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Soluble Catalysts for the Hydrogenation of Olefins¹

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A number of transition metal compounds combined with organometallic derivatives have been found to be soluble catalysts for the hydrogenation of olefins. Transition metals in groups IV–VIII, mostly as acetylacetonates or as alkoxides, have been found to be active when combined with, preferably, a trialkylaluminum compound. Mono-, di-, tri-, and tetrasubstituted olefins have been hydrogenated. The kinetics of the reaction have been studied briefly, and a mechanism is suggested.

Introduction

There has been considerable interest in soluble hydrogenation catalysts in recent years. From a theoretical point of view, it has been felt that the study of soluble catalysts should shed some light on the mechanism of heterogeneous hydrogenation. Practically, soluble catalysts might show higher activity, be less susceptible to poisoning, and be useful for the reduction of polymers.

Relatively few soluble hydrogenation catalysts are reported in the literature. The older work is covered in several review articles.² Recently, hydrogenations catalyzed by the pentacyanocobaltate(II) ion,³ ruthenium(II) ion,⁴ boron alkyls,⁵ and even *t*-butoxide ion⁶ have been reported. The work described in this communication resulted from our interest in learning whether hydrocarbon-soluble, Ziegler-type catalysts would activate hydrogen for hydrogenation of organic molecules.

Results and Discussion

Inasmuch as the usual Ziegler catalysts are heterogeneous, initial experiments were carried out with the soluble system bis(cyclopentadienyl)-titanium dichloride–triethylaluminum.⁷ This combination gave a 70% yield of *n*-octane from 1-octene on standing overnight at room temperature under an initial hydrogen pressure of 4.4 atm., using 3 mmoles of titanium and an aluminum–titanium ratio of 1.2:1. This initial success led to an investigation of other soluble Ziegler-type catalysts.

A 3:1 triisobutylaluminum–tetraisopropyl titanate catalyst, which is soluble in *n*-heptane,^{8,9} was used in conjunction with cyclohexene. Cyclohexene was reduced quantitatively with this catalyst in heptane solution when treated under the conditions above; also, 1-octene was reduced to *n*-octane in 94% yield. The catalyst level was 2–4 mole % of transition metal based on the olefin.

Success with these catalyst systems suggested that derivatives of other transition metals could be made to function as soluble catalysts in the same way. To test the hypothesis, derivatives of the following metals were examined: Co(II and III), Cr(III), Cu(II), Fe(III), Mn(II and III), Mo(VI), Ni(II), Pd(II), Ru(III), V(V), and Zr(IV). With the exception of derivatives of Cu(II), successful hydrogenations under mild conditions (30–50°, 3.7 atm. of hydrogen) of one or more of the

olefins: cyclohexene, 1-octene, 2-methyl-2-butene, 2-pentene, tetramethylethylene, and stilbene, were achieved with derivatives of all of the metals in combination with aluminum trialkyls (Table I). For most of the transition metals that were tested, the acetylacetonate (acac) derivatives were employed because of their ready availability. A few halogen derivatives were used successfully; however, in general the presence of halogen led to insoluble systems. Either heptane or toluene was used as the solvent. In all but two experiments (21 and 22), 20 mmoles of olefin was used, the ratio of olefin to transition metal being 50–100:1. The times recorded for complete reduction in certain experiments are maxima. Catalysts based on iron and cobalt acetylacetonates plus triisobutylaluminum were still active after reducing 0.2 mole of olefin (expt. 21 and 22), equivalent to 1.4 moles of olefin per millimole of catalyst. These high rates and catalyst lifetimes may indicate practical applications for these combinations.

The most active catalysts appeared to be Co(III) > Fe(III) > Cr(III) acetylacetonates, combined with triisobutylaluminum (see also Table III). Triethylaluminum and diisobutylaluminum hydride were essentially equivalent to triisobutylaluminum as the organometallic component. Other organometallics investigated were diethylaluminum chloride, triethylboron, tetraethyltin, tri-*n*-butylphosphine, diethylzinc, *n*-butylmagnesium bromide, and *n*-butyllithium. With the exception of *n*-butyllithium, either no reaction occurred between members of the above list and the transition metal derivatives, or when it did the result was an insoluble material which did not catalyze hydrogenation at 30–50° and 3.7 atm. of hydrogen. Although *n*-butyllithium formed soluble catalysts with tetraisopropyl titanate, triethyl vanadate, and chromic, cobaltic, and ferric acetylacetonates, the rates of hydrogenation with these were considerably slower than with the triisobutylaluminum-containing counterparts.

