Catalytic Hydrogenation of Vegetable Oils I-Hydrogenation of Soybean Oil Catalyzed by Rh- and Ir- Complexes

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ABSTRACT

The rate and selectivity found for the hydrogenation reaction of soybean oil using a series of soluble rhodium and iridium-phosphine complexes can be correlated to the number of phosphine ligands coordinated to the metal. This study shows the possibility of obtaining a wide range of products by varying the reaction time and the catalyst composition. For example, a low stearate content can be obtained using $IrCl(C_8H_{12})PPh_3$, whereas a low double-bond conjugation can be obtained with $[Rh(C_8H_{12})(PPh_3)_2]BPh_4$.

INTRODUCTION

It is well known that many difficulties, mainly due to the separation of a soluble catalyst, suggest a general use of heterogeneous catalysts in industrial processes. However, there is today also a trend to use homogeneous catalysis in a wide field of chemical reactions due to the possibility of obtaining a certain reaction pattern by varying the composition and structure of the catalysts.

Recent work in the partial hydrogenation of vegetable oils leads to the study of stereo-and polyene-selective catalysts able to give the desired products in high yields. Thus, Frankel and coworkers have found very low content of trans-isomers and good trienediene selectivity by using a series of M(arene) $(CO)_3$ complexes (M=Cr, Mo, W) in the hydrogenation of soybean oil, (1-3). The same research group and others explored the activity of different metal carbonyls, metal phosphine (4-11) and metal chelate (12) complexes. Following research on the synthesis of transition metal hydrido complexes and on their use in the catalytic hydrogenation of unsaturated substrates (13-15), we have tested the activity of a series of rhodium and iridium complexes containing different triphenylphosphine/metal ratio as catalysts for the hydrogenation of the soybean oil.

From this study we have attempted to make new correlations of catalytic activity and molecular structure among a series of very similar catalysts.

EXPERIMENTAL PROCEDURES

The soybean oil was a crude product having the following composition C16:0 = 11.1%; C18:0 = 4.5%; C18:1 = 23.5%; C18:2 = 53.5%; C18:3 = 7.5% and I.V. (glc) 131.7. The oil, solvents and catalysts were kept under nitrogen atmosphere until analytical determinations. I.R. analysis for total trans isomer was done according to reported methods (16,17) using a Perkin-Elmer 577 instrument, and the analysis for conjugated dienes, by the U.V. method (16,18), using a C. Zeiss DMR 21 instrument. Gas chromatographic determinations were carried out with a Hewlett-Packard 5750 apparatus connected to a Hewlett-Packard 3380 A integrator using an EGSS X (10% on Chrom P) column (1.7m x 1/8"). C18 methyl esters, purchased from C. Erba, were used as standard. Transesterification to methyl esters was done by using BF_3 in CH_3OH. Selectivities SL_o and SL_n were calculated according to Butterfield and Dutton (19), using a digital computer program for a Hewlett-Packard model 9825 A computer, assuming that hydrogenation follows the simplified steps: triene → diene → monoene → stearate. Selectivity values at any I.V. were calculated with respect to the starting composition by considering the *total amount* of dienes (conjugated + nonconjugated isomers). The amount of monoenes and nonconjugated dienes (various positional and stereo-isomers) were calculated by GLC data, whereas the trienes were calculated by subtracting the amount of total conjugated isomers (by u.v. method) from the amount of trienes + conjugated dienes calculated by GLC (overlapped peaks) (1).

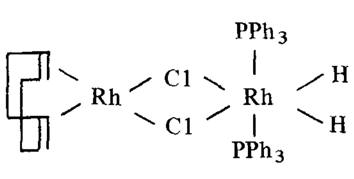
The preparation of the Rh- and Ir- catalysts was performed according to the literature (Table I). The hydrogenation reactions were carried out in a thermostatted glass cell (50 ml), provided with magnetic stirrer, connected to a graduated gas burette which contained pure H_2 (1 ATM) on mercury. Sampling for analyses was done through a rubber septum.

Different amounts of catalysts, dissolved in 2 ml of solvent (Table I) under nitrogen were treated with the oil (10 ml) to obtain a 2.7 10^{-3} metal molarity.

RESULTS AND DISCUSSION

The complexes tested for catalytic hydrogenation of soybean oil (Table I) are active under mild conditions (T = 80C; P_{H_2} = 1 ATM) as shown by the results in Figures 1-5.

