JOURNAL OF CATALYSIS 27, 397-404 (1972)

Nickel Arsenide for Selective Hydrogenation of Diolefins

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Received April 19, 1972

Precipitated nickel arsenate on alumina after reduction in hydrogen at 420°C to nickel arsenide, nominally Ni_3As_{2+x}, is a very active and selective catalyst for hydrogenation of diolefins to the corresponding olefin, provided some catalyst modifier is present. Kinetic data obtained by following the hydrogenation of 1,5-cyclooctadiene, using carbon monoxide as a catalyst modifier, indicate the reaction proceeds by a series of reversible isomerization steps to the 1,3-conjugated diene which is hydrogenated to the corresponding olefin. Integrated rate equations which correlate the conversion-flow rate data show the reaction rates to be fractional order in both hydrogen and diene concentrations with isomerization and hydrogenation steps inhibited by carbon monoxide. It appears that carbon monoxide competes with dienes for sites and is more tightly held than the monoene. In effect, the adsorption of carbon monoxide excludes the monoene from further reaction on nickel arsenide.

INTRODUCTION

Selective hydrogenation of diolefins is an important route to preparing olefins not directly available by other means. Cyclopentadiene, available in large amounts as a byproduct from naphtha crackers, can be selectively hydrogenated to cyclopentene in high yields (*1*). Cyclooctene and cyclododecene can be prepared by selective hydrogenation of the cyclic dimers and trimers of 1,3-butadiene (*2*). All such conversions require special catalysts, close control of operating conditions and, in those cases where excess hydrogen is used to obtain complete conversion of the diene, addition of small amounts of a polar material to improve selectivity or limit the formation of completely saturated material. One of the better catalysts for selective hydrogenation is nickel sulfide on alumina, nominally Ni_3S_2, which, under suitable conditions, gives nearly quantitative diolefin conversion to the corresponding monoenes (*3*).

Nickel also forms compounds with arsenic having stoichiometry similar to nickel subsulfide. The catalytic activity for olefin hydrogenation of the arsenic analogs has not been systematically studied. We wish to report the results of an investigation of the use of nickel arsenide on alumina for diolefin hydrogenation using 1,5-cyclooctadiene as a reactant.

NOMENCLATURE

B	$\dfrac{\pi(N^\circ_H/N^\circ_T)^{2/3}(N^\circ_{1,5}/N^\circ_T)^{1/3}}{1 + K\pi(N^\circ_{CO}/N_T)}$, Atmos
k_1,k_2,k_4,k_5	Rate constants for reversible isomerization reaction
k_3	Rate constant for hydrogenation of 1,3-COD to cyclooctene
K	Adsorption equilibrium constant for carbon monoxide, $atmos^{-1}$
M	Mass of catalyst, gms
$N^\circ_{H_2},N^\circ_{CO},N^\circ_{1,5}$	Molar feed rates for hydrogen, carbon monoxide and 1,5-COD, respectively, $moles\text{-}Hr^{-1}$
π	Reactor pressure, atmos

EXPERIMENTAL

Apparatus and Procedure

The reactor consisted of a vertically suspended stainless steel tube, with a 1-in. diameter, heated by means of a 26-in, three-section electric furnace. The top and bottom were packed with glass beads or α-alumina, the middle section with catalysts diluted with one of the above inerts for near-isothermal operation. Four thermocouples inserted in a coaxial thermocouple well allowed temperature measurements throughout the catalyst bed.

Both the gaseous and liquid feeds entered at the top of the reactor. The reactor pressure was controlled by means of a motor valve placed at the reactor exit which reduced the pressure to ambient conditions. Gas feed rates were controlled by a fine needle valve, using a wet-test meter downstream of a wet ice trap to establish flow rates. Liquid feed rates were determined by means of a buret located upstream of a Lapp pump. Liquid samples for analysis were collected in the wet ice trap.

Carbon monoxide was introduced by either equilibrating the liquid feed with carbon monoxide under pressure or using hydrogen–carbon monoxide gas mixtures. The latter were obtained from the Matheson Company or prepared here at Phillips.