Generally for the acetylacetonate and alkoxide derivatives of the transition metals, an aluminum–metal ratio corresponding to one aluminum for each oxygen present was employed. However, for the triisobutylaluminum–Cr(acac)₃ catalyst in the reduction of cyclohexene, the rate was later found to rise steadily as the Al/Cr ratio rises from 1 to 10 and then to remain constant, or possibly decrease slightly, as the ratio is increased further. For the triisobutylaluminum complexes with VO(OC₂H₅)₃ and Ti(O-*i*-C₃H₇)₄, rate maxima occurred at aluminum–metal ratios of 3:4. It is interesting that for the latter of these the optimum ratio is the same as that reported for the polymerization of ethylene with triethylaluminum–tetraethyl titanate.⁸

The solubility of several of the catalyst systems has been documented in the literature: R₃Al–Ti(OR)₄,⁸ R₃Al–Cr(acac)₃,¹⁰ R₃Al–MoO₂(acac)₂,¹⁰ and R₃Al–(C₅H₅)₂TiCl₂.⁷ In other combinations, a decision as to solubility was reached by visual examination and the

(1) Presented at the Fourteenth Delaware Science Symposium, Newark, Del., February 23, 1963.

(2) (a) J. Halpern, *Quart. Rev. (London)*, **10**, 463 (1956); (b) S. W. Weller and G. A. Mills, *Advances in Catalysis*, **8**, 163 (1956).

(3) J. Kwiatek, I. L. Mador, and J. K. Seyler, *J. Am. Chem. Soc.*, **84**, 304 (1962).

(4) H. Halpern, J. F. Harrod, and B. R. James, *ibid.*, **83**, 753 (1961).

(5) (a) R. Köster, G. Bruno, and P. Binger, *Ann.*, **644**, 1 (1961); (b) E. J. DeWitt, P. L. Ramp, and L. E. Trapasso, *J. Am. Chem. Soc.*, **83**, 4672 (1961).

(6) C. Walling and L. Bollyky, *ibid.*, **83**, 2968 (1961).

(7) D. S. Breslow and N. R. Newburg, *ibid.*, **81**, 81 (1959).

(8) C. E. H. Bawn and R. Symcox, *J. Polymer Sci.*, **34**, 139 (1959).

(9) M. Farina and M. Ragazzini, *Chim. ind. (Milan)*, **40**, 816 (1958); *Angew. Chem.*, **70**, 600 (1958).

(10) G. Natta, *J. Polymer Sci.*, **48**, 219 (1960).

TABLE I
 HYDROGENATION OF OLEFINS WITH SOLUBLE HYDROGENATION CATALYSTS^a

Expt.	Transition metal compound	Catalyst alkylating agent	Ratio ^b	Concn., ^c mM	Olefin	Temp., °C.	Time, hr.	Conversion, %
1	Ti(O- <i>i</i> -C ₃ H ₇) ₄	(<i>i</i> -C ₄ H ₉) ₃ Al	3.3	16.5	Cyclohexene	25	<20	100
2	Ti(O- <i>i</i> -C ₃ H ₇) ₄	(<i>i</i> -C ₄ H ₉) ₃ Al	3.3	16.5	1-Octene	25	<20	94
3	Ti(O- <i>i</i> -C ₃ H ₇) ₄	(<i>i</i> -C ₄ H ₉) ₃ Al	3.3	18.5	<i>trans</i> -Stilbene	25	<22	50
4	Ti(O- <i>i</i> -C ₃ H ₇) ₄	<i>n</i> -C ₄ H ₉ Li	9.9	15.5	Cyclohexene	50	22	6
5	(C ₅ H ₅) ₂ TiCl ₂	(C ₂ H ₅) ₃ Al	1.2	23.2	1-Octene	25	16	70
6	(C ₅ H ₅) ₂ ZrCl ₂	(<i>i</i> -C ₄ H ₉) ₃ Al	2.9	16.8	Cyclohexene	25	17	24.5
7	VO(OC ₂ H ₅) ₃	(<i>i</i> -C ₄ H ₉) ₃ Al	4.2	17.3	Cyclohexene	30	1.08	50
8	VO(O- <i>n</i> -C ₄ H ₉) ₃	(<i>i</i> -C ₄ H ₉) ₃ Al	3.9	19.3	Cyclohexene	40	<20	100
9	VO(O- <i>n</i> -C ₄ H ₉) ₃	(<i>i</i> -C ₄ H ₉) ₃ Al	3.9	19.3	1-Octene	40	<20	100
10	VO(OC ₂ H ₅) ₃	(C ₂ H ₅) ₃ Al	4.0	17.9	Cyclohexene	30	1.08	46.5
11	VO(OC ₂ H ₅) ₃	(<i>i</i> -C ₄ H ₉) ₂ AlH	4.1	18.3	Cyclohexene	30	1.08	43.5
12	Cr(acac) ₃	(<i>i</i> -C ₄ H ₉) ₃ Al	6.0	9.5	Cyclohexene	31.5	2	100
13	Cr(acac) ₃	(<i>i</i> -C ₄ H ₉) ₃ Al	6.0	4.0	1-Octene	30	1.17	55
14	Cr(acac) ₃	(<i>i</i> -C ₄ H ₉) ₃ Al	6.0	7.7	2-Methyl-2-butene	30	0.83	16.5
15	Cr(acac) ₃	(<i>i</i> -C ₄ H ₉) ₃ Al	6.0	4.0	<i>trans</i> -2-Pentene	30	0.83	50
16	Cr(acac) ₃	(<i>i</i> -C ₄ H ₉) ₃ Al	6.3	12.4	Tetramethylethylene	50	18	75
17	MoO ₂ (acac) ₂	(<i>i</i> -C ₄ H ₉) ₃ Al	7.1	15.7	Cyclohexene	30	<16	100
18	MoO ₂ (acac) ₂	(<i>i</i> -C ₄ H ₉) ₃ Al	7.1	14.9	1-Octene	30	<21	100
19	Mn(acac) ₃	(<i>i</i> -C ₄ H ₉) ₃ Al	6.0	15.9	Cyclohexene	30	<16	100
20	Mn(acac) ₂	(<i>i</i> -C ₄ H ₉) ₃ Al	6.0	21.8	Cyclohexene	31	0.45	12.5
21	Fe(acac) ₃	(<i>i</i> -C ₄ H ₉) ₃ Al	6.2	5.6	1-Hexene	30	5 ^d	100
22	Co(acac) ₃	(<i>i</i> -C ₄ H ₉) ₃ Al	6.0	5.7	1-Hexene	30	2 ^d	100
23	Co(acac) ₃	(<i>i</i> -C ₄ H ₉) ₃ Al	6.0	4.0	Cyclohexene	30	0.33	100
24	Co(acac) ₃	<i>n</i> -C ₄ H ₉ Li	12.6	16.3	Cyclohexene	50	22	69
25	Co[(C ₅ H ₅) ₃ P] ₂ Cl ₂	(<i>i</i> -C ₄ H ₉) ₃ Al	3.5	12.5	Cyclohexene	25	16	33.5
26	Ni[(<i>n</i> -C ₄ H ₉) ₃ P] ₂ Cl ₂	(<i>i</i> -C ₄ H ₉) ₃ Al	4.3	12.6	1-Hexene	25	19	57.5
27	Pd[(<i>n</i> -C ₄ H ₉) ₃ P] ₂ Cl ₂	(<i>i</i> -C ₄ H ₉) ₃ Al	4.2	13.0	1-Hexene	25	19	25.5
28	Ru(acac) ₃	(<i>i</i> -C ₄ H ₉) ₃ Al	7.1	15.5	1-Octene	40	<16	100