Among the Rh- series the rate of H_2 consumption gradually increases with the number of phosphine ligands from 0 to 3 (Fig. 1). This trend can be correlated to the easier oxidative addition of molecular hydrogen to rhodium complexes rich in phosphorus ligands such as $[RhCl(PPh_3)_2]_2$ and $RhCl(PPh_3)_3$ (20) (which favors subsequent hydrogen transfer to olefins), compared to the slower hydrogen activation shown by inert tetracoordinated Rh(I) complexes such as $RhCl(C_8H_{12})PPh_3$. In fact, our previous work has shown that the reactivity toward H_2 can be obtained, in this latter case, only at high temperature and with modification of the original compound which produces an unsymmetrical binuclear complex of formula



where two hydrogens are bonded to the rhodium atom stabilized by two phosphine ligands (21). We think that the cyclooctadiene ligand does not play a significant role in the catalyst activity because it can be easy substituted by the unsaturated reactants (22-26).

The relatively high hydrogenation rate observed with $Rh_2Cl_2(C_8H_{12})_2$ is caused by a slow decomposition of the catalyst which produces a finely dispersed metal behaving as an active catalyst.

A different catalyst modification can also be obtained by eliminating the chloro ligand. Thus, using the cation $[Rh(C_8H_{12})(PPh_3)_2]^+$ we can compare its activity with that of $[RhCl(PPh_3)_2]_2$: as expected, the absence of the strong coordinating chloro ligand favors easier coordination

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TABLE I

Catalytic System Used for the Hydrogenation of Soybean Oil

Catalyst	P/M[a]	Solvent	Method of Preparation
$RhCl(PPh_3)_3$	3	Toluene	20
$Rh_2Cl_2(PPh_3)_4$	2	Toluene	20
$RhCl(C_8H_{12})PPh_3$	1	Toluene	21
$Rh_2Cl_2(C_8H_{12})_2$	0	None	22
$[Rh(C_8H_{12})(PPh_3)_2]^+BPh_4^-$	2	Hexan-3-one	23
$IrH_2Cl(PPh_3)_3$	3	Toluene	24
$IrCl(C_8H_{12})PPh_3$	1	Toluene	21
$Ir_2Cl_2(C_8H_{12})_2$	0	None	22
$[Ir(C_8H_{12})(PPh_3)_2]^+BPh_4^-$	2	Hexan-3-one	23

[a] Number of phosphineligands per metal atom.

of the reactants to the metal, and the positive charge, which induces a higher reactivity toward the nucleophilic unsaturated esters, produces a higher hydrogenation rate.

In the series of the rhodium complexes trans- isomer formation is also influenced by the catalyst composition. The active phosphine-rich catalysts produce also a high amount of trans isomers (Fig. 3). However, the complex $RhCl(PPh_3)_3$, which shows the highest hydrogenation rate (Fig. 1), is the most selective because it produces the lowest trans content at any I.V. (Fig. 3).

The values of the selectivities S_{Ln} and S_{Lo}, calculated as described in the experimental part, have been reported for different catalysts. In the Rh- series, the S_{Ln} values are always higher than those of S_{Lo}, and both varied during the course of reactions (Fig. 2a, 2d and 2e).

This latter behavior, which was also observed by other authors (12), can be probably caused by chemical modifications suffered by the unsaturated glycerides (formation of trans isomers and of conjugated dienes). However, no logical relations between catalysts' composition and selectivity can be derived from our data.

A very different trend in hydrogenation rate is observed with use of the iridium derivatives (Fig. 4). In fact, in the series of neutral complexes, the correlation between phosphine-ligands and reactivity is just the opposite of that found with Rh-complexes, because the most active catalyst contains only one triphenylphosphine ligand and the less active three triphenylphosphine ligands. Moreover, the cation $[Ir(C_8H_{12})(PPh_3)_2]^+$ is less active than the neutral system containing two phosphine ligands. In this case, however, the P/Ir = 2 ratio was obtained by adding one mole of free triphenylphosphine per mole of $IrCl(C_8H_{12})PPh_3$, owing to the fact that a neutral bis(triphenyphosphine)iridium complex is not known. Thus, in the absence of a more detailed study of this catalytic system, we have to assume two possibilities: 1) that a bis-triphenylphosphine complex stabilized by the unsaturated esters is the actual catalyst; and 2) that equimolar amount of $IrCl(C_8H_{12})PPh_3$ and $IrH_2Cl(PPh_3)_3$ are the active species. These latter, in fact, can be generated by the following reactions (13,14):

