Anal. Calcd. for $C_{21}H_{26}O_2N_2$: C, 74.51; H, 7.75; N, 8.28. Found: C, 74.53; H, 7.52; N, 8.67.

The sodium bicarbonate solution was acidified with dilute hydrochloric acid. The precipitate of crude monoanilide was crystallized twice from 40% ethanol and melted at 119.5–120.5°.

Anal. Calcd. for $C_{15}H_{21}O_3N$: C, 68.45; H, 8.04; N, 5.32. Found: C, 68.42; H, 7.62; N, 5.42.

(B) 4.1 g. of II was refluxed for 24 hours with 40 ml. of concentrated hydrochloric acid. The clear solution was concentrated *in vacuo* to about 20 ml. and an oil separated. The mixture was extracted with two 30-ml. portions of ether. The combined ether extracts were washed with four 10-ml. portions of water and the ether layer was dried over anhydrous sodium sulfate. Filtration and evaporation of the ether yielded 1.8 g. of viscous, oily VIII which solidified on cooling; m.p. 36.5–39.5°.

Ethyl α-Acetamido-α-carbethoxy-α′-cyanopimelate (III).—The condensation–reduction reaction employing crude γ-acetamido-γ,γ-dicarbethoxy-butyraldehyde[11] (84.7 g.) and ethyl cyanoacetate (36.2 g.) was carried out essentially as described under II. The crude reaction product weighed 121.5 g. Distillation of 86 g. of the crude oil yielded 28.4 g. of product collected at 210–220° (0.8 mm.). A large amount of a dark brown residue remained. Redistillation yielded 22 g. of III collected at 195–198° (0.25 mm.) (27%).

α-Aminopimelic Acid (IX).—A portion (5.2 g.) of the redistilled III was refluxed with 50 cc. of concentrated hydrochloric acid for a period of 24 hours. After filtration, the reaction mixture was concentrated *in vacuo*. The residue was dissolved in 8 cc. of water and neutralized to a *p*H of 3.1 with aqueous sodium hydroxide solution. The resulting solution was heated and filtered. When the filtrate was permitted to cool slowly, it yielded a crystalline product which was melted at 216° with decomposition.

Anal. Calcd. for $C_{17}H_{13}O_4N$: C, 47.98; H, 7.48; N, 8.00. Found: C, 47.90; H, 7.28; N, 7.95.

The α-aminopimelic acid was further characterized as the N-benzoyl derivative which melted at 164–165°.

Anal. Calcd. for $C_{14}H_{17}O_5N$: C, 60.18; H, 6.13; N, 5.02. Found: C, 60.44; H, 5.82; N, 5.34.

Ethyl α-Cyano-ε,ε-dicarbethoxyhexadecanoate (IV).—The condensation–reduction reaction was carried out using 51.9 g. of crude γ-decyl-γ,γ-dicarbethoxybutyraldehyde[9] and 20.3 g. of ethyl cyanoacetate essentially as described under II. Distillation of the reaction product yielded 29 g. of IV collected at 200–205° (0.7–0.8 mm.). Redistillation yielded 21 g. (32%) of IV collected at 189–198° (0.12 mm.). An analytical sample was prepared by collecting a middle cut from another distillation at 176° (0.06 mm.), $n^{25}D$ 1.4515.

Anal. Calcd. for $C_{25}H_{43}O_6N$: C, 66.22; H, 9.49; N, 3.09. Found: C, 66.27; H, 9.36; N, 3.49.

Ethyl α-Acetoxy-α-carbethoxy-α′-cyanopimelate (V).—Crude γ-acetoxy-γ,γ-dicarbethoxybutyraldehyde[9] (27 g.) was condensed with ethyl cyanoacetate (12.5 g.) essentially as described under II. In the first distillation, 19 g. of crude V was collected at 167–182° (0.2–0.3 mm.). Upon redistillation, 13 g. (35%) was collected at 160–168° (0.1 mm.). A center fraction was collected at 162.5–163° (0.1 mm.); $n^{25}D$ 1.4512.

Anal. Calcd. for $C_{17}H_{25}O_8N$: C, 54.95; H, 6.79; N, 3.78. Found: C, 54.77; H, 6.66; N, 3.64.

