reactions, by their carbonyl infrared spectra, and by electron microscopy.

### Introduction

Catalysts used in many processes are small metal particles stably dispersed on a support like silica or alumina. Preparation of a supported-metal catalyst involves (1) impregnation of the support with a solution of a metal salt or ion exchange of a metal, (2) calcination, and (3) reduction (e.g., with hydrogen) leading to migration and agglomeration of metal on the support and formation of an array of particles of varying sizes and structures, typically having hundreds or thousands of atoms and referred to as crystallites. The reduction and agglomeration processes are poorly understood, there being almost no experimental evidence of the metal entities smaller than about 15 Å, the ones large enough to be characterized by electron microscopy; surface titration with hydrogen determines the dispersion (the fraction of metal atoms accessible on a surface), but it is nearly unity for all crystallites smaller than 15 Å.<sup>2</sup>

Recent efforts to prepare small, well-defined metal entities supported on surfaces have taken advantage of metal-cluster compounds; for example Ichikawa<sup>3</sup> brought platinum and nickel carbonyl clusters into contact with silica and alumina, producing highly dispersed metal catalysts, but the cluster-surface interactions and the pyrolytic agglomeration processes remain uncharacterized. Collman et al.<sup>4a</sup> allowed  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Rh}_6(\text{CO})_{16}$  to react with poly(styrene-divinylbenzene) resins functionalized with  $\text{PPh}_2$  groups, and the ensuing ligand-exchange reactions produced attached rhodium clusters of undetermined structures. Oxidation with air led to loss of the carbonyl spectrum and yielded catalysts having activity for arene hydrogenation at 25 °C and 1 atm; similar catalytic behavior was exhibited by a commercial catalyst consisting of Rh crystallites (having an average dimension of about 20 Å) supported on alumina ( $\text{Rh}/\text{Al}_2\text{O}_3$ ). Collman's and related results<sup>4</sup> provided a starting point into the research described here, since they indicated that chelation by the polymer matrix might allow stable bonding of small metal clusters to a solid support. The present study focused on the process of aggregation of the metal entities; the characterization of the metal

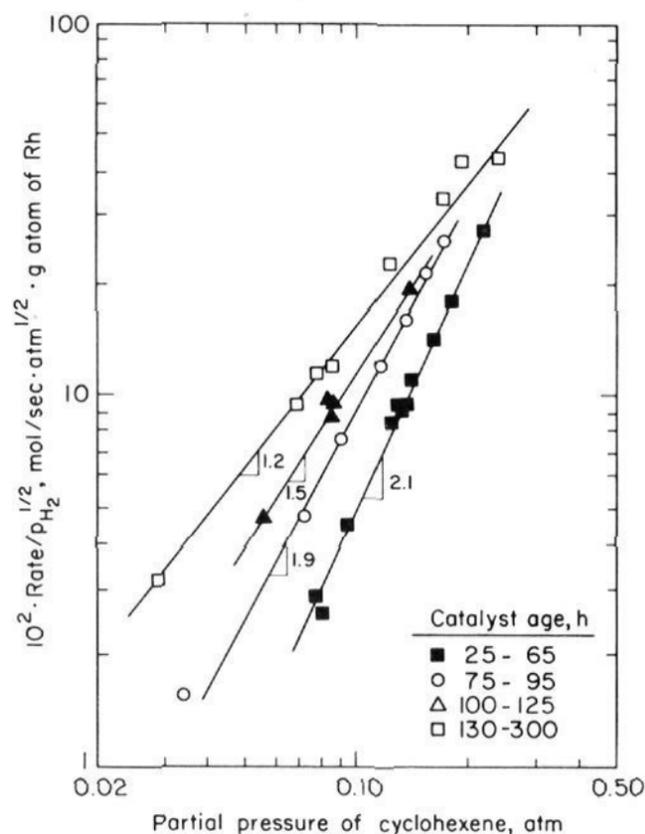
included infrared spectroscopy of carbonylated species, electron microscopy, and kinetics of catalytic hydrogenation reactions.