^a Reactions were generally carried out with 20 mmoles of olefin in 20–25 ml. of *n*-heptane or toluene solution in a vessel having a void volume of 230–240 ml. under an initial hydrogen pressure of 3.5–3.7 atm., except where indicated. ^b Ratio of organometallic to transition metal concentration. ^c Based on transition metal. ^d Time to reduce 0.2 mole of olefin in the absence of solvent under a constant hydrogen pressure of 2.4 atm.

absence of settled solid material after catalyst aging. However, several of the transition metals, derivatives of which were used as catalyst components, are themselves efficient hydrogenation catalysts, *e.g.*, cobalt, ruthenium, nickel, and palladium. To investigate the possibility that these hydrogenations might have been catalyzed by colloidal metal, preformed catalyst mixtures were "killed" with acetone or ethanol and then used for olefin hydrogenation. For all catalysts listed in Table I, under these conditions, no hydrogenations were observed, indicating that the hydrogenations in the absence of alcohol or acetone were not catalyzed by metal. Cupric acetylacetonate precipitated copper with triisobutylaluminum, but hydrogenation did not occur.

For the triisobutylaluminum–chromic acetylacetonate catalyst system, some preliminary kinetic experiments have been carried out, which indicate that the hydrogenation reaction is first order with respect to hydrogen and zero order in olefin, or over-all first order (exclusive of catalyst terms). This is the same rate behavior observed in many heterogeneous hydrogenations.

A typical rate experiment illustrating the first-order nature of the reaction is presented in the Experimental section. The experiments in Table II show that the observed rates are reproducible and roughly proportional to the chromium concentration at a constant Al/Cr ratio (at least when the chromium concentration is less than $4 \times 10^{-3} M$). These facts indicate that we are probably operating in a range where diffusion-controlled processes are not important. It should be noted that these rate constants are specific for these experimental conditions, since the observed rate is dependent on the void volume of the system in this type of reaction.¹¹ The zero-order dependence on olefin is illustrated by

(11) H. A. Smith and J. F. Fuzek, *J. Am. Chem. Soc.*, **70**, 3743 (1948).

the fact that in the hydrogenation of cyclohexene the initial rate was unchanged at constant pressure when the cyclohexene concentration was varied by a factor of two.

 TABLE II
 RATES OF HYDROGENATION OF CYCLOHEXENE WITH THE TRI-ISOBUTYLALUMINUM–CHROMIC ACETYLACETONATE CATALYST IN HEPTANE AT 30°^a

Cr concn., 10 ³ M	No. of runs	10 ² k, min. ⁻¹
2.0	1	0.74
4.0	2	1.8 ± 0.2
8.0	2	2.4 ± 0.1

^a Cyclohexene, 1.04 M; Al/Cr, 6.0; initial pressure, 3.7 atm.