Reagents

Commercial grade electrolytic hydrogen from National Cylinder Gas was used in all experiments. The 1,5-cyclooctadiene was obtained from Columbia Carbon. The 2,3-trimethyl-1,4-pentadiene was obtained from Chemical Samples Co. The 3,3-dimethyl-1,4-pentadiene was synthesized here at Phillips. Other reagents were Phillips 98% materials. No attempt was made to purify any of the reagents.

Catalysts

Impregnated. Nickel arsenate was prepared by impregnating $-6/+20$ mesh nickel oxide on γ-alumina with aqueous solutions of H_3AsO_4, drying at 110°C, and calcining in air at 650°C for 2 hr.

Precipitated. Nickel arsenate was precipitated from a solution of $0.32\,M$ $Ni(NO_3)_2$ and $0.22\,M$ H_3AsO_4 containing suspended Alon-C alumina by slow addition of diluted NH_4OH until a pH of 7 was reached. The slurry was filtered, washed by reslurrying the filter cake in distilled water, and then refiltered. Following drying overnight at 100°C the catalyst was calcined at 535°C for 30 min, cooled to room temperature, and sized to $-10/+20$ mesh for use in a fixed-bed reactor.

Analysis of a typical batch of catalyst prepared by the above method gave 8.6 wt % As and 8.6 wt % Ni, with a BET surface area of 83 m^2/g, a pore volume of 0.73 ml/g, and an ABD of .68 g/cm^3.

Final activation of each catalyst was carried out in the fixed-bed reactor at 300–420°C for 4–16 hr under a slow stream of H_2 or the mixture of H_2 and CO. This reduction under H_2 converts the yellow-green nickel arsenate to a black, active catalyst.

Sample Analysis

Samples collected from the 1,5-cyclooctadiene hydrogenation were analyzed by glc using a Perkin-Elmer Model 880 gas chromatograph equipped with a 1,2,3-tris(2-cyanoethoxy) propane column. The 3,3-dimethyl-1,4-pentadiene hydrogenation products were analyzed using a Model 5750-B Hewlett-Packard instrument equipped with UCON columns. The 2,3,3-trimethyl-1,4-pentadiene hydrogenation product was analyzed using the Hewlett-Packard instrument equipped with an Apiezon N column.

The possible presence of structural isomers was checked by complete hydrogenation of products using the Adams catalyst in acetic acid and analyzing the hydrogenated product with glc.

RESULTS

Impregnated Catalysts

In initial work, a catalyst prepared by impregnation was tested for selective hydrogenation of diolefins using 4-vinylcyclohexene diluted in cyclohexane. The data

TABLE 1

Selective Hydrogenation of 4-Vinylcyclohexene, Impregnated Catalyst

Catalyst	Ni_3S_2	Ni_3As_{2+x}	
Process conditions			
Temperature (°C)	243	232	279
Reactor pressure (psig)	100	100	100
V(l.h.s.)(ml/ml · hr)	2	2	2
Product analysis (mole %)			
Ethylcyclohexane	1.70	.86	10.7
1-Ethylcyclohexene	60.5	62.6	51.6
3-Ethylcyclohexene	23.7	19.3	15.7
4-Ethylcyclohexene	9.3	8.2	5.9
Ethylbenzene	4.3	7.8	12.2
Vinylcyclohexane	.46	.50	—
4-Vinylcyclohexene	—	—	—
Ethylidinecyclohexane	—	.68	3.9

given in Table 1 indicate this catalyst to be the approximate equivalent of commercially available nickel sulfide on alumina. However, attempts to employ a similar impregnated catalyst for selective hydrogenation of 1,5-cyclooctadiene gave excessive saturation except in the presence of catalyst modifiers. Using a 10 wt % solution of 1,5-cyclooctadiene in cyclohexane and operating at 0.5 V(l.h.s.), 1000 psig, and 200°C gave a C_8 product consisting of 29% cyclooctane, 66% cyclooctene, 4% of the mixed cyclooctadiene isomers and 1% of a product tentatively identified as bicyclo [3.3.0]octene-2. A second sequence of tests was made using a 10% solution of 1,5-cyclooctadiene in *n*-pentane, saturating this solution with carbon monoxide at pressures of 75 and 145 psig. The analysis of the reactor effluent after steady state conditions had been reached indicated marked improvement in selectivity to cyclooctene with increased amounts of carbon monoxide improving the selectivity to the monoenes. These results are summarized in Table 2.