$$2\,IrCl(C_8H_{12})PPh_3 + 2H_2 \rightarrow Ir_2H_2Cl_2(C_8H_{12})(PPh_3)_2 + C_8H_{14}$$

$$Ir_2H_2Cl_2(C_8H_{12})(PPh_3)_2 + 2PPh_3 \rightarrow IrCl(C_8H_{12})PPh_3 + IrH_2Cl(PPh_3)_3.$$

Both these assumptions agree with the observed hydrogenation rate which is intermediate between that observed with $IrCl(C_8H_{12})PPh_3$ and with $IrH_2Cl(PPh_3)_3$ (Fig. 4).

The low activity of the triphenylphosphine-rich Ir-complexes can be explained by the high stability of the hydrido-complexes, containing many phosphine ligands, which does not facilitate ligand dissociation and consequent olefin activation.

The trans-formation caused by these Ir- catalysts is similar to that of Rh- compounds. In fact, we can form a low trans-isomers' content by using the most active catalysts having a P/M=2 and 1, as shown in Fig. 5.

As expected (14), the neutral Ir-complexes shown a diene/monoene selectivity (S_{Lo}) higher that the Rh-complexes; also for these catalysts, the selectivity values varied during the hydrogenation reaction (Fig. 2f - 2j).

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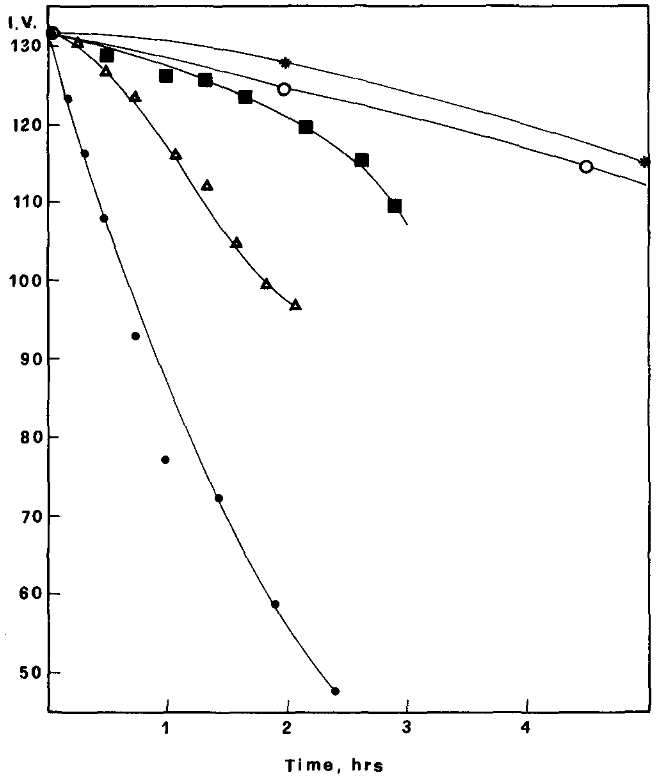


FIG. 1. Variation of i.v. in hydrogenation of soybean oil catalyzed by rhodium complexes. Key: ● = $RhCl(PPh_3)_3$; ○ = $Rh_2Cl_2(PPh_3)_4$; * = $RhCl(C_8H_{12})PPh_3$; ■ = $[RhCl(C_8H_{12})]_2$; △ = $Rh(C_8H_{12})(PPh_3)_2BPh_4$.