In order to determine how olefin structure influences rate of hydrogenation, the triisobutylaluminum–Cr(acac)₃ catalyst was tested with a series of olefins of varying double bond substitution. The results are given in Table III, together with similar results from a few other catalyst systems. From the data, it appears that mono- and disubstituted acyclic ethylenes are hydrogenated at similar rates. There is a much sharper break between the disubstituted and trisubstituted double bond as represented by 2-methyl-2-butene, its rate of hydrogenation being low even at a larger than usual catalyst concentration. Tetrasubstituted double bonds are hydrogenated very slowly, as illustrated by the fact that even after twenty-four hours no hydrogenation of tetramethylethylene was detected at 30°; slow hydrogenation did occur at 50°. It is interesting that cyclohexene reacts somewhat faster than 1-octene, a terminal olefin, in contrast to the results with heterogeneous catalysts, for example, Raney nickel, where it is found that disubstituted ethylenes, including cyclo-

hexene, are hydrogenated slower than are terminal olefins.¹²

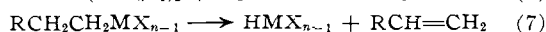
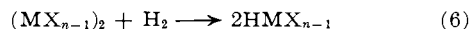
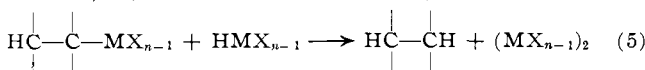
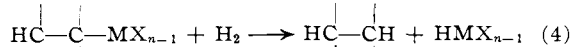
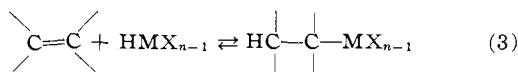
The hydrogenation of substituted acetylenes with soluble catalysts was sometimes found to be complicated by a competing cyclization to a substituted benzene derivative. Thus, although phenylacetylene was reduced quantitatively to ethylbenzene with a triisobutylaluminum-tetraisopropyl titanate catalyst, a 23% yield of hexaethylbenzene was isolated from the reduction of 3-hexyne in the presence of triisobutylaluminum-Cr(acac)₃, 34% of the theoretical amount of hydrogen being absorbed. Other catalysts had the same effect on 3-hexyne, as evidenced by the less than theoretical amount of hydrogen absorbed. Since hydrogen was absorbed in all of the experiments, however, reduction of the acetylene did occur. Several examples of the cyclization of acetylenes by Ziegler catalysts have been reported.¹³ A variety of other compounds, including ketones, aldehydes, nitriles, nitro compounds, azo compounds, and esters, were not reduced with the soluble catalysts.

TABLE III
RATES OF OLEFIN HYDROGENATION WITH SOLUBLE CATALYSTS

Olefin	Catalyst, Al/M = 6.0	Transition metal concn., mM	mmole/min. at 3.5 atm.
Cyclohexene	(<i>i</i> -C ₄ H ₉) ₃ Al-Cr(acac) ₃	3.9	0.66 ± 0.07
1-Octene	(<i>i</i> -C ₄ H ₉) ₃ Al-Cr(acac) ₃	3.9	.36 ± .03
<i>trans</i> -2-Pentene	(<i>i</i> -C ₄ H ₉) ₃ Al-Cr(acac) ₃	3.9	.30 ± .03
2-Methyl-2-butene	(<i>i</i> -C ₄ H ₉) ₃ Al-Cr(acac) ₃	7.6	.050
Cyclohexene	(<i>i</i> -C ₄ H ₉) ₃ Al-Cr(acac) ₃	2.0	.33
Cyclohexene	(<i>i</i> -C ₄ H ₉) ₃ Al-Fe(acac) ₃	2.0	1.1
Cyclohexene	(<i>i</i> -C ₄ H ₉) ₃ Al-Co(acac) ₃	2.9	3.1
Cyclohexene	(<i>i</i> -C ₄ H ₉) ₃ Al-VO(OC ₂ H ₅) ₃ ^a	7.9	0.04

^a Al/V = 3.5.

A postulated mechanism for hydrogenation with the soluble catalysts must be speculative, since the structures of the various catalysts are largely uninvestigated.¹⁴ Nevertheless, it now seems to be well established that reaction of transition metal derivatives with aluminum alkyls has as its first step alkylation of the transition metal derivative (1).⁷ We consider that this step is followed by hydrogenolysis of the metal-alkyl bond formed to yield a metal hydride (2), which then adds to an olefin, forming a new metal alkyl (3). Hydrogenolysis of the latter yields saturated hydrocarbon with regeneration of the metal hydride (4). Alternatively, the hydrogenolysis of eq. 4 might take place *via* another molecule of hydride (5) with sub-



sequent reduction by hydrogen of the transition metal

(12) C. A. Brown and H. C. Brown, *J. Am. Chem. Soc.*, **85**, 1003, 1005 (1963).