Precipitated Catalysts

As results obtained with impregnated catalysts showed variation in activity and selectivity, other methods of catalyst preparation were investigated. Catalysts prepared by precipitation of nickel arsenate on γ-alumina gave good results with little batch-to-batch variation in performance. Typical high conversion results for the precipitated catalyst using carbon monoxide to improve selectivity are shown in Table 3. As shown here, it is possible to reduce diene content to less than 0.05% and obtain yields of 97.5% cyclooctene with this system. Tests were made using a wide range of carbon monoxide contents to determine reaction rate and product distribution. As indicated in Table 4, increased carbon monoxide content reduces hydrogenation and diene isomerization activity. There appears to be little justification for using carbon monoxide molar feed rates in excess of the molar feed rate of 1,5-cyclooctadiene for selective hydrogenation, since increases in CO concentration above 5% in hydrogen reduced the reaction

TABLE 2

Selective Hydrogenation of 1,5-Cyclooctadiene, Impregnated Catalyst

Process conditions					
Temperature (°C)	206	206	206	206	222
Reactor pressure (psig)	100	200	400	400	400
(l.h.s.) (ml/ml · hr)	4.7	4.2	4.8	3.1	3.5
Mole ratio, 1,5-Cyclooctadiene/CO[a]	7	7	7	3.5	3.5
Mole ratio, H_2/1,5-Cyclooctadiene	36	32	28	48	53
Product analyses (mole %)					
Cyclooctane	2.5	2.7	4.5	3.0	6.7
Cyclooctene	28.0	40.8	90.6	92.0	92.7
1,3-Cyclooctadiene	35.8	33.8	3.1	4.1	.4
1,4-Cyclooctadiene	14.7	11.5	.7	.4	.1
1,5-Cyclooctadiene	18.9	11.2	1.2	.4	.2

[a] Estimated from solubility data of CO in *n*-C5.

TABLE 3
SELECTIVE HYDROGENATION OF 1,5-CYCLOOCTADIENE, PRECIPITATED CATALYST

Process conditions									
Temperature (°C)	182	182	182	182	182	182	182	182	182
Pressure (psig)	100	100	100	200	200	200	200	300	300
Feed rates (moles/hr)									
H_2	1.050	.954	.448	1.070	1.100	0.563	.513	1.050	1.080
CO	.050	.046	.022	.051	.053	.027	.024	.052	.053
Cyclohexane	.254	.599	.602	.262	.569	.255	.565	.251	.602
1,5-Cyclooctadiene	.023	.052	.053	.025	.049	.018	.049	.022	.052
Catalyst (g)	13.9	13.9	13.9	13.9	13.9	13.9	13.9	13.9	13.9
(l.h.s.)(ml/ml·hr)	1.41	3.50	3.51	1.46	3.14	1.43	3.14	1.41	3.34
C_8-Product distribution (mole %)									
Cyclooctane	2.76	1.24	1.09	5.04	2.39	7.10	2.42	8.64	2.94
Cyclooctene	96.95	97.60	97.68	94.87	97.60	92.89	97.56	91.39	97.06
1,3-Cyclooctadiene	.19	1.13	1.19	.05	.01	.01	<.01	<.01	<.01
1,4-Cyclooctadiene	.01	.07	.03	.01	<.01	<.01	<.01	<.01	<.01
1,5-Cyclooctadiene	.01	.06	.01	.04	<.01	<.01	<.01	<.01	<.01

rates significantly with little improvement in selectivity at comparable conversions.

