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EQUILIBRATION OF *ortho*- AND *para*-HYDROGEN BY HOMOGENEOUS HYDROGENATION CATALYSTS IN SOLUTION; A TEST FOR THE REVERSIBILITY OF HYDROGEN ADDITION USING RAMAN SPECTROSCOPY

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Summary

para-Enriched hydrogen is converted into the *ortho–para* equilibrium mixture by tris(triphenylphosphine)rhodium chloride in toluene solution. The rotational Raman effect can be used to show that this equilibration occurs during the course of hydrogenation of cyclohexene by the above catalyst. The methanol solvate formed by reduction of 1,4-bis(diphenylphosphino)butanebicyclo[2.2.1] heptadienerhodium tetrafluoroborate also catalyses the *ortho–para* equilibration of hydrogen, in common with related cationic rhodium complexes. No equilibration occurs, however, during the course of hydrogenation of (*Z*)-α-benzamidocinnamic acid by cationic chelate rhodium complexes, including that derived from the chiral ligand (*R*,*R*)-1,2-bis(*o*-methoxyphenylphenyl)ethane (DIPAMP), thus demonstrating that addition of hydrogen to rhodium is irreversible.

Introduction

The mechanism of homogeneous hydrogenation by Wilkinson's catalyst, tris(triphenylphosphine)rhodium chloride, has been established through careful kinetic [1] and spectroscopic [2] studies with theoretical support [3]. The addition of hydrogen occurs predominantly to $ClRh(PPh_3)_2$ present at very low concentration and the resulting dihydride $ClH_2Rh(PPh_3)_2$ complexes an olefin prior to hydride transfer in the rate-limiting step. A second minor pathway involves a chloro-bridged dimer formed in equilibrium with monomeric complexes. It is implicit in this mechanism that hydrogen addition is reversible, and both Ohtani [1], Tolman [2] and their respective co-workers report that loss of hydrogen from the coordinatively saturated

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complex $ClH_2Rh(PPh_3)_3$ can be followed spectroscopically. This overall mechanism involving addition of substrate to a reversibly formed rhodium dihydride is not followed during the reduction of dehydroaminoacid derivatives by chelate biphosphine rhodium complexes since substrate coordination is here the first step of the catalytic cycle [4]. In the latter case there is no means of knowing whether hydrogen addition is reversible or not, and we sought a general test. Reversible addition must lead to equilibration of *ortho-* and *para*-hydrogen, a well-established phenomenon for surfaces and dissolved paramagnetic species but one only rarely observed [5] for diamagnetic complexes in solution until recently. Whilst our own work was in progress Tadros and Vaska [6] published a very comprehensive study of *ortho–para* hydrogen equilibration by iridium, ruthenium and platinum complexes. They observed that oxidative addition is a prerequisite to equilibration and that platinum complexes which are inert to hydrogen addition do not catalyse the reaction.

Hydrogenations by tris(triphenylphosphine)rhodium chloride

A *para*-enriched sample of hydrogen was readily prepared by standing pure oxygen-free hydrogen over magnetite at −196°C for 20 min and then transferring the gas to a magnetically stirred vessel (see Experimental section) which contained the catalyst and reactant solution maintained at −80°C and which carried a side-arm arranged for observation by laser-Raman spectroscopy. The two rotational isomers of hydrogen are then readily distinguished by their Stokes emissions at $\Delta\nu$ 587 (*ortho*) and 354 cm^{-1} (*para*). The reaction vessel was allowed to reach ambient temperature, stirring commenced and the appropriate regions of the Raman spec-