(13) (a) E. F. Lutz, *ibid.*, **83**, 2551 (1961); (b) W. R. Smith, U. S. Patent 2,990,434 (1961).

(14) The structure of triethylaluminum-chromic acetylacetonate has been investigated [G. Sartori and G. Costa, *Z. Elektrochem.*, **63**, 105 (1959)] with the conclusion that the chromium is zero-valent. However, the data are open to alternative explanations, one of which is the presence of a chromium hydride.

moiety formed (6). As an alternative to eq. 2, initial formation of the transition metal hydride could be by elimination from the metal alkyl (7).

Certainly, eq. 1-7 are highly simplified. It is likely that in some situations reduction of the transition metal valence state occurs, and that the transition metal moieties are complexed with aluminum species. Also likely is the occurrence of additional intermediates between the steps listed here. For example, the addition of transition metal hydride to olefin (3) is probably preceded by complex formation between the olefin and the transition metal.¹⁵ In fact, the possibility that the transition metal hydride-olefin complex is formed directly by hydrogenation of a transition metal alkyl-olefin complex cannot be excluded. The postulation of metal hydrides as intermediates in homogeneously catalyzed hydrogenations is not new^{2a, 3, 16}; in this connection our mechanism differs in detail but not in concept from that proposed by Halpern for hydrogenations catalyzed by Ru⁺⁺.¹⁷

The first two steps of the postulated mechanism find precedent in the work of Hein and co-workers who isolated Li₃CrPh₆ from reaction of phenyllithium with Cr(acac)₃ and found that its reaction with excess hydrogen led to a substance of the formula Li₃Cr₂H₃Ph₆.¹⁸ Other examples of the hydrogenolysis of transition metal alkyls are known also.¹⁹ Furthermore, the addition of transition metal hydrides to olefins is well precedented,^{15, 19-21} and a definable hydride is known for each of the transition metals considered here.²²

Several experiments designed to gather information on the role of transition metal hydrides in these hydrogenations were carried out. In the first, 2-methyl-2-butene was treated with deuterium in the presence of the triisobutylaluminum-Cr(acac)₃ catalyst. The resulting isopentane when analyzed by mass spectrometry exhibited mass peaks at 75, 74, and 73 in larger than natural abundance amounts. These values correspond to tri-, di-, and monodeuterated species, respectively. Unfortunately, the relative amounts of each species and the position of the deuterium were not determinable because of lack of standards. Nevertheless, the results do indicate that exchange of hydrogens on the substrate occurs and that a simple one-step transfer of a molecule of hydrogen from the catalyst to the double bond does not take place. It is reasonable to explain these results in terms of a reversible addition of a metal hydride to the olefins. Thus, the first intermediate is formed by addition of a metal deuteride to the olefin. The resulting metal alkyl either can be cleaved by deuterium (or another molecule of metal deuteride) to give dideuterated product, or can undergo elimination of metal hydride to give a monodeuterated olefin. Repetition of the addition-cleavage steps on the latter olefin would yield a trideuterated product. The monodeuterated product presumably arises from deuterium cleavage of a metal alkyl formed by addi-

(15) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).

(16) Since submission of this manuscript, two other complex hydrogenation catalysts which may involve metal hydrides have been reported: the stannous chloride-chloroplatinic acid system: R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *ibid.*, **85**, 1691 (1963); and the triethylaluminum-nickel(II) carboxylate system: S. J. Lapporte and W. R. Scheutt, *J. Org. Chem.*, **28**, 1947 (1963).

(17) J. Halpern and B. R. James, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., 1962, Abstracts, p. 23N.

(18) (a) F. Hein, R. Weiss, B. Heyn, K. H. Barth, and D. Tille, *Monatsber. deut. Akad. Wiss. Berlin*, **1**, 541 (1959); *Chem. Abstr.*, **55**, 17339 (1961); (b) F. Hein and R. Weiss, *Naturwissenschaften*, **46**, 321 (1959).

(19) D. S. Breslow and R. F. Heck, *Chem. Ind. (London)*, 467 (1960).

(20) P. M. Treichel, E. Pitcher, and F. G. A. Stone, *Inorg. Chem.*, **1**, 511 (1962).

(21) R. W. Goetz and M. Orchin, *J. Org. Chem.*, **27**, 3698 (1962).