Compounds other than carbon monoxide can be added to the system to improve selectivity or minimize the formation of cyclooctane by subsequent reaction of cyclooctene. Using as a feed the 10 wt % 1,5-cyclooctadiene, 90 wt % cyclohexane and adding 5 wt % of various modifiers gives the results summarized in Table 5. The conversion of mixed dienes was greater than 99.8% in each case cited in the tabulation. It would appear that a wide variety of carbonyl and polar compounds could be used in lieu of carbon monoxide. All such compounds reduce the reaction rate and improve selectivity to cyclooctene. There is, however, a partial conversion of aldehydes and ketones to alcohols and subsequent product purification would be more difficult than with carbon monoxide. It should also be noted that the results obtained with the precipitated catalyst in the absence of a modifier are significantly better than those cited earlier with impregnated catalysts.

TABLE 4
1,5-CYCLOOCTADIENE HYDROGENATION, EFFECT OF CARBON MONOXIDE CONTENT

Process conditions			
Temperature (°C)	190	190	190
Pressure (psig)	100	100	100
Feed rates (moles/hr)			
H_2	1.181	1.456	.568
CO	.069	.104	.653
Cyclohexane	.833	.825	.816
1,5-Cyclooctadiene	.0719	.0712	.0704
(l.h.s.)	8.2	8.1	8.0
Catalyst (g)	8	8	8
C_8-Product distribution (mole %)			
Cyclooctane	.19	.06	.01
Cyclooctene	57.69	31.63	10.22
1,3-Cyclooctadiene	38.40	53.14	34.31
1,4-Cyclooctadiene	2.87	8.56	26.25
1,5-Cyclooctadiene	.87	6.61	29.22

CATALYST COMPOSITION AND STABILITY

Adding ammonium hydroxide to a solution of a nickel salt and orthoarsenic acid in a slurry of alumina gives precipitated catalysts with a nickel to arsenic weight ratio near 1. This does not correspond to the stoichiometry for $Ni_3(AsO_4)_2 \cdot 5\ H_2O$ nor $NiHAsO_4 \cdot 2\ H_2O$ with nickel to arsenic weight ratios of 0.78 and 1.175, respectively. It appears that the method of catalyst preparation gives a mixture of

TABLE 5
MODIFIERS FOR 1,5-CYCLOOCTADIENE HYDROGENATION[a]

Modifier	Cyclooctene	Cyclooctane
Acetic acid	97.2	2.1
Acetone	97.2	1.9
Acetaldehyde	96.1	2.8
Methanol	92.7	6.9
None, dry feed	82.0	18.0
H_2O saturated at 32°C	82.0	18.0

[a] 400 psig, 204°C.

$NiHAsO_4 \cdot 2\ H_2O$ and $Ni_3(AsO_4)_2 \cdot 5\ H_2O$. The complexity of the nickel–arsenate system has been cited by Guerin *et al.* (*4*), and our results appear to be in agreement with his generalization concerning the difficulty of preparing $Ni_3(AsO_4)_2 \cdot 5\ H_2O$ as a pure compound.

Samples of calcined nickel arsenate on alumina were suspended in a porous silica container and dried under N_2 to a constant weight at various temperatures between 300 and 425°C. When CP hydrogen was substituted for the N_2 an immediate loss in weight occurred and continued until the weight loss corresponded to reduction of ortho- and pyro-nickel arsenate to the metal arsenide. That is, a sample containing 9.6 wt % As and 10.0 wt % Ni reached a constant weight loss of 7.5% at 425°C in a matter of several minutes. This analysis corresponds to a mixture of 0.52 moles $Ni_2As_2O_7$ per mole of $Ni_3(AsO_4)_2$ with a calculated weight loss of 7.4% on reduction to $Ni_3As_{2.26}$. Alternate oxidation and reduction for five cycles did not alter the composition within analytical precision, nor did sustained treatment under hydrogen for 60 hr at 425°C result in a change in weight.

At higher temperatures near 550°C there is a continual weight loss from the catalyst during the oxidation and reduction cycles. Thus, temperatures in this region should be avoided during regeneration and activation.

X-ray diffraction patterns of the active catalyst show the presence of γ-alumina and NiAs. Lines for the Ni/As–σ phase that correspond to $(Ni_{11}As_8)_4$ were not present, although the phase diagram for the Ni/As system given by Heyding and Calver (*5*) indicates both NiAs and $Ni_{11}As_8$ to be present in this composition range of 50–50 wt % Ni/As.