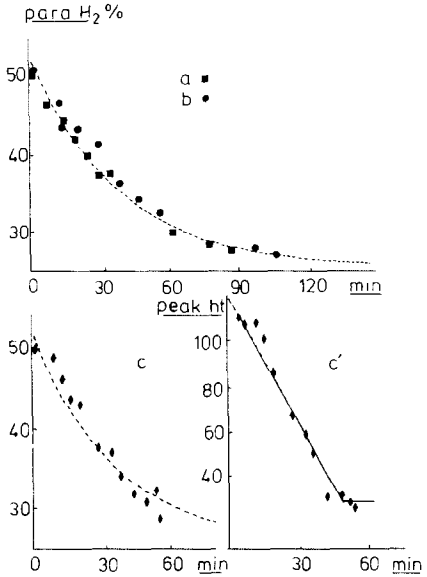


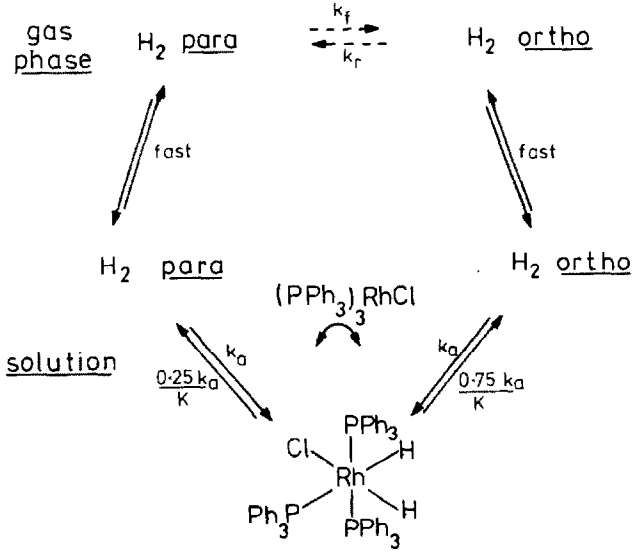
Fig. 1. Reactions of *para*-hydrogen (140 ml, ~1 atm) with $ClRh(PPh_3)_3$ (50 mg) in toluene (8–10 ml) at 20°C. Runs (a) and (b) are duplicates with ●, ■ representing experimental points and the computer-drawn line corresponding to $k_f = 0.000105\ s^{-1}$ in eq. 1 and $[H_2]_{0para} = 0.51$ atm. Run (c) is similar with 500 μl added cyclohexene, $k_f = 0.000115\ s^{-1}$ and $[H_2]_{0para} = 0.52$ atm. The points ◆ displayed in c′ represent decay of the total peak height during c.

trum recorded at regular timed intervals. Under our conditions, blank experiments demonstrated that in the absence of catalyst less than 5% equilibration occurred over 2 h.

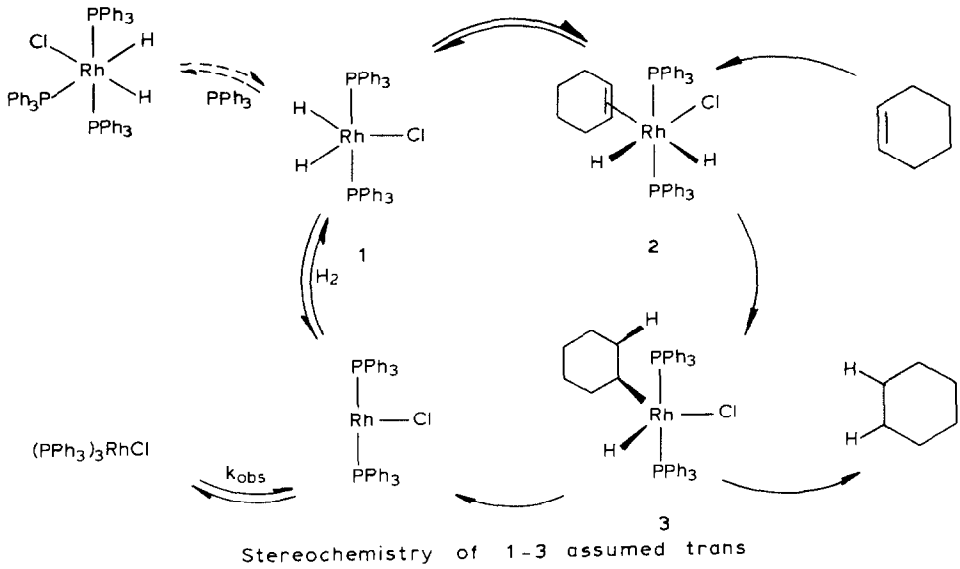
Observations made on toluene solutions of tris(triphenylphosphine)rhodium(I) chloride are recorded in Fig. 1. In the absence of excess triphenylphosphine, the proportion of *para*-hydrogen diminishes steadily with time and equilibrium is obtained in a little more than 1 h at ambient temperature. The reaction vessel is not thermostatically controlled, and this together with the limitations of accuracy in measurement of peak heights precludes determination of accurate rate-constants. Nevertheless, the shape of the decay curve of (% *para*-H_2) versus time is in accord with what is expected for the reversible first-order reaction of equation 1. Computer simulation (Fig. 1) indicated a forward rate-constant k_f of $1.05 \times 10^{-4} s^{-1}$ for experiments in which a solution of $ClRh(PPh_3)_3$ (54 μmol in 8–10 ml toluene) reacted with 140 ml of H_2 (initially 51% *para*) at ambient pressure.