(22) (a) M. L. H. Green, *Angew. Chem.*, **72**, 719 (1960); (b) J. Chatt, *Proc. Chem. Soc.*, 318 (1962).

tion of metal hydride to olefin. The ready reversibility of the addition of metal hydrides to olefins is well established for boron²³ and aluminum²⁴ hydrides, and for cobalt hydrocarbonyl.¹⁵

In another experiment it was determined that the same catalyst (Al/Cr = 6) in 30 hr. at room temperature absorbed more than 7 moles of hydrogen per mole of chromium. Even at this point, although hydrogen absorption became very slow, it did not appear to have stopped completely. At most, reduction of the chromium oxidation state, even from +3 to 0, could account for only 3 moles of hydrogen. Furthermore, it is doubtful that the acetylacetonate ligands were reduced, since ketones were not hydrogenated with this catalyst. There is left as a reasonable possibility the formation of chromium or aluminum hydrides, probably by means of a sequence of reactions analogous to those observed in the phenyllithium-Cr(acac)₃-hydrogen system.¹⁸

In conclusion, it is interesting to point out the possibility of an analogy between the mechanism of heterogeneous hydrogenation and that of hydrogenation with the soluble Ziegler-type catalysts. For the purposes of the comparison, the hydrogen absorbed in a metallic catalyst is analogous to the transition metal hydride; the formation of the "half-hydrogenated" intermediate²⁵ is similar to the formation of the transition metal alkyl by addition of the hydride to olefin; and the conversion of the "half-hydrogenated" intermediate to product is analogous to hydrogenolysis of the transition metal alkyl.

Experimental

Materials.—Aluminum alkyls were purchased from Texas Alkyls, Inc. *n*-Butyllithium was purchased from Lithium Corp. of America. The acetylacetonates of chromium(III), manganese(III), cobalt(III), and iron(III) were purchased from MacKenzie Chem. Works, Inc. The acetylacetonates of molybdenum(VI),²⁶ ruthenium(III)²⁷, manganese(II),²⁸ and palladium(II)²⁷ were prepared by procedures described in the literature, as were bis-(tri-*n*-butylphosphine)-nickel dichloride,²⁹ bis-(tri-*n*-butylphosphine)-palladium dichloride,³⁰ bis-(triphenylphosphine)-cobalt dichloride,³¹ bis-(cyclopentadienyl)-titanium dichloride,³² and bis-(cyclopentadienyl)-zirconium dichloride.³³ Tetraalkyl titanates were purchased from E. I. du Pont de Nemours and Co. The trialkyl vanadates were purchased from Stauffer Chemical Co.

The olefins and acetylenes used for hydrogenation were the purest available commercial materials. Solids were purified by recrystallization. Liquids were purified by distillation and then stored under nitrogen.

Solvents were dried over Molecular Sieves (Linde Corp.) and then stored under nitrogen.

General Hydrogenation Procedure.—The hydrogenation reactions were carried out in 8-oz. pressure bottles closed with self-sealing rubber liners and crown caps. Since in all cases the catalysts were sensitive to air and moisture, all operations were carried out in a nitrogen or hydrogen atmosphere. In general, the bottles were alternately evacuated and flushed with nitrogen, then evacuated again and pressured with hydrogen to 1.4–1.8 atm. The nitrogen-flushed reaction components were then injected by syringe, and the bottles were further filled with hydrogen to the desired pressure, usually 3.7 atm. Solid reagents stable to air were added before the bottles were capped. Pressure changes in the bottles were followed by means of Bourdon gages

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(24) K. Ziegler, W. R. Kroll, W. Larbig, and O. W. Steudel, *Ann.*, **629**, 53 (1960).

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equipped with hypodermic needles. Agitation was provided by means of magnetic stirring in thermostated baths or by means of a shaker at room temperature. Results of a typical experiment are given in Table IV.

TABLE IV

KINETICS OF HYDROGENATION OF CYCLOHEXENE WITH THE TRIISOBUTYLALUMINUM-CHROMIC ACETYLACETONATE CATALYST IN HEPTANE AT 30°^a

Time, min.	Pressure, atm.	Log (P ₀ /P)	10 ² × k, min. ⁻¹
0	3.62	0	
1.0	3.56	0.009	2.0
2.0	3.50	.015	1.7
4.0	3.37	.030	1.7
6.0	3.24	.049	1.9
11.0	2.97	.086	1.8
13.0	2.85	.104	1.8
15.0	2.75	.116	1.8
19.0	2.56	.148	1.8
24.0	2.36	.187	1.8
30.0	2.18	.220	1.7
70.0	1.62		

^a Cyclohexene, 1.04 M; [Cr] = 3.96 × 10⁻⁴ M; Al/Cr = 6.0.

For experiments at constant pressure the bottles were left attached to the hydrogen source at the desired pressure. The rate could be determined by closing off the hydrogen and observing the pressure drop over a short length of time.

Products were analyzed either by isolation and identification or by determining the ratio of olefin to saturated hydrocarbon by mass spectrometry. The instrument used was a Consolidated Electrodynamic Corp. mass spectrometer, Model 21-103. In several experiments the amount of reduction could be calculated from the pressure drop and void volume of the system.

Several typical hydrogenation experiments are described below.