### Results

Catalysts prepared by ligand exchange of  $\text{Rh}_6(\text{CO})_{16}$  with 7- $\mu\text{m}$  thick membranes of poly(styrene-divinylbenzene) functionalized with  $\text{PPh}_2$  groups gave infrared spectra like those reported previously,<sup>4</sup> the results being consistent with the hypothesis that small Rh clusters were attached to the phosphine groups of the polymer.<sup>5</sup> The golden-brown membrane samples could be reversibly carbonylated and decarbonylated in a flow reactor at 80 °C, and they were stable catalysts, experiencing tens of thousands of turnovers and maintaining unchanged activity for hydrogenation of cyclohexene or of ethylene for as long as 80 h of continuous operation, provided that they were exposed to only reactants (olefin +  $\text{H}_2$ ), He, and/or  $\text{CO}$ .<sup>5</sup>

When the catalyst preparation procedure was modified so that a  $\text{Rh}_6(\text{CO})_{16}$ -benzene solution was brought in contact with the functionalized polymer at 50 °C instead of the usual 25 °C, black spots of metallic Rh deposited on the glassware, and the resulting membranes were gray or black. Transmission electron microscopy showed that aggregated metal species were present in the polymer, having an average diameter of about 25–40 Å and consisting of several hundred atoms each. We infer that the aggregation was much slower at 25 °C, the usual temperature of preparation, since the usual membranes were golden-brown and had no metal crystallites observable by electron microscopy.

A group of catalysts (Table I) was used to determine kinetics of catalytic hydrogenation of cyclohexene, ethylene, and benzene vapors at 1 atm and about 80 °C. The observed reaction products were cyclohexane, ethane, and cyclohexane, respectively. Conversions were less than about 4%; they were shown experimentally to be differential, determining reaction rates directly. For each olefin, the rate data were well repre-



**Figure 1.** Aging of the Rh-containing polymer catalyst (sample 1) during cyclohexene hydrogenation at 75 °C and 1 atm. The slope of a line gives the order of reaction in cyclohexene. The decline in this reaction order was accompanied by agglomeration of the Rh.

**Table I.** Analysis of Polymers

sample no.	cross-linking, % divinylbenzene	elemental analysis, wt % of element			color
		Br	P	Rh	
1 <sup>a</sup>	2.0	1.17	0.92	1.69	golden brown
2 <sup>a</sup>	1.9	0.76	0.44	1.59	golden brown
3 <sup>a</sup>	1.9	0.13	0.36	1.55	golden brown
4 <sup>b</sup>	3	8.45	6.21	0.55	light brown
5 <sup>a</sup>	5.4	12.1	0.23	1.27	gray
6 <sup>a</sup>	1.9			1.61	dark gray

<sup>a</sup> Gel-form membrane. <sup>b</sup> Macroporous beads.

sented by kinetics of the form

$$r = kP_{\text{olefin}}^m P_{\text{H}_2}^n \quad (1)$$

where  $P$  is partial pressure and  $k$  is the rate constant. The kinetics results are typified by data of Figure 1 and summarized in Table II. Data for a commercial Rh/Al<sub>2</sub>O<sub>3</sub> catalyst (Strem, 0.5 wt % Rh) are given for comparison in Table II. The Rh/Al<sub>2</sub>O<sub>3</sub> catalyst had a dispersion of 0.72, corresponding to an average crystallite size of about 20 Å.<sup>6</sup>

The freshly prepared catalyst, which incorporated no observable metal crystallites and presumably incorporated small Rh clusters,<sup>4,5</sup> maintained stable catalytic activity only when the reactant stream was purified to remove oxygen by flow through a trap containing particles of supported Cu. When small amounts of oxygen were included in the feed stream, the change in catalytic activity was too rapid to characterize conveniently, and when the standard precautions were taken (see Experimental Methods), the change in activity lasted hundreds of hours. The slowness of this catalyst aging provided the opportunity for this research; as shown below, the change indicated the genesis of a supported-metal catalyst.

Details are given for aging of a typical catalyst in Figure 1 and Table II: the order of cyclohexene hydrogenation in hydrogen was always near 1/2 and that in cyclohexene changed from nearly 2 to nearly 1 as the catalyst aged; the change was so slow that precise kinetics was determined for intermediate states (Figure 1). The kinetics of cyclohexene hydrogenation



A



B

**Figure 2.** (A) Transmission electron micrograph of a section of a membrane (sample 3) after 40 h use as a cyclohexene hydrogenation catalyst. Particles of Rh are just discernible, having dimensions of about 15 Å. (B) Transmission electron micrograph of a section of the membrane characterized by the data of Figure 1 after 350 h use as a cyclohexene hydrogenation catalyst. Rh crystallites about 20–25 Å in dimension are clearly visible.

observed finally was almost the same as the kinetics indicative of the supported-metal catalysts mentioned before, Rh/Al<sub>2</sub>O<sub>3</sub> and Rh/poly(styrene-divinylbenzene) (Table II). Ethylene hydrogenation kinetics, in contrast to cyclohexene hydrogenation kinetics, failed to provide a sensitive probe of catalyst structure (Table II). Benzene hydrogenation was too slow for determination of a rate equation, but rates were determined under standard conditions, mentioned below.