$$H_2\,(para) \underset{k_n}{\overset{k_f}{\rightleftharpoons}} H_2(ortho);\ k_f = 3k_r \qquad (1)$$

The quality of fit observed in this analysis encouraged a more detailed treatment, assuming that $ClRh(PPh_3)_2$ and not the ψ-chloro-bridged dimer is the reacting species. It was further assumed that mass transport between the gas and solution phases is not rate-limiting and that hydrogen was at saturation solubility of 0.0036 *M*. Now Halpern has studied the mechanism of addition of hydrogen to $ClRh(PPh_3)_3$ in some detail [1] and convincingly concludes that in the absence of added ligand the first step is reversible dissociation of PPh_3 followed by H_2 capture by the 14-electron complex $ClRh(PPh_3)_2$. The dissociation step is rate-limiting and thus the overall reaction is independent of $[H_2]$ with an observed rate-constant $k_{obs} = 0.68\ s^{-1}$. Making the assumptions outlined above and no others, it proved possible to simulate our data for *ortho–para* hydrogen interconversion using a rate-constant for PPh_3



SCHEME 1. Kinetic scheme employed for the analysis of *ortho–para* hydrogen interconversion.



SCHEME 2. The mechanism of hydrogenation by $ClRh(PPh_3)_3$ and *ortho–para* hydrogen interconversion therein.

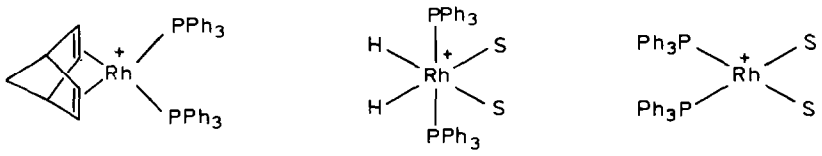
dissociation from Wilkinson's catalyst of $k_a = 0.7\ s^{-1}$ according to Scheme 1. The fit is excellent, and leads us to believe that *ortho–para* hydrogen interconversion is proceeding by the same mechanism (Scheme 2), and involves reversible hydrogen addition to the complex. This result gave us sufficient confidence to test the reversibility of hydrogen addition under catalytic conditions.

Hydrogenation of olefins catalysed by $ClRh(PPh_3)_3$ requires that the substrate adds to the coordinatively unsaturated intermediate $ClH_2Rh(PPh_3)_3$ prior to rate-determining hydride transfer. Our results demonstrate (Fig. 1) that *ortho–para* H_2 interconversion proceeds at essentially the same rate during hydrogenation, implying that H_2 elimination from the intermediate is much faster than its interception by olefin.

In the presence of excess PPh_3 the rate of *ortho–para* H_2 interconversion by $ClRh(PPh_3)_3$ is slowed, particularly during the initial stages, with an apparent induction period. The data could not readily be fitted to a kinetic model.

Hydrogenations by cationic rhodium complexes

(a) From triphenylphosphine. Schrock and Osborn [7] have described a detailed study of homogeneous hydrogenation catalysed by chelating diolefin rhodium bis-phosphine cations, such as **4**. They suggest that in a coordinating solvent rapid hydrogenation of the catalyst produces a *trans*-biphosphine *cis*-dihydride (**5**) which is the only observed species under an H_2 atmosphere. Presumably the substrate then displaces solvent and hydrogenation occurs by *cis*-ligand transfer. Later work [8] has demonstrated that the dihydride may be in equilibrium with a solvate complex **6**, which is evident from ^{31}P NMR after the sample has stood under Ar. Exposure of



4 5 6

all BF_4^-

complex **4** in methanol solution to *para*-enriched hydrogen led to equilibration at a slightly slower rate than was observed for the neutral complex $ClRh(PPh_3)_3$ (Fig. 2), indicating that the reversible loss of hydrogen from **5** occurs at an appreciable rate, $k_f = 6.8 \times 10^{-5}\ s^{-1}$ (eq. 1) for 56 μmol of complex in 8 ml MeOH reacting with 140 ml of H_2 at ambient pressure.