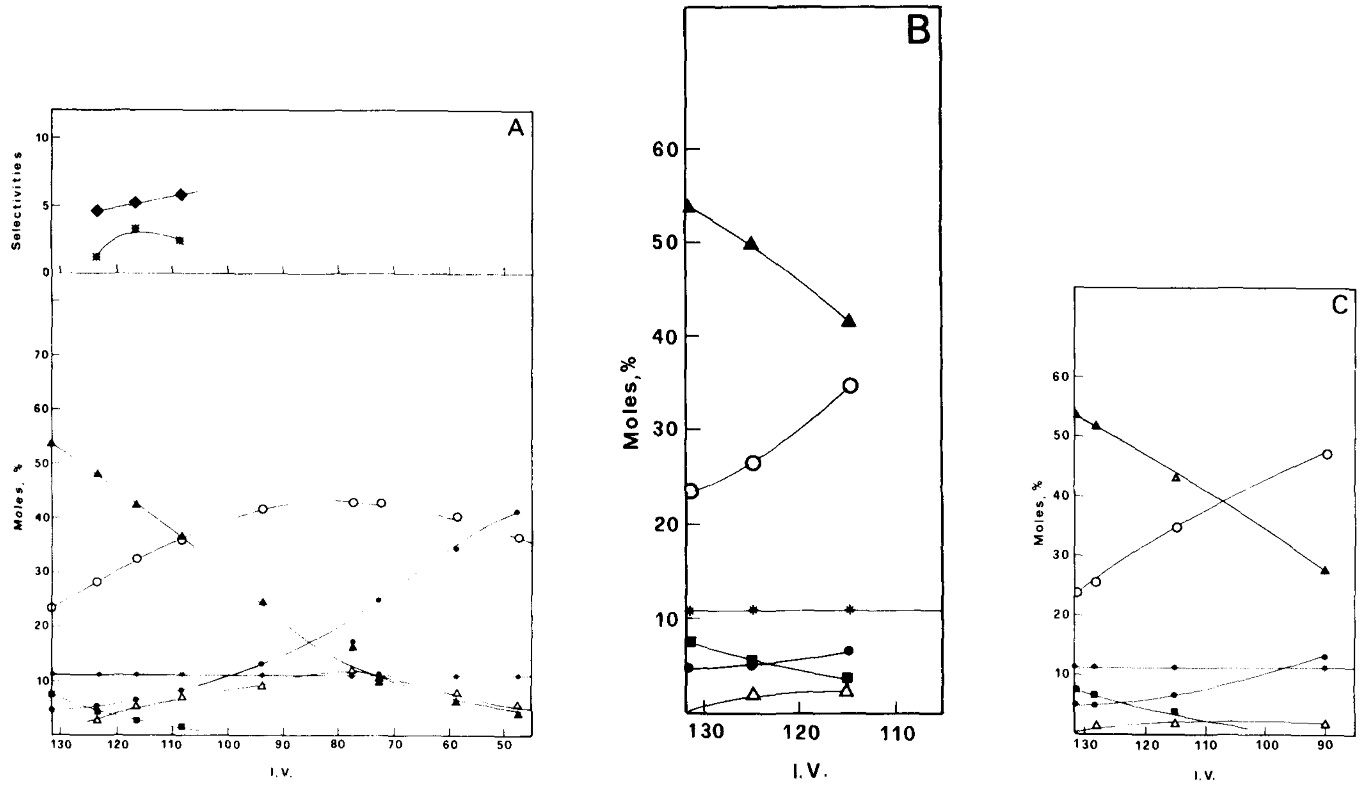