The inference that metal aggregation occurred in the polymers during the catalyst aging in the presence of traces of oxygen was confirmed by the electron micrographs. The Rh catalyst, after a short period of aging, had no discernible crystallites; further aging gave barely discernible crystallites about 15 Å in size and finally crystallites with a nearly uniform distribution in the 20–25 Å size range (Figure 2). The growth of metal crystallites was confirmed by electron microscopy for

Table II. Summary of Olefin Hydrogenation Kinetics<sup>a</sup>

catalyst	Sample no. <sup>b</sup>	cyclohexene hydrogenation at 75 °C			ethylene hydrogenation at 78 °C		
		$k$ , mol/s·g- atom of Rh·atm <sup>m+n</sup>	$m$	$n$	$k$ , mol/s·g- atom of Rh·atm <sup>m+n</sup>	$m$	$n$
Rh cluster attached to poly(styrene-divinylbenzene) membrane	1 <sup>5</sup>	6.1 ± 0.3	2.06 ± 0.03	0.55 ± 0.03	0.57 ± 0.04	0.92 ± 0.04	0.23 ± 0.09
sample 1 used >250 h for hydrogenation of cyclohexene and ethylene	1	3.1 ± 0.2	1.25 ± 0.08	0.43 ± 0.14	0.74 ± 0.07	0.90 ± 0.15	0.25 ± 0.08
Rh cluster attached to poly(styrene-divinylbenzene) membrane	2 <sup>5</sup>	7.4 ± 0.4	2.22 ± 0.05	~0.5 <sup>c</sup>	0.57 ± 0.03	0.80 ± 0.03	0.22 ± 0.07
Rh cluster attached to macroporous poly(styrene-divinylbenzene) particles	4	<i>d</i>	<i>d</i>	<i>d</i>	0.0048 ± 0.0010 <sup>e</sup>	0.61 ± 0.15 <sup>e</sup>	0.91 ± 0.07 <sup>e</sup>
Rh/poly(styrene-divinylbenzene) membrane	6	6.5 ± 1.5	1.37 ± 0.41	~0.5 <sup>c</sup>			
Rh/Al <sub>2</sub> O <sub>3</sub> particles		9.0 ± 0.5	1.03 ± 0.03	0.36 ± 0.09	60 ± 2 <sup>e</sup>	0.98 ± 0.01 <sup>e</sup>	~0.2 <sup>e,f</sup>

<sup>a</sup>  $r = kPm_{\text{olefin}}P_{\text{H}_2}^n$ . <sup>b</sup> Table I. <sup>c</sup> A value of 0.50 was assumed in calculating  $k$  and  $m$ . <sup>d</sup> The catalytic activity was too low to allow measurement of kinetics. <sup>e</sup> Temperature 77 °C. <sup>f</sup> A value of 0.20 was assumed in calculating  $k$  and  $m$ .

each of several samples and for catalyst aging during reaction of cyclohexene and ethylene separately.

Further confirmation of metal aggregation was provided by infrared spectroscopy. Spectra of functioning catalysts were measured routinely but failed to provide any evidence of the metal structure and showed that the metal was not carbonylated. Therefore, kinetics experiments were interrupted periodically as the flow of reactants was replaced by the flow of CO to provide a carbonyl spectrum. The interruptions did not affect the subsequent kinetics, provided that sufficient time was allowed for complete replacement of reaction-inhibiting CO ligands by reactants.<sup>5</sup> The spectra of the carbonylated polymers (Figures 3 and 4) confirm the pattern of formation of the Rh crystallites; the initial spectrum is similar to that of Rh<sub>6</sub>(CO)<sub>13</sub>(PPh<sub>3</sub>)<sub>3</sub>,<sup>4b</sup> and the final spectrum is characteristic of CO adsorbed on Rh, as determined for the membrane initially containing crystallites (Figure 3) and confirmed by the literature for CO adsorbed on Rh/Al<sub>2</sub>O<sub>3</sub>.<sup>8</sup> States of intermediate aggregation are indicated by spectra of Figure 4.