Hydrogenation of *trans*-Stilbene with the Triisobutylaluminum-Cr(acac)₃ Catalyst.—An 8-oz. pressure bottle, charged with 1.80 g. (10 mmoles) of *trans*-stilbene and 0.105 g. (0.30 mmole) of chromic acetylacetonate, was evacuated, flushed with nitrogen several times, and then pressured with hydrogen. Into the bottle were then injected 20.0 ml. of nitrogen-sparged toluene and 1.80 ml. of 0.99 M triisobutylaluminum in *n*-heptane. The hydrogen pressure was adjusted to 3.7 atm., and the resulting red-brown solution was magnetically stirred at room temperature for 20 hr. At the end of this time the pressure was 2.6 atm. This corresponds to complete reduction. The catalyst was destroyed by addition of a few drops of water. After filtration the solvent was removed, and the residue was recrystallized from ethanol. The yield of bibenzyl was 1.40 g. (78%), m.p. 52.0–52.5° (lit.³⁴ m.p. 52°).

In a similar experiment in which 1.2 ml. of acetone was added after the catalyst components were mixed, no olefin hydrogenation took place.

Hydrogenation of Cyclohexene with an *n*-Butyllithium-Co(acac)₃ Catalyst.—In an 8-oz. pressure bottle a solution was prepared from 0.106 g. (0.29 mmole) of cobaltic acetylacetonate, 1.62 g. (19.7 mmoles) of cyclohexene, 1.0 ml. of 2.9 M *n*-butyllithium in *n*-heptane, and 15.0 ml. of *n*-heptane as described in the previous experiment. At an initial hydrogen pressure of 3.4 atm. the bottle was agitated in a rotating bath at 50° for 22 hr. At the end of this time the pressure had dropped to 1.7 atm. After destruction of the catalyst with water, the solution was dried over magnesium sulfate, filtered, and analyzed by mass spectrometry; found: cyclohexane, 14.7 mole %; cyclohexene, 6.6 mole % (69% reduction).

In a similar experiment in which ethanol was added after forming the catalyst, no hydrogenation occurred.

Hydrogenation of 3-Hexyne with a Triisobutylaluminum-Cr(acac)₃ Catalyst.—In an 8-oz. pressure bottle a solution of 0.80 g. (9.8 mmoles) of 3-hexyne, 0.90 g. (0.26 mmole) of chromic acetylacetonate, 1.9 ml. of 0.95 M triisobutylaluminum, and 15.0 ml. of *n*-heptane was prepared under 3.7 atm. of hydrogen as already described. The bottle was agitated at 30° for 24 hr., at the end of which time the pressure was 3.0 atm. This pressure drop is the result of absorption of 6.7 mmoles of hydrogen. The catalyst was decomposed by addition of a few drops of water, and the resulting mixture was dried over magnesium sulfate. Filtration and removal of the solvent yielded 0.356 g. of oily crystals,

(34) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 259.

which after recrystallization from ethanol-water produced 0.182 g. of hexaethylbenzene, m.p. 128.5-129.0° (lit.³⁵ m.p. 129°).

(35) "Dictionary of Organic Compounds," Vol. II, I. Heilbron and H. M. Bunbury, Ed., Oxford University Press, New York, N. Y., 1953, p. 657.

The infrared spectrum was identical with that published for hexaethylbenzene.³⁶

(36) R. E. Richards and H. W. Thompson, *Proc. Roy. Soc. (London)*, **A195**, 4 (1948).

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The Synthesis, Nuclear Magnetic Resonance Spectrum, Resolution, and Rate of Racemization of 1-Fluoro-12-methylbenzo[*c*]phenanthrene¹

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The synthesis and resolution of 1-fluoro-12-methylbenzo[*c*]phenanthrene is described. The rates of racemization in *o*-dichlorobenzene at 130.5, 109.7, and 91.9° were found to be 7.81×10^{-5} , 9.49×10^{-6} , and 1.27×10^{-6} sec.⁻¹, respectively. From these values, the activation energy was calculated to be 31.1 kcal./mole and the entropy of activation at 109.7°, -2.80 ± 0.6 cal./deg./mole. The molecule showed unexpected n.m.r. properties that are attributed to ring distortion.

A review of the structural features required in compounds which owe their asymmetry to intramolecular overcrowding has been made.³ Later, the synthesis and optical properties of hexahelicene were described.⁴ Of the compounds described in these papers, racemization either occurred too easily or too difficultly to allow for convenient measurement. For example, in the benzo[*c*]phenanthrene series the rate of racemization of a 1-methyl derivative⁵ was too rapid (groups in the 1- and 12-positions, CH₃ and H) whereas in 1,12-dimethyl-5-carboxy-methylbenzo[*c*]phenanthrene³ racemization could not be studied because of thermal decomposition of the compound (groups in the 1- and 12-positions, CH₃ and CH₃) at temperatures suitable for racemization study. Hence it seemed likely that if the groups in the 1- and 12-positions were CH₃ and F perhaps the rate of racemization would be measurable. This hypothesis proved to be correct.