MINNEAPOLIS, MINNESOTA

RECEIVED AUGUST 3, 1951

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[11] O. A. Moe and D. T. Warner, THIS JOURNAL, 70, 2763 (1948).

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY, EMERYVILLE, CALIFORNIA]

Selective Hydrogenation of Polyolefins with Metal Sulfide Catalysts in the Liquid Phase

BY R. J. MOORE, R. A. TRIMBLE AND B. S. GREENSFELDER

The use of the sulfides of molybdenum and nickel as liquid phase selective hydrogenation catalysts is described; these materials were found to be highly selective for the hydrogenation of polyolefins to monoölefins. Advantageously, they retain their activity in the presence of as much as one per cent. mercaptan or alkyl sulfide. Evidence is presented to show that hydrogenation proceeds through the conjugated form of the polyolefin, with preliminary catalyzed isomerization of nonconjugated double bonds to this form when structurally permissible.

Although metal sulfides have been proposed as liquid phase olefin hydrogenation catalysts,[1,2] finely divided active metals such as nickel, platinum, etc., have remained the most widely used catalysts for this type of reaction. It is very difficult, however, to hydrogenate an olefin with these metal catalysts in the presence of common sulfur compounds, except for some limited reactions involving thiophenes. In view of the successful development and application of metal sulfide catalysts for commercial high temperature vapor phase hydrogenation and dehydrogenation, the use of catalysts of this type with sufficient activity for liquid phase reactions at low to moderate temperatures was investigated.

When operating in the range 100 to 200°, metal sulfides, notably the sulfides of nickel and molybdenum, have been found to have a remarkable activity and selectivity for hydrogenation of certain polyolefins to monoölefins in the liquid phase, but are virtually inactive for hydrogenation of monoolefins or of the benzene ring. However, only those polyolefins which are conjugated or are capable of conjugation by double bond shift isomerization were found to be susceptible to this selective hydrogenation. These catalysts are highly selective in that the rate of monoölefin hydrogenation is so low as to be negligible under the applied conditions. In contrast, previous work with elementary metals[3] appears to be based on relatively smaller differences in reactivity in favor of the more unsaturated component, and the reaction must be externally interrupted at the desired extent of hydrogenation.

Experimental Part

Preparation of Catalysts.—The catalysts used here were prepared by impregnating a porous support with an aqueous solution of a readily decomposable metal salt. The dried mixture was then heated with hydrogen sulfide to convert the metal to the sulfide. In general, the finished catalysts contained about 10% metal by weight.

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[1] U. S. Patent 1,908,286, E. Dorrer (to I. G. Farbenindustrie, A. G.), May 9, 1933; U. S. Patent 2,402,493, B. S. Greensfelder and W. H. Peterson (to Shell Development Co.), June 18, 1946; U. S. Patent 2,488,145, W. M. Smith and R. B. Mason (to Standard Oil Development Co.), November 15, 1949.

[2] W. A. Lazier, F. K. Signaigo and co-workers have described the preparation of various sulfide hydrogenation catalysts and their use in introducing sulfur into organic compounds, as covered by U. S. Patents 2,402,613 to −15; −39 to −45; −85 and −86 (to E. I. du Pont de Nemours and Co.).

[3] K. N. Campbell and B. K. Campbell, *Chem. Revs.*, 31, 77 (1942).

A typical preparation of supported molybdenum sulfide follows: 21.8 g. of Baker C.P. ammonium molybdate was dissolved in 45 ml. of 10% ammonium hydroxide and used to impregnate 100 g. of "Alorco" F-1 alumina (α-alumina monohydrate, <0.8% Na_2O, <0.1% SiO_2). After drying at 110°, the material was treated with hydrogen sulfide at 300°, then with hydrogen to reduce the sulfide to MoS_2. To facilitate suspension in a liquid medium, the catalyst was ground to pass a 100-mesh screen. A similar preparation of active nickel sulfide was made using nickel nitrate.