MECHANISM AND KINETICS OF SELECTIVE DIENE HYDROGENATION

The data for 1,5-cyclooctadiene hydrogenation at various conversions suggest that the reaction proceeds by a series of isomerization steps to a conjugated 1,3-diolefin which is hydrogenated to the corresponding olefin. Consistent with this generalization are the facts that (1) the addition of a double bond isomerization catalyst, MgO, to a fixed amount of nickel arsenide on alumina results in increased conversion to cyclooctene, and (2) where the possibility of forming a conjugated system is eliminated, very little conversion of the diolefin to the olefin occurs. The excellent double-bond isomerization activity of nickel arsenide was verified by a series of experiments using pentene-1 (Phillips Petroleum Co. pure grade). At conditions where extensive conversion of 1,5-cyclooctadiene to cyclooctene is obtained, pentene-1 is isomerized to a mixture of *cis*- and *trans*-pentene-2 while only small amounts of normal pentane are formed. Under similar conditions, 3,3-dimethyl-1,4-pentadiene and 2,3,3-trimethyl-1,4-pentadiene, in which the formation of a conjugated system is blocked, give only minor amounts of monoenes and paraffin (carbon monoxide was used in the pentene and branched diolefin work as a catalyst modifier). This demonstrates that carbon–carbon double bond isomerization is rapid over nickel arsenide and there is a strong preference for hydrogenation of conjugated diolefin over nonconjugated diolefins and monoenes.

An effort was made to correlate the flow rate–product distribution data obtained at conditions giving less than complete conversion. Several rate constants are required since, in addition to the hydrogenation steps, there are the isomerization steps and carbon monoxide inhibition to be included in the rate expression. For a flow reactor a material balance over an incremental mass of catalyst, dM, gives the following equations for the reaction sequence depicted below:

$$\text{1,5-COD} \underset{k_4}{\overset{k_1}{\rightleftarrows}} \text{1,4-COD} \underset{k_5}{\overset{k_2}{\rightleftarrows}} \text{1,3-COD} \underset{H_2}{\overset{k_3}{\rightleftarrows}} \text{Cyclooctene.}$$

$$r_1 dM = -N^{\circ}_{1,5} d(N_{1,5}/N^{\circ}_{1,5}); \qquad (1)$$

$$r_2 dM = N^{\circ}_{1,5} d(N_{1,4}/N^{\circ}_{1,5}); \qquad (2)$$

$$r_3 dM = N^{\circ}_{1,5} d(N_{1,3}/N^{\circ}_{1,5}); \qquad (3)$$

$$r_4 dM = N^{\circ}_{1,5} d(N_p/N^{\circ}_{1,5}). \qquad (4)$$

The variables r_1, r_2, r_3, and r_4 are the rates of disappearance of 1,5-cyclooctadiene, the formation of 1,4-cyclooctadiene, 1,3-cyclooctadiene, and hydrogenated product per

TABLE 6

SELECTIVE HYDROGENATION OF 1,5-CYCLOOCTADIENE, PRECIPITATED CATALYSTS

Process conditions									
Temperature (°C)	191	191	191	191	191	191	191	191	191
Pressure (atm)	7.82	7.82	7.82	7.82	7.82	7.82	7.82	7.82	7.82
Feed rate (moles/hr)									
H_2	.661	.663	1.456	1.181	.563	.568	1.393	1.411	1.411
CO	.119	.120	.104	.069	.647	.653	.557	.564	.564
Cyclohexane	.378	.825	.825	.833	.374	.816	.816	.366	.593
1,5-Cyclooctadiene	.0326	.0712	.0712	.0719	.0323	.0704	.0704	0.316	.0500
Product distribution (mole %)									
Cyclooctane	.12	.04	.06	.06	.03	.01	.02	.05	.04
Cyclooctene	64.44	21.19	31.63	28.32	34.81	10.22	17.78	46.40	31.79
1,3-Cyclooctadiene	33.65	54.08	53.14	53.01	53.30	34.31	46.58	46.16	50.73
1,4-Cyclooctadiene	1.20	13.59	8.56	10.67	7.42	26.25	17.96	4.83	10.12
1,5-Cyclooctadiene	.59	11.11	6.61	7.94	4.44	29.22	17.66	2.56	7.32
$B(M/N^\circ_{1,5})$	398	159	180	186	218	104	149	299	202