Hydrogenation of (*Z*)-benzamidocinnamic acid in the presence of *para*-enriched H_2 under the same conditions occurs too rapidly to provide an unambiguous result. Nevertheless, it appears that *ortho–para* interconversion only begins when hydrogenation of the substrate is complete. This is much more clearly demonstrated by other cationic complexes described below.

(b) From bis(1,2-diphenylphosphino)ethane and bis(1,4-diphenylphosphino)butane. The original work of Halpern and co-workers [9] and Slack and Baird [10] demonstrated that hydrogenation of chelate biphosphine complexes analogous to **4** led only to solvate complexes and hydridic species were not observed under neutral conditions. Thus [9] bicyclo[2.2.1]heptadiene bis(1,2-diphenylphosphino)ethanerhodium

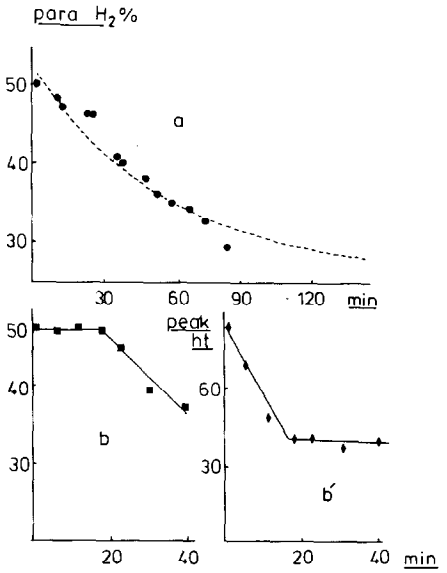
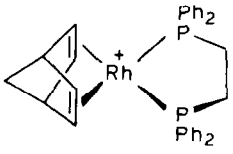


Fig. 2. Reactions of *para*-hydrogen (140 ml, 1 atm) with cationic rhodium complexes derived from **4** (45 mg) in methanol (8 ml) at 20°C. Run (a) was carried out in the absence of substrate with ● representing experimental points and the computer-drawn line corresponding to $k_f = 0.000068\ s^{-1}$ and $[H_2]_{0_{para}} = 0.515$ atm. Run (b) was carried out in the presence of 0.5 g (*Z*)-α-acetamidocinnamic acid and ■, ◆ represent $[H_2]_{para}$ and Σ [peak heights] respectively.

tetrafluoroborate (7) reacted quantitatively with 2 mol of hydrogen in methanol solution to give the solvate **8**. This observation tells us that hydride formation is thermodynamically unfavourable, but not whether it occurs reversibly with a low equilibrium constant. We studied the equilibration of *para*- and *ortho*-hydrogen in the presence of **8** and demonstrate that reversible addition of hydrogen must occur (Fig. 3). Under the reaction conditions, complex **8** is the only species detectable by ^{31}P NMR [4] and a reasonable interpretation of the result is that addition of hydrogen occurs to give an undetectable concentration of dihydride **9**, with rapid



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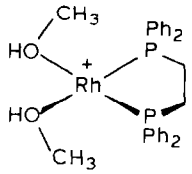

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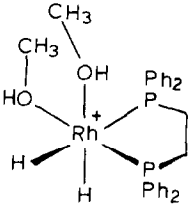

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reversal. The formation of dihydrides from solvates closely related to **8** is unknown, but gains credence from the formation of **10** under similar conditions [11], rhodium hydride formation being favoured here by the more basic phosphine. The existence of bridging rhodium hydride complexes where the counter-ligand is a chelating phosphite provides further supportive evidence [12].