Hydrogenation in an Autoclave.—The hydrogenation equipment consisted of a 325-ml. capacity stainless steel bomb with heating and shaking devices of the type described by Adkins.[4] Temperatures were maintained automatically within 3° of the specified temperature, and pressures were observed on a calibrated gage. The reactant and solvent totaling 100 or 150 ml., and 50 g. of catalyst (*ca.* 5 g. metal) were charged to the bomb, air was flushed out with hydrogen, and hydrogen was admitted to the desired pressure.[5] The vessel was heated to reaction temperature (usually within 40 minutes) with shaking and the rate of hydrogenation was estimated from the observed pressure drop. When hydrogen was no longer absorbed, the vessel was cooled, the excess hydrogen released, and the product recovered from the catalyst by filtration.

In those experiments in which appreciable hydrogenation took place, the rate of hydrogenation at 150° with an initial pressure of 100 atm. was about 0.5 to 1.0 mole per hour. These rates appear to be unaffected by as much as 1% mercaptan or alkyl sulfide.

Extent of hydrogenation and reaction selectivity were estimated from the total amount of hydrogen absorbed and by determination of the bromine number of the product. These values checked within a few tenths of a per cent. in most cases and gave values corresponding to 100% hydrogenation of all but one double bond. In some instances, infrared absorption analysis was used to study the structures of feed and product hydrocarbons.

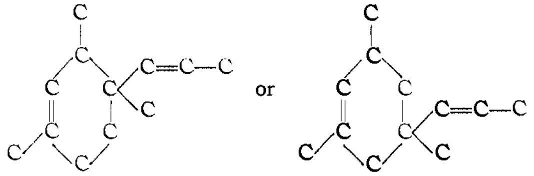
Hydrocarbons.—*d*-**Limonene** (1-methyl-4-isopropenylcyclohexene) (Eastman Kodak Co.) was fractionated under reduced pressure, the fraction used boiling at 177°, $n^{20}D$ 1.4739.

1,5-Hexadiene was prepared by the method of M. S. Kharasch,[6] boiling range 59.6–59.7°, $n^{20}D$ 1.4043. Infrared absorption analysis showed no conjugated diolefin and only α-olefin type bonds.

Myrcene (2-methyl-6-methylene-2,7-octadiene) obtained from the Glidden Company was distilled under reduced pressure, the fraction used boiling at 167° (cor.).

Cyclohexene (Eastman Kodak Co.).—**1,3-Cyclohexadiene** was prepared by dehydration of cyclohexen-3-ol, which in turn was obtained by the two-step process, substitutive chlorination of cyclohexene followed by caustic hydrolysis; boiling range 79–80°.

"Dihexene" was prepared by dimerization of a commercial mixture of 2- and 4-methyl-1,3-pentadiene. Boiling range 198–200°, $n^{20}D$ 1.4764. Proposed structures for this material, which are supported by infrared absorption analysis,[7] are shown below (I).



I

The other hydrocarbons were standard laboratory materials of greater than 99% purity.

Discussion

The data summarized in Table I show the high selectivity of the sulfide type catalysts for hydrogenation of certain polyolefins. Those compounds which were susceptible to hydrogenation, such as 1,5-hexadiene and limonene, readily reacted under relatively mild conditions (125–150°) to form the corresponding monoölefin. Similarly, myrcene, a decatriene, was hydrogenated to a decene. In contrast, benzene showed no detectable change in 6 hours and cyclohexene was hydrogenated to the extent of only 5% in 24 hours at 150°.

TABLE I

LIQUID PHASE HYDROGENATION WITH METAL SULFIDE CATALYSTS

(A) MoS_2/alumina; (B) NiS/alumina; temperature, 150°; initial hydrogen pressure, 100 atm.

Hydrocarbon	Number of double bonds	Moles H_2 absorbed per mole hydrocarbon		Catalysts
		From pressure drop	From bromine no.	
Limonene[a]	2	1.0	1.0	A,B
1,5-Hexadiene	2	1.0	1.0	A,B
Myrcene	3	1.9	1.8	B
1,3-Cyclohexadiene	2	1.0	1.0	B
2-Pentene	1	[b]	[b]	B
1-Hexene	1	[b]	[b]	B
Cyclohexene	1	0.05	0.05	B
Benzene	3	Nil	. .	B
2-Methylpentadiene	2	[c]	[c]	A,B
Dihexene	2	0.10	0.10	A

[a] 90% of hydrogenated product contained the $—CH_2—CR=CH_2—$ group in the ring by infrared analysis.
[b] No reaction observed at 150°; 20% hydrogenation observed in 20 hours at 200°. No double bond isomerization.
[c] 50% of original diolefin converted to dimer; remainder was isohexenes.