In this paper the synthesis of 1-fluoro-12-methylbenzo[*c*]phenanthrene (VI) and the measurement of its rate of racemization at three temperatures are described. Thus, for the first time, the energy of activation and entropy of activation for the racemization of a compound which owes its asymmetry to intramolecular overcrowding⁶ have been determined.

The synthetic route illustrated was that of Newman and Wolf⁷ modified as described in later similar syntheses.^{3,4,8} The steps from I to III_d proceeded in excellent yields. However, difficulty was experienced in the double ring closure to IV, as in the best cases only about 30-44% yields were obtained. The remainder was a keto acid VII of unproved structure⁹ which was not readily cyclized to the desired diketone IV. Reduction of IV to the diol V proceeded well. Conversion of V to VI was accomplished in 40% yield by heating in refluxing xylene with a small amount of iodine for over 100 hr. Thus, VI was prepared from I in 9.2% over-all yield.

The ultraviolet absorption spectrum of VI is almost the same as that of 1,12-dimethylbenzo[*c*]phenanthrene.⁷ The values are listed in Table I.

(1) This work was taken from the Ph.D. thesis of R. G. M., The Ohio State University, 1962.

(2) We are indebted to the National Science Foundation and The U. S. Public Health Service for support of this work.

(3) M. S. Newman and R. M. Wise, *J. Am. Chem. Soc.*, **78**, 450 (1956).

(4) M. S. Newman and D. Lednicer, *ibid.*, **78**, 4765 (1956).

(5) M. S. Newman and W. Wheatley, *ibid.*, **70**, 1913 (1948).

(6) F. Bell and D. H. Waring, *J. Chem. Soc.*, 2689 (1949).

(7) M. S. Newman and M. Wolf, *J. Am. Chem. Soc.*, **74**, 3225 (1952).

(8) M. S. Newman and D. Phillips, *ibid.*, **81**, 3667 (1959).

(9) We favor the structure 3-carboxymethyl-4-*o*-fluorophenyl-5-methyl- α -tetralone rather than the isomeric structure involving ring closure into the fluorine-containing ring because ring closure *meta* to an aromatic fluorine atom should occur less easily than ring closure *meta* to a methyl group.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA			
1-Fluoro-12-methylbenzo[<i>c</i>]-phenanthrene		1,12-Dimethylbenzo[<i>c</i>]-phenanthrene	
λ , m μ	log ϵ	λ , m μ	log ϵ
212	4.32 (min.)	215	4.46 (min.)
221	4.55 (max.)	224	4.60 (max.)
240	4.05 (min.)	244	4.07 (min.)
248	4.10 (max.)	250	4.08 (max.)
255	4.09 (min.)	254	4.05 (min.)
289	4.73 (max.)	292	4.78 (max.)
322	3.87 (min.)	324	3.91 (min.)
326	3.88 (max.)	328	3.92 (max.)
361	2.49 (min.)	363	2.46 (min.)
367	2.51 (max.)	370	2.50 (max.)

The resolution of VI was accomplished by the use of (-)- α -(2,4,5,7-tetranitro-9-fluorenylideneaminoxy)-propionic acid¹⁰ as in a similar case.⁴ The maximum resolution afforded VI with [α]_D²⁵ ± 580 ± 15° in chloroform. The rates of racemization in *o*-dichlorobenzene were 7.81×10^{-5} at 130.5°, 9.49×10^{-6} at 109.7°, and 1.27×10^{-6} sec.⁻¹ at 91.9°. From these values, the activation energy was calculated to be 31.3 kcal./mole and the entropy of activation at 109.7° calculated to be -2.8 ± 0.6 cal./deg./mole. Thus it appears that the transition state for racemization is only slightly more rigid than the reactant.

The variations in the methyl group absorptions of 1-methylbenzo[*c*]phenanthrene, 1-fluoro-12-methylbenzo[*c*]phenanthrene, and 1,12-dimethylbenzo[*c*]phenanthrene in the n.m.r. spectra are of interest.¹¹ The spectrum of 1-methylbenzo[*c*]phenanthrene showed a complex multiplet of relative area eleven centered at about 7.7 δ and 50 c.p.s. in width which was attributed to the aromatic hydrogens. Unlike benzo[*c*]phenanthrene, it lacked unique absorption farther downfield.¹² In the methyl region it showed a singlet of relative area three at 2.36 δ . This methyl absorption was not very greatly shifted (from that for toluene at 2.32 δ) by the presence of the additional rings with their associated ring currents. These results could be attributed to the forcing of the methyl group out of the plane of maximum deshielding anisotropy of the opposing aromatic ring.¹³

(10) M. S. Newman and W. B. Lutz, *J. Am. Chem. Soc.*, **78**, 2469 (1956).

(11) The work on spectra of these compounds and their interpretation was done by Dr. George Slomp of the Upjohn Co., Kalamazoo, Mich. The discussion in our text was written by him. We are much indebted to him for this work. The spectra were taken on deuteriochloroform solutions with a Varian A-60 spectrometer.

(12) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 249.