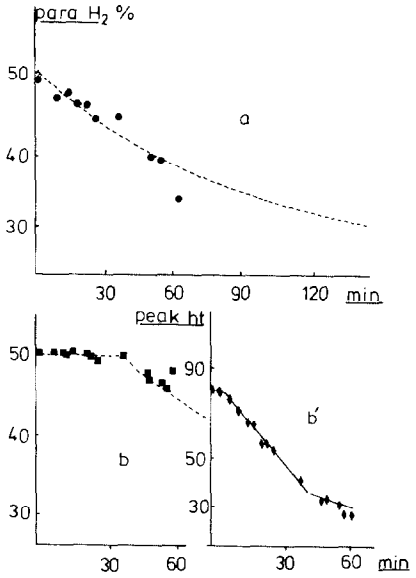
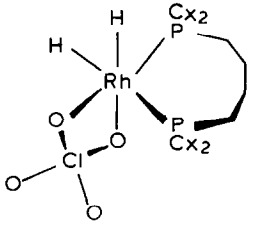


Fig. 3. Reactions of *para*-enriched hydrogen with chelate cationic complexes derived from **8** (40 mg) in methanol (8 ml) at 20°C. Run (a) is for **8** in the absence of substrate with ● representing experimental points and the computer-drawn line corresponding to $k_f = 0.000042\ s^{-1}$ and $[H_2]_{0para} = 0.51$ atm. Run (b) was monitored under similar conditions with 0.555 g added (*Z*)-α-acetamidocinnamic acid (■). The computer-drawn line corresponds to $k_f = 2 \times 10^{-6}\ s^{-1}$ for 42 min and $k_f = 0.000042\ s^{-1}$ subsequently. The decay of Σ[peak heights] during this run is shown as ◆ (in b').

For homogeneous hydrogenation catalysed by complex **8** in methanol solution, coordination of the substrate may precede the addition of hydrogen. This is certainly the case in reduction of dehydroamino acids (enamides) and the resulting chelate complexes, e.g. **11**, have been characterised by X-ray crystallography [13] and solution NMR. In the catalytic cycle, addition of hydrogen is subsequent to formation of complex **11** and although the dihydride is not observed, the species **12**



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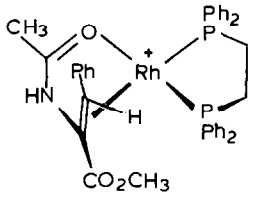

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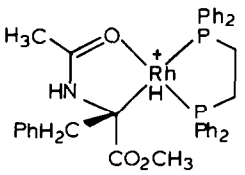

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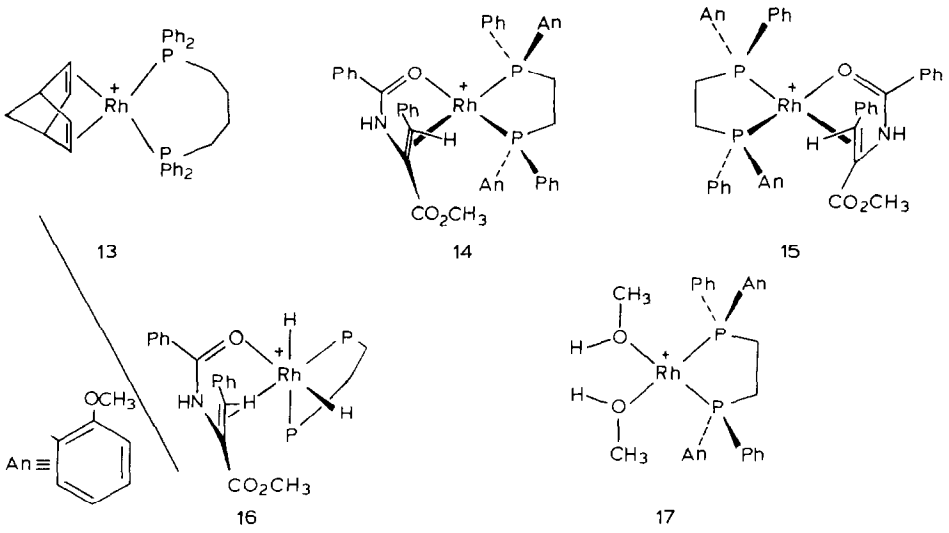
resulting from internal hydride transfer has been characterised by ^{1}H, ^{13}C and ^{31}P NMR at low temperature [13,14]. To test for reversibility of hydrogen addition, hydrogenation of (*Z*)-benzamidocinnamic acid in the presence of catalyst **8** (derived by hydrogenation of complex **7** in situ) was carried out with *para*-enriched hydrogen as before. In contrast to the previous observations, no *ortho–para* equilibration occurred until reduction was complete. This means that addition of hydrogen to **11**, which is the resting-state of the catalyst under ambient conditions, occurs irreversibly. Entirely similar observations were made with the catalyst derived from complex **13** although reduction of *Z*-benzamidocinnamic acid occurs much more rapidly [15] with the 7-membered ring chelate complex (Fig. 3).