The spectra gave no indication of the phosphine groups in the polymer, presumably because the peaks were obscured by the more intense poly(styrene-divinylbenzene) peaks.<sup>9</sup> After the catalysts had been aged by oxygen contamination and formation of metal crystallites had occurred, however, weak bands appeared at 1120 and 1170 cm<sup>-1</sup>, almost matching the locations of the two most intense bands of triphenylphosphine oxide at 1120 and 1190 cm<sup>-1</sup>.<sup>10</sup> We conclude that phosphine ligands in the polymer were oxidized to phosphine oxide during the aging process.<sup>11</sup>

The catalytic reaction experiments provided another, qualitative, distinction between the cluster- and crystallite-containing catalysts in addition to the kinetics: the effect of traces of oxygen in the reactant stream was a sensitive indicator of catalyst structure. When the catalyst was freshly prepared, containing Rh presumably as clusters, the effect was the slow oxidation of the phosphine groups and agglomeration of the metal, mentioned previously; there was no immediate effect on the kinetics of hydrogenation. In contrast, after the catalyst had been aged and metal crystallites had formed (or when the catalyst was Rh/Al<sub>2</sub>O<sub>3</sub>), the introduction of oxygen into the feed stream caused an activation of the catalyst, e.g., a doubling of the activity in 2 h after the temperature of the Cu trap for oxygen removal was reduced from 100 °C to 25 °C. The change could be reversed by reinstating stringent purification of the feed stream.<sup>12,13</sup>

The work of Collman et al.<sup>4a</sup> included investigation of the

catalytic nature of the Rh using arene hydrogenation, which occurs rapidly on many metal surfaces,<sup>15</sup> but which evidently occurs in association with only one known mononuclear complex.<sup>16</sup> It is tempting to consider the occurrence of arene hydrogenation as a demonstration of the presence of catalytic species having metal-metal bonds.<sup>17</sup> In our experiments, hydrogen plus benzene vapors flowed over the various catalysts described above, which were characterized by their activities under standard conditions of 75 °C, 0.9 atm H<sub>2</sub> partial pressure, and 0.13 atm benzene partial pressure. The results (Table III) show that the supported-metal catalysts, including those formed from clusters in the above-mentioned catalyst-aging experiments, all had approximately the same activity for benzene hydrogenation relative to cyclohexene hydrogenation (Table III). This result suggests that the attached clusters were active for benzene hydrogenation, but it is more probably an indication that agglomeration of the metal had occurred to a small extent (undetected by the infrared and microscopic techniques) prior to the aging experiments.

One catalyst membrane was prepared from the complex RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub> (instead of the usual Rh cluster carbonyl) by a ligand-exchange method similar to that used for the cluster compound.<sup>18</sup> When the usual feed purification methods were applied to exclude oxygen, the catalyst prepared from the complex aged much more rapidly than those prepared from the cluster compound. After an initial period of inconsistent operation, the former catalyst became gray and catalyzed hydrogenation of both cyclohexene and benzene at 75 °C and 1 atm, exhibiting an activity similar to that of Rh/Al<sub>2</sub>O<sub>3</sub>. We conclude that the metal complex species agglomerated more rapidly than the clusters.