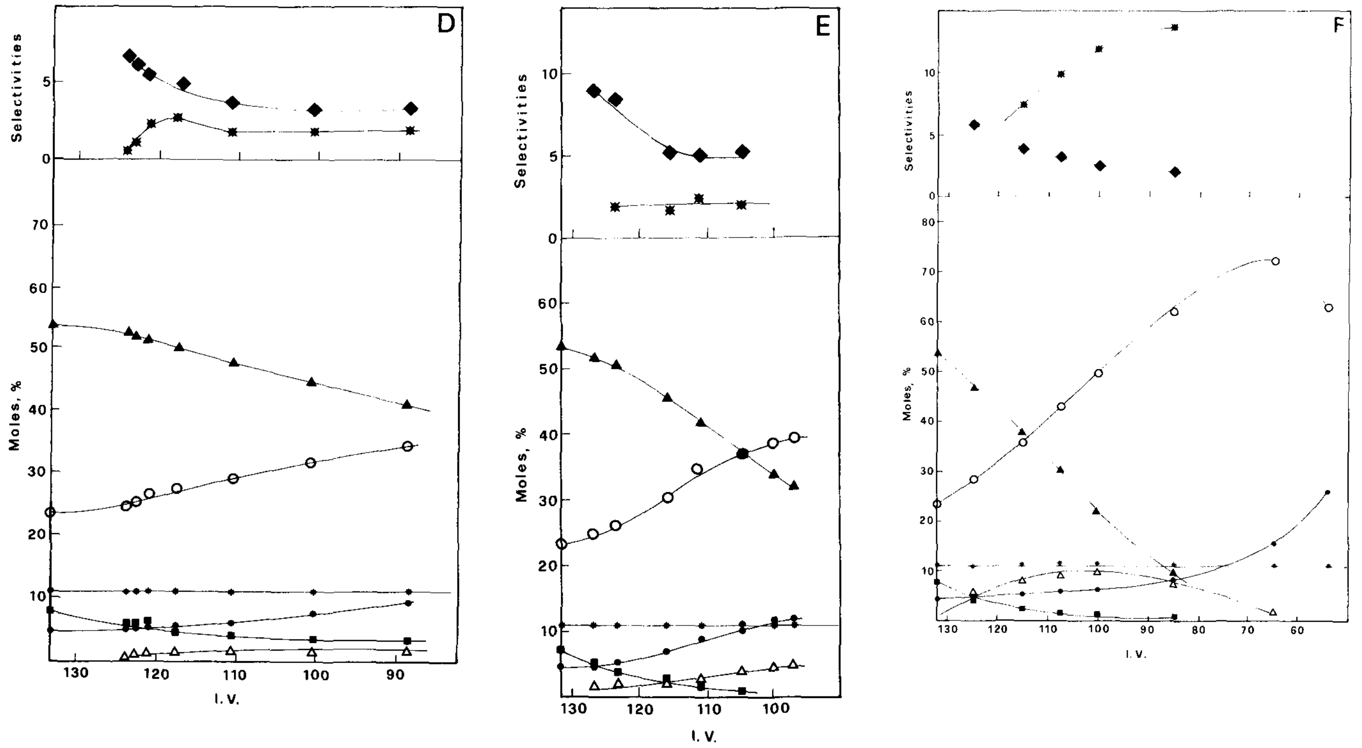