(c) From (R,R)-bis(1,2-o-methoxyphenylphenylphosphino)ethane. Asymmetric hydrogenation of dehydroamino acids by chelate biphosphinerhodium complexes involves the formation of two diastereomeric rhodium enamide complexes which are in rapid equilibrium. In two cases [14] where definite evidence exists there is a strong preponderance of one diastereomer which is unreactive, but the catalytic cycle involves the disfavoured species. Complexes **14** and **15** derived from (*R,R*)-bis(1,2-*o*-methoxyphenylphenylphosphino)ethane (DIPAMP) are present in ratio 92/8 at room temperature in MeOH solution and the latter complex reacts selectively with hydrogen at low temperatures. The origin of this specificity is not immediately apparent, and molecular models do not reveal any strong steric preference. Each diastereomeric complex has two pathways for hydrogen addition involving the alternative faces, and stereoelectronic factors dictate that **16** should be the preferred precursor of product with the correct disposition of Rh–H and C=C bonds. This means that unproductive reversible addition of hydrogen to complex **14** or to the lower face of complex **15** has to be considered. Experiment reveals otherwise, however. Addition of *para*-enriched hydrogen to a solution of solvate **17** (prepared in situ from dinorbornadienerhodium tetrafluoroborate and the ligand in MeOH) containing excess (*Z*)-α-acetamidocinnamic acid occurred smoothly without concomitant *ortho–para* equilibration. This means that H_2 addition is stereospecific and always occurs in the productive sense, or alternatively that conformational and configurational equilibria may occur in the H_2 adduct faster than the configuration



13 14 15 16 17

is fixed by hydride transfer from rhodium to carbon.

Solvate **17**, again prepared in situ, is an effective catalyst for *ortho–para* equilibration in the absence of substrate with $k_f = 0.0008\ s^{-1}$ in eq. 1.

Experimental

Rhodium complexes were prepared by previously described procedures [7]. Catalytically active complexes derived from the ligand DIPAMP were generated in situ from equimolar quantities of the biphosphine and bis(bicyclo[2.2.1]heptadiene)-rhodium(I) tetrafluoroborate in MeOH with prehydrogenation [4]. Purified solvents were degassed several times under argon before use. *para*-Enriched hydrogen was generated in the apparatus shown in Fig. 4, containing magnetite (Fe_3O_4) in the large Schlenk tube A and organometallic complex in solvent together with a magnetic stirrer bar in the side-arm vessel B, which was held at −80°C. Tube A was evacuated and filled with argon three times, and then evacuated and filled with hydrogen three times, finally to an overpressure of 13 cmHg. This was then cooled to −196°C in liquid nitrogen for twenty minutes. During this time vessel B was cooled to −80°C, evacuated to tap C and filled with argon via tap D.

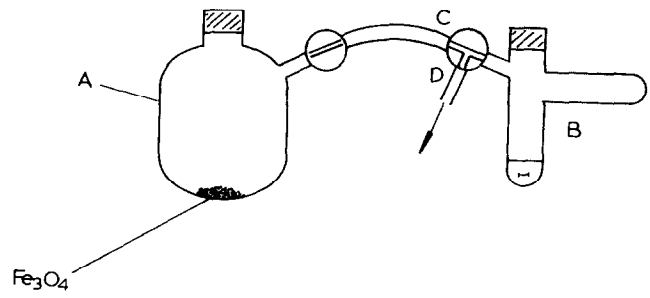


Fig. 4. Apparatus for the preparation of *para*-enriched hydrogen and subsequent hydrogenation.