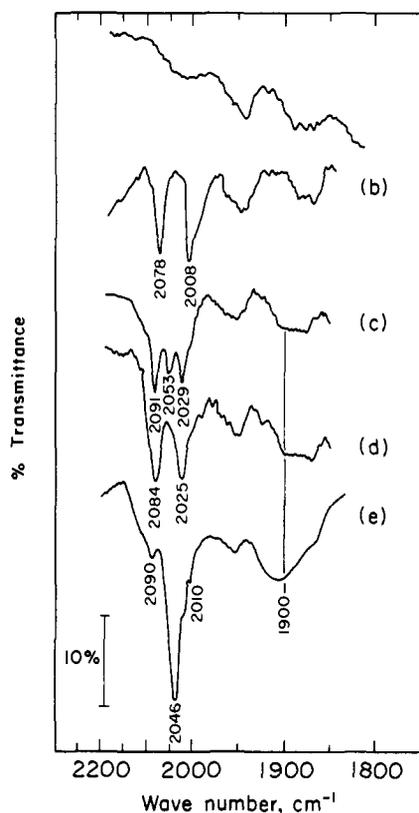
## Discussion

A unique property of the polymer with PPh<sub>2</sub> groups as a catalyst support is its ability to chelate a metal species, allowing stabilization of coordinative unsaturation of the metal and, consequently, catalytic activity.<sup>4,5</sup> We conclude from the results that when oxygen was allowed to contact the catalyst containing Rh clusters, the chelating phosphine ligands were oxidized to phosphine oxide, destroying the coordinative bonds between the support and the metal. Consequently, the less restricted metal migrated in the polymer matrix and approached coordinative saturation by formation of metal-metal bonds. This interpretation was confirmed by results with a polymer<sup>19</sup> having an unusually high phosphine to rhodium ratio, about 40 instead of the usual 1-2; this catalyst retained

**Table III.** Relative Activities of Catalysts for Hydrogenation of Cyclohexene and Benzene<sup>a</sup>

catalyst	sample no.	$10^3 \times$ benzene hydrogenation rate, mol/s-g-atom of Rh	rate of cyclohexene hydrogenation/rate of benzene hydrogenation
Rh/Al <sub>2</sub> O <sub>3</sub>		3.77	26
Rh cluster attached to poly(styrene-divinylbenzene) membrane	1	0.14	70
Rh/poly(styrene-divinylbenzene)	6	1.91	33

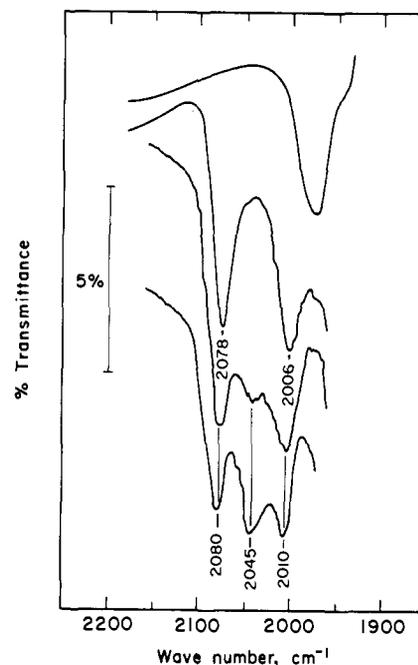
<sup>a</sup> Reactants were studied (separately) at 75 °C and 0.9 atm H<sub>2</sub> partial pressure and 0.13 atm hydrocarbon partial pressure.



**Figure 3.** Metal carbonyl spectra of a series of membranes prior to use as catalysts: (a) A freshly prepared membrane catalyst in the decarbonylated state. Infrared absorptions are those of the polymer support. (b) The freshly prepared membrane catalyst characterized by the data of Figure 1 following carbonylation by exposure to flowing CO for 3 h at 75 °C. It was golden-brown and evidently lacked Rh crystallites; the metal carbonyl spectrum closely resembles that of Rh<sub>6</sub>(CO)<sub>13</sub>(PPh<sub>3</sub>)<sub>3</sub>. (c) A membrane containing metal crystallites about 25 Å in diameter (sample 5) after carbonylation by exposure to flowing CO for 3 h at 75 °C. The band at 2053 cm<sup>-1</sup> is identified with CO bonded to Rh in a crystallite face. (d) The membrane (sample 6) of (c) following partial decarbonylation by exposure to flowing He for 12 h at 40 °C. The result indicates that CO bonded to Rh atoms in a crystallite face was more easily removed than CO bonded to Rh edge atoms. (e) A freshly prepared, carbonylated membrane which was black and contained crystallites of Rh approximately 40 Å in size, as determined by electron microscopy; there were far more Rh atoms on crystal faces than on edges.

its activity even after it had been held in air for several days at 125 °C. We infer that it remained a good chelating polymer even after oxidation of a large number of phosphine groups, since many still remained and could bond to the metal. Corresponding to the high stability of the polymer having a high phosphine to Rh ratio was a low catalytic activity (Table II), which we attribute to inhibition of the hydrogenation reaction by the excess phosphine groups.

Reasoning by analogy with solution chemistry,<sup>20</sup> we suggest that the oxidation of the phosphine ligands was catalyzed by the rhodium in the polymer; Grubbs and Su<sup>21</sup> similarly found



**Figure 4.** Metal carbonyl spectra of the membrane catalyst characterized by the data of Figure 1. The upper spectrum is of the unused, uncarbonylated catalyst, and the others (from top to bottom) are of the carbonylated catalyst following use in cyclohexene hydrogenation for 0, 120, and 250 h, respectively. The evolution of the spectrum indicates agglomeration of Rh in the catalyst.

that mononuclear Rh bonded to polymer-attached phosphine groups rapidly catalyzed the oxidation of the phosphine.