FIG. 2. Molar percentage of fatty acid methyl esters and selectivities versus i.v. in the hydrogenation of soybean oil catalyzed by rhodium and iridium complexes. a) $RhCl(PPh_3)_3$; b) $Rh_2Cl_2(PPh_3)_4$; c) $RhCl(C_8H_{12})PPh_3$; d) $Rh_2Cl_2(C_8H_{12})_2$; e) $[Rh(C_8H_{12})(PPh_3)_2]BPh_4$; f) $IrCl(C_8H_{12})PPh_3$; g) $IrCl(C_8H_{12})PPh_3+PPh_3$; h) $IrH_2Cl(PPh_3)_3$; i) $Ir_2Cl_2(C_8H_{12})_2$; j) $[Ir(C_8H_{12})(PPh_3)_2]BPh_4$. Key: * = C16:0; ●=C18:0; ○=C18:1; ▲=C18:2; ■=C18:3; △=conjugated diene; ◆=triene:diene selectivity (S_{ln}); ★=diene:monoene selectivity (S_{lo}).



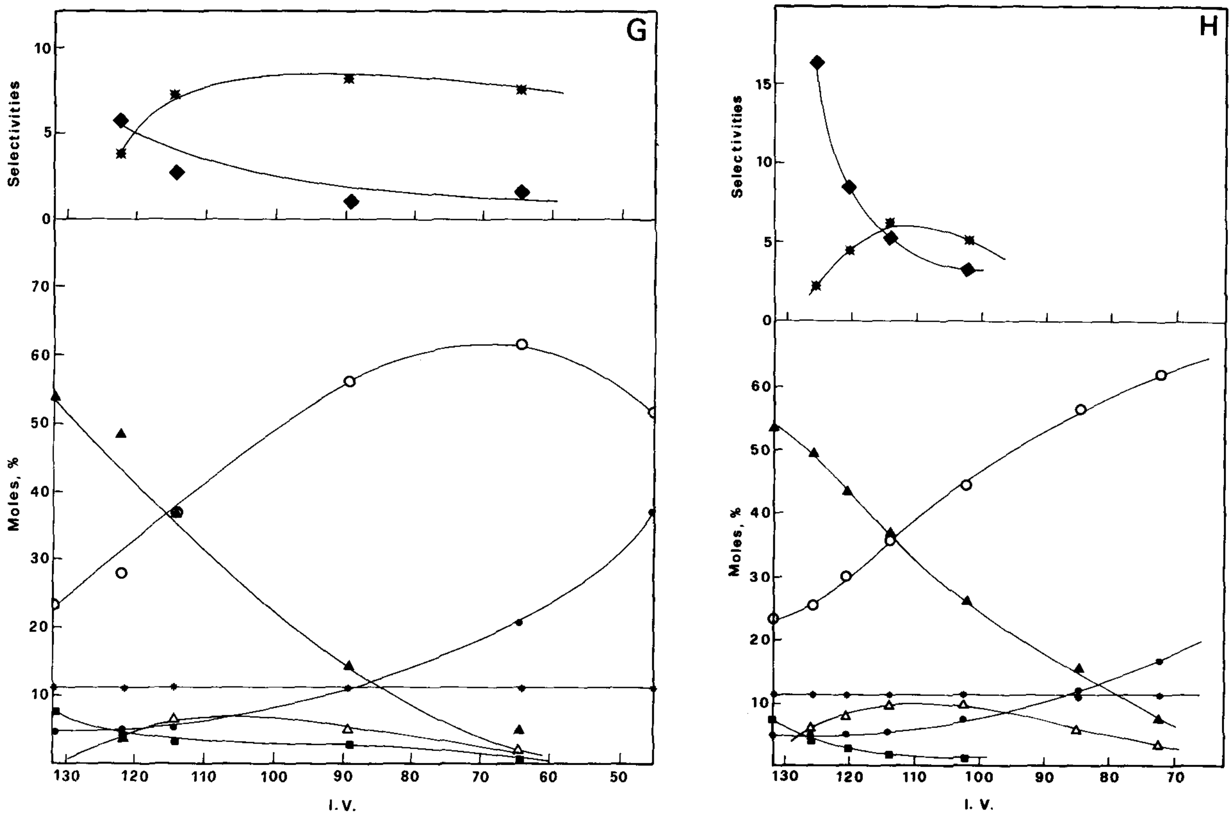
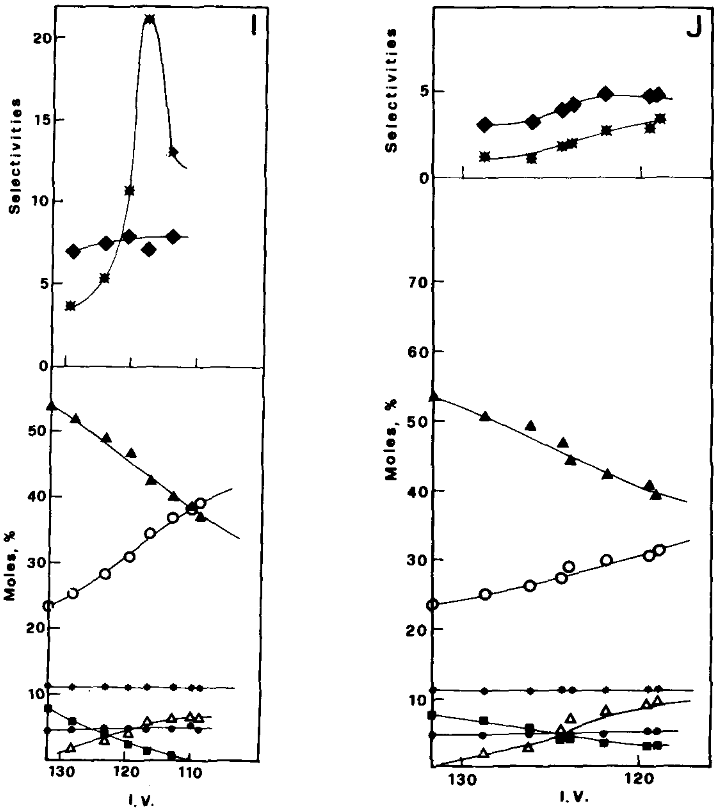


FIG. 2. Continued.