This procedure was repeated three times, and the vessel evacuated. Tap C was opened and the Schlenk tube warmed to room temperature. Tap D was then closed and the vessel detached. It was mounted with the incident laser beam of the Raman assembly (a Spex Ramalog 5) focused at the centre of the side-arm and the mixture in the main chamber of the vessel was rapidly warmed to room temperature with fast stirring. The rotational Raman scattering of the hydrogen gas was excited at λ 514.5 nm using the output of Spectra-Physics Model 165 Ar^+ laser; the incident radiation made but a single traverse of the sample at a power level typically in the order of 400 mW. The experiments made repeated scans of the emissions at Δ_v 587 and 354 cm^{-1} due to *ortho-* and *para*-hydrogen, respectively. Peak heights were measured graphically and data transferred to an HP 85 microcomputer. Kinetic simulation was carried out using programs available from the authors on request.

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References

1 J. Halpern and C.S. Wong, J. Chem. Soc. Chem. Commun., (1973) 629; J. Halpern, T. Okamoto, and A. Zakhariev, J. Molec. Cat., 2 (1977) 65; C. Rousseau, M. Evrard and F. Petit, ibid., 3 (1978) 309; M.H.J.M. de Croon, P.F.M.T. van Nisselrooij, H.J.A.M. Kuipers and J.W.E. Coenen, ibid., 4 (1978) 325; Y. Ohtani, M. Fujimoto and A. Yamagishi Bull. Chem. Soc. Japan, 49 (1976) 1871; 50 (1977) 1453.
2 C.A. Tolman, P.Z. Meakin, D.L. Lindner and J.P. Jesson, J. Amer. Chem. Soc., 96 (1974) 2762; Y. Ohtani, M. Fujimoto and A. Yamagishi, Bull. Chem. Soc. Japan, 52 (1979) 69.
3 A. Dedieu, Inorg. Chem., 20 (1981) 2803; 19 (1980) 375; A. Dedieu and A. Strich, ibid., 18 (1979) 2940.
4 J.M. Brown and P.A. Chaloner, J. Amer. Chem. Soc., 102 (1980) 3040; J. Chem. Soc. Perkin II, (1982) 711; I. Ojima, T. Kogure and N. Yoda, J. Org. Chem., 45 (1980) 4728.
5 M. Calvin, Trans. Farad. Soc., 34 (1938) 1181; W.K. Wilmarth and M.K. Barsh, J. Amer. Chem. Soc., 75 (1953) 2237.
6 M.E. Tadros and L. Vaska, J. Colloid Interface Sci., 85 (1982) 389.
7 R.R. Schrock and J.A. Osborn, J. Amer. Chem. Soc., 98 (1976) 2134, 2143.
8 J.M. Brown, P.A. Chaloner, A.G. Kent, B.A. Murrer, P.N. Nicholson, D. Parker and P.J. Sidebottom, J. Organomet. Chem., 216 (1981) 263.
9 J. Halpern, D.P. Riley, A.S.C. Chan and J.J. Pluth, J. Amer. Chem. Soc., 99 (1977) 8055.
10 D.A. Slack, I. Greveling and M.C. Baird, Inorg. Chem. 18 (1979) 3125.
11 K. Tani, K. Suwa, E. Tanigawa, T. Yoshida, T. Okano and S. Otsuka, Chem. Lett., (1982) 261; K. Tani, K. Suwa, T. Yamagata and S. Otsuka, ibid., (1982) 265.
12 M.D. Fryzuk, Organometallics, 1 (1982) 408.
13 A.S.C. Chan, J.J. Pluth and J. Halpern, Inorg. Chim. Acta, 37 (1979) L477; idem, J. Amer. Chem. Soc., 102 (1980) 5952.
14 J.M. Brown and P.A. Chaloner, J. Chem. Soc. Chem. Commun., (1980) 344; A.S.C. Chan and J. Halpern, J. Amer. Chem. Soc., 102 (1980) 838.
15 J.-C. Poulin, T.-P. Dang and H.B. Kagan, J. Organomet. Chem., 84 (1975) 87.