The metal clusters in the polymer must have had some coordinative unsaturation to be catalytically active, but we expect that the phosphine groups were not the only ones forming bonds with the metal. The phenyl rings of the polymer backbone are expected to have bonded to the metal also,<sup>22</sup> and this expectation finds some support in the result that benzene was a reaction inhibitor when the catalyst was Rh/Al<sub>2</sub>O<sub>3</sub> but not when it was Rh/poly(styrene-divinylbenzene). The former catalyst was several times more active than the latter (Table II), and this small difference might be explained by self-inhibition by the phenyl rings in the latter; catalysts contacted with CO only slowly developed a carbonyl spectrum, providing further evidence of such a polymer-metal interaction.<sup>5</sup>

Other ligands associated with the metal included hydrogen and hydrocarbon, since these were catalytically converted. The reaction orders in hydrogen suggest that it was dissociatively bonded, but the nature of the hydrocarbon intermediates remains obscure; even though the kinetics results were evidently free from the influence of mass transfer,<sup>14</sup> they are still far from sufficient to establish the details of the reaction mechanism. All we may conclude is that the data for the Rh-crystallite catalysts are consistent with a mechanism involving the rate-determining combination of surface H and hydrocarbon ligands, which is perhaps the most generally ac-

cepted mechanism for metal-surface-catalyzed hydrogenation.<sup>23</sup> Most such olefin hydrogenations are approximately zero order in olefin (reflecting the strong adsorption of this reactant), but the kinetics results of Table I suggest that the olefins were relatively weakly bonded to Rh at 75 °C. An explanation for the second-order dependence of rate on cyclohexene partial pressure has been suggested elsewhere.<sup>5</sup>

Although the data are not sufficient to provide a determination of the structures of the metal species present during the evolution of the freshly prepared catalyst, the spectra do yield some structural information. The catalysts which incorporated no observable metal crystallites had two sharp bands, one at 2078 cm<sup>-1</sup> and the other in the region 2015–1995 cm<sup>-1</sup> (the position differed somewhat from sample to sample and depended on the extent of carbonylation<sup>5</sup>). These are identified as the stretching frequencies of terminal carbonyl ligands on Rh; since they are close to the 2079- and 2005-cm<sup>-1</sup> bands of Rh<sub>6</sub>(CO)<sub>13</sub>(PPh<sub>3</sub>)<sub>3</sub> (reported by Iwatate et al.<sup>4b</sup>) we have proceeded under the assumption that the Rh carbonyl species were small clusters. As the phosphine ligands were oxidized and the Rh agglomerated, these two bands shifted slightly and decreased in intensity and a new, broad band formed at about 2045 cm<sup>-1</sup> (Figure 4), coinciding with that characterizing the polymer initially containing crystallites (Figure 3).

The band at about 2045 cm<sup>-1</sup> has been assigned to vibrations of CO bonded to a Rh atom on a crystal face,<sup>8</sup> and from the above discussion, the bands at about 2078 and 2008 cm<sup>-1</sup> are assigned to vibrations of CO bonded to Rh atoms at the edges of small Rh entities including those between the undefined limits of clusters and crystallites. The band at about 1900 cm<sup>-1</sup> (Figure 3) is assigned to a bridging CO.<sup>8</sup>

These assignments, combined with the result that the crystallite size distributions (Figure 2) appeared to be nearly uniform at two different degrees of catalyst aging, lead us to the suggestion that genesis of the supported-metal catalyst involved the gradual agglomeration of Rh in the polymer matrix in such a way that the metal entities were nearly uniform in size at each stage of the process. This suggestion is speculative and in need of critical examination by further experimentation, but it is important because, if it proves to be correct, the means are at hand for preparation of graded sets of catalysts having nearly unique metal entities in just the critical size range which has eluded systematic characterization. We expect that the preparation method could be extended to other metal-cluster compounds (including bimetallics) and a variety of polymeric supports; the physical properties of the support (e.g., the resistance to diffusion, influenced by the cross-link density) are expected to affect the metal agglomeration rate. Supported-metal catalysts prepared in this way can be expected to yield to structural determination by EXAFS<sup>24</sup> (which has recently provided the structure of the polymer-bound analogue of Wilkinson's catalyst<sup>25</sup>) and laser Raman spectroscopy (which may provide evidence of the metal-metal bonds<sup>26</sup>).

