

Solvent Assisted Regioselective and Stereospecific Hydrogenation of Dienes, at Ambient Temperatures and Pressures Catalyzed by (Naphthalene)Cr(CO)₃. Nature of the Active Catalytic Species

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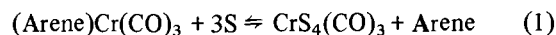
The use of arenechromium tricarbonyl compounds as catalysts for the regioselective hydrogenation of dienes to monoenes¹⁻⁴ is of special interest in view of the high stereospecificity of products attained in the reaction. Linear conjugated dienes give^{1,2} almost entirely *cis*-monoenes by 1-4 addition; norbornadiene gives⁵ norbornene (82%) and norbornene (18%) by *cis-endo* addition; tricyclo[4.2.2.0^{2,5}] deca-3,9-diene gives⁵ both monoenes by *endo* addition; 12-oxa-12-oxa[4.4.3]propella-2,4,7,9-tetraene gives⁶ preferentially the symmetric tetrahydrodiene (70%), with addition from the direction of the ether oxygen. However the experimental procedure meets with practical disadvantages since the required¹⁻⁴ operating conditions are relatively vigorous ($T > 100^\circ\text{C}$, $p > 10$ atm).

We now wish to report a modified form of the catalytic system which operates efficiently even at atmospheric pressures and ambient temperatures. This development has come as a result of our studies on the nature of the active catalytic species generated during the induction period that invariably precedes the hydrogenation reaction.

Based on indirect evidence, it has previously been assumed^{2,4} that arene displacement (total or partial) was implied in the thermally stimulated induction step. In order to obtain direct spectroscopic and chemical evidence on the identity of the species formed during induction, and on their connection with catalytic activity, we sought a suitable combination of a coordinating solvent, and an arene compound with a kinetically labile π -bonded ligand, that would undergo the expected arene displacement reaction under milder conditions (without forming new kinetically inert species that would inhibit the hydrogenation). The arenechromium tricarbonyl complexes which appeared to be particularly adequate for this purpose

were the polycyclic derivatives LCr(CO)_3 (L = anthracene (1), naphthalene (2), and phenanthrene (3)), which had been found to show singularly high catalytic activity⁷, and were known from early descriptive and kinetic evidence to decompose or react more readily than monocyclic derivatives. Thus, 1, which is difficult to obtain, has been reported⁸ to decompose rapidly in organic solvents. The more readily accessible 2⁹ has been found to undergo ligand exchange with free naphthalene at faster rates than the benzene analogue¹⁰. A simple interpretation of the lower stabilities of polycyclic aromatics π -bonded to Cr has been proposed¹¹, using localization energies with a Hückel type approximation. A possible connection between X-ray structural features of these complexes and their catalytic reactivities has been suggested⁷.

We have found that in coordinating solvents such as THF, acetone, dioxane, glyme, ethyl acetate, acetonitrile, and others, the compounds 1-3 undergo facile solvolysis (eq. 1, S = solvent):



With strong ligands such as CH_3CN , the reaction proceeds fast to completion*. With weaker donors (e.g. ethers) conversion is incomplete and an equilibrium is reached. Parallel with reaction (1), the newly formed and highly reactive 4 undergoes decomposition, rapidly by interaction with traces of oxygen, or slowly by reaction with oxygen donors, with ultimate formation of Cr_2O_3 and the higher carbonylated species $\text{S}_n\text{Cr(CO)}_{6-n}$ (mainly $n = 2$ (5)). In THF the new species 4 and 5 were identified by i.r. (ν_{CO} : 4, 1920 and 1773 cm^{-1} ; 5, 2018, 1900, 1884 and 1836 cm^{-1}), as well as chemically by quantitatively converting them *in situ* into (cycloheptatriene)Cr(CO)₃, and (norbornadiene)Cr(CO)₄, respectively, by addition of an excess of the corresponding olefins to the mixture.

In THF, both rates and equilibria for (1) were found to increase along the series $1 > 2 > 3$, in line with predictions¹¹. Thus, at room temperature, 1 reacts with nearly complete conversion in 5 min, 2 reaches equilibrium (55% conversion) in approximately 40 min, and

*In dichloroethane we found that 2 reacts with CH_3CN following a 2nd order rate law with $k_2 = 5.77 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ (30 $^\circ\text{C}$), $\Delta E^\ddagger = 16.8 \text{ kcal/mol}$; $\Delta S^\ddagger = -20 \text{ e.u.}$

3 requires hours (and was too slow to be studied without interference of the decay leading to 5).

The link between facile displacement of arene in complexes 1-3 and catalytic activity was established by the following hydrogenation experiments in THF, at 30 °C and 1 atm. total pressure. A solution of 2 ($5 \times 10^{-3} M$) and of diene substrate (0.5 M methyl sorbate), after a short induction period of 6 min, was observed to take up H₂ at steadily increasing rates up to a maximum (0.54 mM/min for an 80 ml solution) after 22 min (16% conversion), parallel with the growth of concentrations of 4 in the reaction mixture; when 4 approached equilibrium the uptake rates decreased following reagents consumption. By allowing the complex 2 to interact with the solvent to equilibrium before introduction of substrate, the induction and acceleration periods were found to be bypassed and the hydrogenation was observed to set in immediately at maximum initial rate (1.32 mM/min). On the other hand, the addition of an excess of naphthalene at onset was found to inhibit hydrogenation by shifting the position of equilibrium of (1) to the left.

The role of 4 was further demonstrated by generating it in THF from other suitable precursors and noting the correlation between concentrations of this species and rates. When either Cr(CO)₃(CH₃CN)₃, a yellow, air- and moisture-sensitive solid¹², or 1 (purple crystals) was dissolved in THF, orange-coloured solutions of 4 were obtained, with nearly complete conversion. Hydrogenation with these solutions (all concentrations as before) proceeded at the high initial rate of 3mM/min (higher by a factor of 2.2. relative to the initial rates with equilibrium concentrations of 4 from 2). A recent report¹³ describes briefly the use of Cr(CO)₃(CH₃CN)₃ as hydrogenation catalyst, although at slightly higher pressures, and requiring longer reaction times, than those described here, doubtless needed to overcome the

inhibiting effect of the strongly coordinating acetonitrile introduced as solvent.

We believe that the readily available and air stable 2 is at present the best practical precursor for the generation of catalytically effective concentrations of the active species 4, for hydrogenation in coordinating solvents at low temperatures and pressures. Furthermore, the mild operating conditions described above, now open the way to new experimental approaches for mechanistic studies of this reaction.

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