unit mass of catalyst, respectively. $N^\circ_{1,5}$ is the molar feed-rate of 1,5-cyclooctadiene, and the terms $N_{1,5}/N^\circ_{1,5}$, $N_{1,4}/N^\circ_{1,5}$, $N_{1,3}/N^\circ_{1,5}$, and $N_p/N^\circ_{1,5}$ represent the fraction of 1,5-cyclooctadiene converted to various products. Satisfactory correlation of the data shown in Table 6 was obtained using a hybrid digital–analog computer to obtain a solution to the nonlinear equations that result from Eq. 1–4 when the rates are expressed as follows:

$$r_1 = \frac{\pi(N^\circ_H/N^\circ_T)^{2/3}(N^\circ_{1,5}/N^\circ_T)^{1/3}}{[1 + K\pi(N^\circ_{CO}/N^\circ_T)]} \times \left[k_1\left(\frac{N_{1,5}}{N^\circ_{1,5}}\right)^{1/3} - k_4\left(\frac{N_{1,4}}{N^\circ_{1,5}}\right)^{1/3}\right]$$

$$r_1 = B[k_1(N_{1,5}/N^\circ_{1,5})^{1/3} - k_4(N_{1,4}/N^\circ_{1,5})^{1/3}];$$

$$r_2 = B[k_1(N_{1,5}/N^\circ_{1,5})^{1/3} - k_4(N_{1,4}/N^\circ_{1,5})^{1/3} - k_2(N_{1,4}/N^\circ_{1,5})^{1/3} + k_5(N_{1,3}/N^\circ_{1,5})^{1/3}];$$

$$r_3 = B[k_2(N_{1,4}/N^\circ_{1,5})^{1/3} - k_3(N_{1,3}/N^\circ_{1,5})^{1/3} - k_5(N_{1,3}/N^\circ_{1,5})^{1/3}];$$

$$r_4 = B[k_3(N_{1,3}/N^\circ_{1,5})^{1/3}].$$

This model assumes that the rate of 1,5-cyclooctadiene reaction is 2/3-order in hydrogen concentration and 1/3-order in diolefin concentration. The term $[1 + K\Pi(N^\circ_{CO}/N^\circ_T)]^{-1}$ denotes the reduction in rate due to carbon monoxide and can be interpreted as representing the fraction of sites covered by carbon monoxide. The assumptions that the total number of moles, N°_T, does not change with reaction and that isomerization and hydrogenation steps are inhibited in the same manner by the presence of carbon monoxide are obvious simplifications required for a tractable analysis. This leads to the following equations on substitution in Eqs. (1)–(4):

$$\int_1^{N_{1,5}/N^\circ_{1,5}} \frac{d(N_{1,5}/N^\circ_{1,5})}{k_1(N_{1,5}/N^\circ_{1,5})^{1/3} - k_4(N_{1,4}/N^\circ_{1,5})^{1/3}} = B(M/N^\circ_{1,5}); \qquad (1\text{-}1)$$

$$\int_0^{N_{1,4}/N^\circ_{1,5}} \frac{d(N_{1,4}/N^\circ_{1,5})}{k_1(N_{1,5}/N^\circ_{1,5})^{1/3} - (k_4 + k_2)(N_{1,4}/N^\circ_{1,5})^{1/3} + k_5(N_{1,3}/N^\circ_{1,5})^{1/3}} = B(M/N^\circ_{1,5}); \qquad (2\text{-}1)$$

$$\int_0^{N_{1,3}/N^\circ_{1,5}} \frac{d(N_{1,3}/N^\circ_{1,5})}{k_2(N_{1,4}/N^\circ_{1,5})^{1/3} - k_5(N_{1,3}/N^\circ_{1,5})^{1/3} - k_3(N_{1,3}/N^\circ_{1,5})^{1/3}} = B(M/N^\circ_{1,5}); \qquad (3\text{-}1)$$

$$\int_0^{N_{1,3}/N^\circ_{1,5}} \frac{d(N_p/N^\circ_{1,5})}{k_3(N_{1,3}/N^\circ_{1,5})^{1/3}} = B(M/N^\circ_{1,5}). \qquad (4\text{-}1)$$