### Experimental Section<sup>5,14</sup>

Polymer membranes having a thickness of approximately 7 μm were synthesized from the monomers styrene, divinylbenzene, and *p*-bromostyrene.<sup>27</sup> Treatment with LiPPh<sub>2</sub> in refluxing THF under N<sub>2</sub> for about 2 days led to replacement of a small fraction of the -Br groups with -PPh<sub>2</sub> groups. Each resulting membrane was brought in contact with a solution of Rh<sub>6</sub>(CO)<sub>16</sub> (Strem) in benzene; the ensuing reaction led to the incorporation of Rh into the polymer. Each sample was analyzed by Galbraith Laboratories, Knoxville, Tenn., for Rh, P, and Br. Occasionally, brominated macroporous beads of poly(styrene-divinylbenzene) (Aldrich) were used in the synthesis instead of the membranes, which lacked macropores.

Transmission electron microscopy was used to investigate samples embedded in epoxy resin; microtomed sections were supported on a

carbon film and a Cu grid in the electron beam of a Philips EM-200 microscope.

The hydrogenation reactions were carried out in a flow reactor system allowing simultaneous measurement of reaction rates and infrared spectra of a functioning catalyst membrane.<sup>18</sup> The reactant stream contained vaporized cyclohexene or benzene (redistilled from LiAlH<sub>4</sub> under N<sub>2</sub>) fed from a syringe pump, or ethylene fed from a high-pressure cylinder; the stream also contained H<sub>2</sub>, He, and/or CO, which flowed from cylinders through an oxygen trap of particles of supported Cu at 300 °C (Harshaw, Cu-0803T catalyst, activated in flowing H<sub>2</sub> at 200 °C for 2 h) and through a water trap of particles of zeolite 5A (Linde, activated in flowing He at 400 °C for 2 h). The reactant vapors passed through a thermostated gas cell held in the sample compartment of a Beckman IR-12 infrared spectrophotometer. The cell held a catalyst membrane perpendicular to the beam of infrared radiation. Product vapors flowed from this cell (the reactor) through a compensating gas cell, and conversions were so low that spectra of the vapors in the two cells nearly canceled. Therefore, the observed spectra were indicative of the catalyst membrane. Product vapors flowing from the reference cell were periodically sampled for quantitative analysis by gas chromatography.

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## Mechanisms of Chlorine Oxidation of Hydrogen Peroxide

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**Abstract:** Kinetic parameters for two-electron oxidation of hydrogen peroxide by hypochlorous acid have been determined. Reaction with HOCl proceeds according to the rate law  $d[O_2]/dt = k_2[HOCl][H^+][Cl^-]$ ; with  $OCl^-$  ion,  $d[O_2]/dt = k_3[H_2O_2][OCl^-]$ . For the alkaline ( $k_3$ ) pathway, the primary yield of electronically excited oxygen was measured by chemical trapping with 2,5-dimethylfuran (DMFu); results indicate essentially 100% initial formation of ( $^1\Delta$ ) $O_2$ . The rate law for reaction with HOCl is identical with that found for halogenation of DMFu and other reactive organic molecules and, possibly, for conversion of HOCl to  $Cl_2$ . Kinetic arguments are presented supporting the view that these reactions proceed by rate-limiting formation of a common reactive intermediate whose stoichiometry is  $H_2OCl_2$ . From consideration of available thermodynamic parameters, molecular mechanisms and activated complex geometries for the various pathways are proposed.

### Introduction

Oxidation of hydrogen peroxide by hypochlorite ion forms electronically excited molecular oxygen.<sup>1,2</sup> The reaction has been used extensively as a source of  $^1\Delta$  oxygen both for analytical<sup>3</sup> and synthetic purposes,<sup>4</sup> and has been proposed to play a central role in biological disinfection processes.<sup>5</sup>