A determination of structure of all of the reaction products was not attempted. However, the position of the remaining double bond in hydrogenated 1,5-hexadiene was established to study the course of the hydrogenation reaction. Estimation of double bond type by infrared absorption analysis and by ozonization of the hexene product to a mixture of acetic, propionic and butyric acids showed that on hydrogenation of 1,5-hexadiene, 2- and 3-hexene but no 1-hexene had been formed. Since it was also shown in another experiment that double bond shift isomerization of *monoölefin* does not take place under the experimental conditions used,

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(4) H. Adkins, *Ind. Eng. Chem., Anal. Ed.*, **4**, 342 (1932).

(5) Over the range 15–100 atm., there appeared to be no effect of hydrogen pressure on the rate of hydrogenation.

(6) M. S. Kharasch, *J. Org. Chem.*, **9**, 364 (1944).

(7) The original 1,3-methylpentadiene was stated to contain about 85% of the 2-methyl and 15% of the 4-methyl isomer. The latter is relatively unreactive compared to the former. Now, sixteen possible co- and cross-dimers can be obtained from a mixture of the two isomers. Infrared spectroscopic analysis of distilled dimer showed (1) no conjugated double bonds; (2) no normal alpha double bonds; (3) only 14 mole % tertiary alpha ($CH_2=CR_2$) bonds; (4) 41 mole % *trans*-secondary (RCH=CHR) bonds; and (5) an unspecified large amount of internal tertiary ($RCH=CR_2$) bonds. It is assumed that (6) 41 mole % *cis*-secondary (RCH=CHR) bonds (not detectable by infrared analysis) are present, equal to the *trans*-secondary.

Four structures may be eliminated on the basis of (2); four more are assigned minor importance from (3); two co-dimers of the 4-methyl isomer are excluded because of low reactivity of this isomer. Of the six remaining structures, only two fulfill simultaneously (4), (5) and (6); these two correspond to the structures (I) shown, and they are the preferred Diels–Alder co-dimers of the reactive 2-methyl isomer. However, it is also possible to satisfy the latter spectroscopic results (4), (5), (6), by assuming a mixture of two pairs of cross-dimers, the first pair containing solely internal tertiary bonds in both the ring and side-chain, the second pair containing solely *cis*- and *trans*-secondary bonds in both the ring and side-chain. Therefore, the proof of structure is not conclusive.

Hydrogen absorption, checked by bromine number, was 0.1 mole H_2 per mole dihexene (Table I); this value is not far from the expected absorption of 0.14 mole H_2 per mole deduced from structures corresponding to (3).

either (a) preliminary isomerization of the double bonds to the conjugated form, or (b) 1,6-hydrogenation is required to account for appearance of the remaining double bond at other than the alpha position. Attempts to effect a catalytic isomerization of 1,5-hexadiene with active sulfide catalyst in the presence of an inert gas were fruitless; after 6 hours at 150° in the presence of nitrogen, the hydrocarbon and catalyst were recovered essentially unchanged, and no conjugated diene could be detected by ultraviolet absorption analysis. It would appear, therefore, that if isomerization does occur, hydrogen is required as in the catalytic isomerization of polyunsaturated acids.[8] This has been found to be the case in the double bond shift isomerization of butenes over metal film catalysts at room temperature in these laboratories,[9] as well as over unsupported metal sulfide catalysts[10] at 250°. In the latter experiments, atmospheric pressure was used and hydrogenation of double bonds was rapid. In the present work (at 150°), pentene-2 and hexene-1 were not isomerized and only very slowly hydrogenated. Any double bond isomerization with 1,5-hexadiene is unfortunately obscured in the present case by concomitant hydrogenation. However, by combining the hydrogenation products from a number of experiments and removing the hexene by distillation, a small amount of material equivalent to about 10% of the original hexadiene was recovered boiling in the range expected for the hexadiene dimer (200°) and having a terpene-like odor. This indicates that at least some conjugated diene is formed, permitting dimerization *via* a Diels–Alder type reaction.