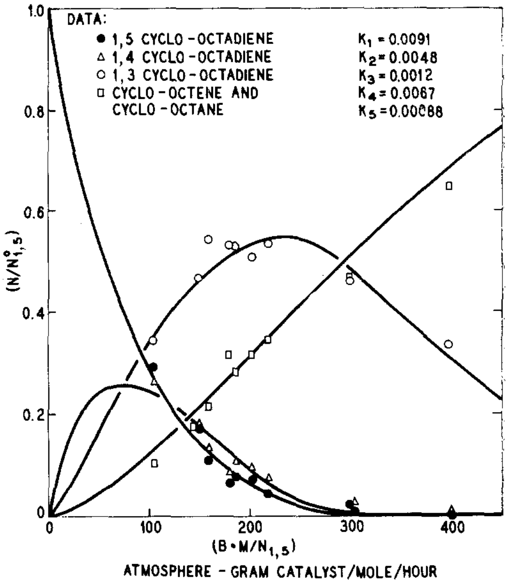

FIG. 1. Computer determination of rate constants in selective diene hydrogenation.

Concentrations of all the cyclic C_8 compounds are determined by a value of the term $B(M/N^\circ_{1,5})$ and the rate constants for the reaction sequence at a fixed temperature.

The results of a hybrid computer determination of the reaction rate constants are given in Fig. 1. The rate constants were determined by least-squares fit to the data in Table 6, also plotted in Fig. 1. The differential equations in the kinetic model were programmed and solved on an EAI 680 analog computer. Operation of the analog and selection of parameter values (reaction rate constants) were under control of the digital computer, an EAI 8400. The digital program used a form of the Hooke and

Jeeves pattern search (*6*) in obtaining the least-squares fit.

The computer search for the reaction rate constants did not result in a clearly unique set of values. The form of the kinetic model and the run conditions resulted in a relatively flat sum of squares in the region around the minimum. However, the variations in the reaction rate constants that result in small variations in the sum of squares are to be expected with this kinetic model. The reversible reactions can have both the forward and reverse rate constants changed in the same direction (e.g., increased) with only minor changes in the sum of squares. Computer results for the irreversible formation of cyclooctene from 1,3-cyclooctadiene were relatively constant. Changing the order of the reaction from 1/3 order in olefin and 2/3 order in hydrogen by plus or minus 20% of these values gave less satisfactory correlation of the data.

CONCLUSION

In conclusion, it appears that nickel arsenide on alumina is similar to supported nickel sulfide in its catalytic properties. Both systems are active for double-bond isomerization, preferentially hydrogenate conjugated diolefins over the nonconjugated diolefins and monoenes, give little structural isomerization or cleavage of carbon to carbon bonds and do not hydrogenate aromatics (7). The nickel arsenide system requires the addition of some polar material to give highly selective diolefin hydrogenation and avoid paraffin formation by subsequent hydrogenation of monenes. The system appears to be stable with no detected arsenic loss and, as contrasted with Ni_3S_2, can be used without the contamination of products from sulfur compounds. For hydrogenation of 1,5-cyclooctadiene to cyclooctene, the nickel arsenide catalysts modified by carbon monoxide are more selective than the nickel sulfide on alumina catalysts used by Zuech (*2*).

ACKNOWLEDGMENTS

The thermogravimetric analyses were made by Dr. H. D. Johnston. Many of the experimental catalysts were prepared by D. W. Walker. W. H. Buckhannan used the analog simulator to help model the kinetics of 1,5-cyclooctadiene hydrogenation.

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