In 1947, Connick made a careful study of the reaction in acidic aqueous media.<sup>6</sup> In addition to providing a kinetic description of hydrogen peroxide oxidation by molecular chlorine, he was able to detect two additional pathways, one identified as the hydrogen peroxide-hypochlorite ion reaction and another whose rate law and reaction stoichiometry were only ill defined. The  $H_2O_2-Cl_2$  reaction has been given alternative mechanistic interpretations;<sup>6,7</sup> observation of chemiluminescence arising from radiative deactivation of singlet oxygen produced in the reaction has been claimed,<sup>8</sup> but could not be reproduced.<sup>9</sup> More recently, Kajiwara and Kearns have reported results from a cursory study of the reaction in alkaline solution<sup>9</sup> for which apparently straightforward overall second-order kinetics were observed in  $H_2O$ , but quite complex kinetic behavior was noted in  $D_2O$ . Chemiluminescence measurements allowed identification of the  $H_2O_2-OCl^-$  pathway as the origin of singlet oxygen; the product yield could not be established.

With the intention of clarifying these points we have undertaken a rigorous examination of the redox reactions. From the results described herein it has proved possible to draw numerous mechanistic inferences regarding the nature of the activated complexes associated with the various pathways. Additionally, based upon our perception of a reactive intermediate common to several diverse reactions involving hypochlorous acid, we propose what is hopefully a useful unifying view of these reactions.

### Experimental Section

**Reaction Rates and Stoichiometries.** The reactions of hypochlorous acid with hydrogen peroxide and 2,5-dimethylfuran (DMFu) were studied using a variable speed drive assembly<sup>10</sup> coupled to 0.1-1.0-cm optical cells in a Cary 16 recording spectrophotometer. Loss of  $OCl^-$

ions was followed at 290 nm,<sup>11</sup> loss of DMFu at 215 nm, and appearance and decay of intermediates in the DMFu oxidation reaction at 240 nm. Additional measurements of the relatively rapid  $H_2O_2-OCl^-$  reaction were made on a Gibson-Durrum stopped-flow instrument. Oxygen concentrations were measured polarographically using a Clark-type oxygen electrode (Yellow Springs Instrument Co., Model YS-4004). The electrode was inserted into a Pyrex-jacketed cell (Figure 1) maintained at constant temperature by the circulation of water from a thermostated bath through the jacket. Response was monitored with a 1-mV recorder interfaced to the electrode by the circuit shown in Figure 1. The instrument was calibrated by the injection of a known volume of oxygen-saturated or air-saturated solvent, and by the addition of hydrogen peroxide followed by catalase.<sup>12</sup> The system response was tested under a variety of conditions and no deviations from linearity were found for the pH and salt concentrations used in the experiments. Changes in sensitivity with solvent composition and temperature were dealt with by recalibration. Oxygen formation rates were determined by injection of hypochlorite reagent into hydrogen peroxide solutions which had previously been deoxygenated by bubbling with nitrogen. Concentrations were adjusted to ensure that electrode response times were not rate limiting.

Stoichiometries for the  $H_2O_2-HOCl$  reaction were established by determination of oxygen yields, by determination of chloride ion formation using an ion-selective electrode, and by standard iodometric titration.<sup>13</sup> For the last method, known quantities of reactants were mixed with hydrogen peroxide in slight excess. Hydrogen peroxide remaining after reaction ceased was determined by  $I_2$ -thiosulfate titration. Reactant concentrations for kinetic runs were determined by direct iodometric titration and/or absorption spectrometry.

**Determination of  $^1\Delta$ -Oxygen Yields by Chemical Trapping.** Singlet oxygen yields were measured by determining the extent of  $O_2$  trapping by acceptor molecules accompanying chlorine oxidation of  $H_2O_2$ . Assuming the mechanism given in Scheme I, fractional yields of singlet oxygen initially formed ( $Y_1$ ) are given by  $Y_1 = k_i/(k_i + k_{ii})$ . Yields of  $AO_2$  formed during reaction ( $Y_{AO_2}$ ) depend both upon  $Y_1$  and upon partitioning of the intermediate over its various decomposition pathways, steps iii-v, i.e.,  $Y_{AO_2} = Y_1[k_{iv}[A]/(k_{iii} + k_{iv}[A] + k_v)]$ . In reciprocal form,  $Y_{AO_2}^{-1} = Y_1^{-1}(1 + \beta/[A])$ , where  $\beta = (k_{iii} + k_v)/k_{iv}$ . The equations are formally analogous to those used in analysis of photosensitized generation of singlet oxygen;<sup>3b,14</sup> measurement of  $Y_{AO_2}$  as a function of  $[A]$  permits determination of  $Y_1$ .

The compound 2,5-dimethylfuran was chosen as chemical trapping