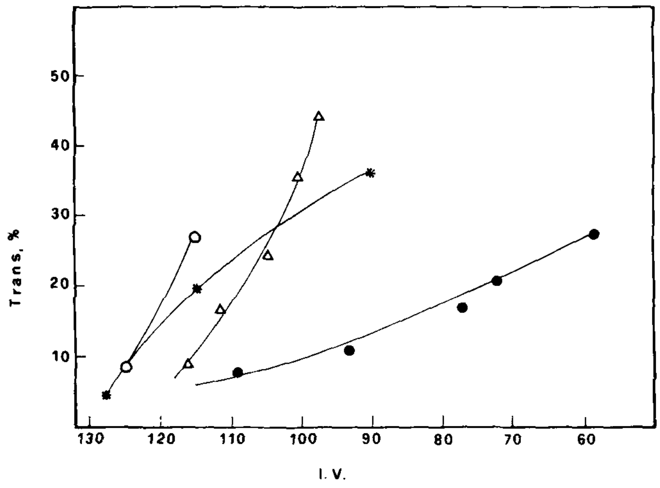


FIG. 3. Percentage of trans isomers (as methyl elaidate) vs. I.V. in the hydrogenation of soybean oil catalyzed by rhodium complexes. Key: ● = $RhCl(PPh_3)_3$; △ = $Rh(C_8H_{12})(PPh_3)_2BPh_4$; ○ = $Rh_2Cl_2(PPh_3)_4$; * = $RhCl(C_8H_{12})PPh_3$.

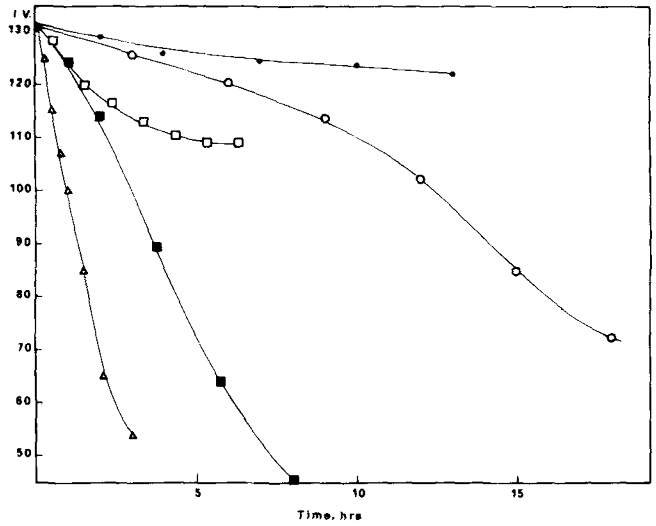


FIG. 4. Variation of I.V. in the hydrogenation of soybean oil catalyzed by iridium complexes. Key: △ = $IrCl(C_8H_{12})PPh_3$; ■ = $IrCl(C_8H_{12})PPh_3+PPh_3$; □ = $[IrCl(C_8H_{12})]_2$; ○ = $IrH_2Cl(PPh_3)_3$; ● = $Ir(C_8H_{12})(PPh_3)_2BPh_4$.

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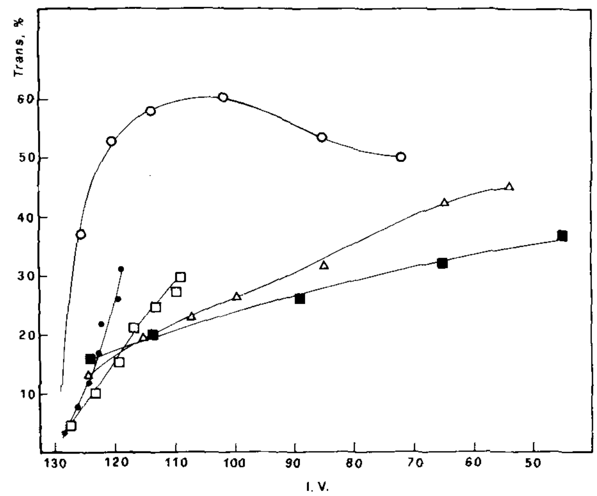

FIG. 5. Percentage of trans isomers (as methyl elaidate) vs. I.V. in the hydrogenation of soybean oil catalyzed by iridium complexes. Key: △=$IrCl(C_8H_{12})PPh_3$; ○=$IrH_2Cl(PPh_3)_3$;■=$IrCl(C_8H_{12})PPh_3+PPh_3$; □ = $[IrCl(C_8H_{12})]_2$; ● = $Ir(C_8H_{12})(PPh_3)_2BPh_4$.

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