In order to establish whether or not conjugation of multiple double bonds must precede hydrogenation over the sulfide type catalysts, as in (a) above, a hydrocarbon which could not become conjugated by virtue of its structure was studied. Dihexene (I), the dimer of 2-methyl-1,3-pentadiene, having a geminally substituted carbon atom between the two double bonds, cannot be isomerized by simple double bond shift *via* the movement of successive adjacent hydrogen atoms to the conjugated form. When this compound was subjected to hydrogenating conditions only a small absorption of hydrogen was found.[7] It is concluded, therefore, that selective hydrogenation with sulfide type catalysts occurs only with conjugated systems or those which first become conjugated over the catalyst through double bond isomerization in the presence of hydrogen.

Acknowledgment.—The authors are indebted to other members of the staff of Shell Development Company, in particular, to R. C. Morris for providing samples of cyclohexadiene and dihexene, to W. R. Harp, Jr., and F. S. Mortimer for spectroscopic analysis of dihexene, and to S. G. Balestrieri and Miss M. B. Hofacker for assistance in experimental work.

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[8] G. H. Twigg, *Proc. Roy. Soc.* (*London*), **A178**, 106 (1941).

[9] O. Beeck, *et al.*, unpublished results.

[10] B. S. Greensfelder, R. M. Roberts and F. T. Eggertsen, Emeryville Laboratories of Shell Development Company, unpublished results.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Transfer of Oxygen Atoms in Oxidation–Reduction Reactions. III. The Reaction of Halogenates with Sulfite in Aqueous Solution

BY JOSEPH HALPERIN[1] AND HENRY TAUBE

The extent of transfer of oxygen atoms from the oxidizing agent to the reducing agent on the reaction of various halogenates with sulfite in aqueous solution has been measured with O^{18} as tracer element. The number of oxygen atoms transferred per mole of halogenate on complete reduction to halide ion was observed to be 2.29 for ClO_3^-, 1.50 for ClO_2, 1.55 for ClO_2^-, 0.36 for Cl_2O and 2.20 for BrO_3^-, for a solution 0.1 *M* in HCl at 25°. Except for Cl_2O, which was not intensively studied, it was found that the values for transfer are independent of the order of mixing, and decrease slightly as the *p*H increases. The data are interpreted on the basis that reduction takes place stepwise (*e.g.*, $ClO_3^- \rightarrow ClO_2^- \rightarrow ClO^- \rightarrow Cl^- \rightarrow$) and that the defect from complete transfer takes place in the hypochlorite stage. With ClO_2, the first step is a process bimolecular in ClO_2, forming ClO_2^- of the same isotopic composition as ClO_2. The interpretation is consistent with rate laws where they have been determined, and with the chemistry of the systems. When ClO_2 disproportionates in alkali, the ClO_2^- formed has isotopic composition almost identical with the original ClO_2, with only a minor dilution by solvent oxygen.

In the reaction of oxy-oxidizing agents such as ClO_3^-, NO_3^-, MnO_4^- with reducing agents in an oxide labile solvent such as water, either the solvent or the oxidizing agent may be the source of oxygen which is added to the reducing agent on oxidation. Experiments using O^{18} as tracer have shown[2] that in the oxidation of sulfite by nitrite, the oxygen appearing on the sulfite is derived from the solvent. Preliminary tracer experiments[3] in the reaction of chlorate with sulfite showed that in this reaction, a part but not all of the oxygen added to sulfite is derived from the oxidizing agent.

The experimental technique has been considerably refined since publication of the preliminary results on the chlorate–sulfite system, and the observations on the system have been amplified. The tracer method has been applied also to the reactions with sulfite of other halogenates, namely, ClO_2, ClO_2^-, HClO, Cl_2O and BrO_3^-. In the present paper the experimental methods are described, pertinent exchange data are presented and the results of the tracer experiments reported. Observations made on the path of oxygen in the disproportionation of ClO_2 by alkali are also included.

Experimental Method

The steps involved in carrying out a tracer experiment on the oxidation of sulfite by halogenates were: preparation of

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[1] A.E.C. Predoctoral Fellow, 1949–1950.

[2] A. C. Rutenberg, J. Halperin and H. Taube, THIS JOURNAL, **73**, 4487 (1951).

[3] J. Halperin and H. Taube, *ibid.*, **72**, 3319 (1950).