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(54) PROMOTING THE CATALYTIC PROCESS FOR MAKING POLYHYDRIC ALCOHOLS

(71) We, UNION CARBIDE CORPORATION, a corporation organized and existing under the laws of the State of New York, United States of America, of 270 Park Avenue, New York, State of New York 10017, United States of America, (assignee of LEONARD KAPLAN), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to the manufacture of polyhydric alcohols.

It is known that monofunctional compounds such as methanol can be obtained by reaction between carbon monoxide and hydrogen at elevated pressures, e.g., up to about 1000 atmospheres, and temperatures ranging from 250°C to 500°C, using mixtures of copper, chromium and zinc oxides as the catalyst therefor. It is disclosed in U.S. Patent No. 2,451,333 that polyhydroxyl compounds are produced by reaction of formaldehyde, carbon monoxide, and hydrogen in the presence of hydrogenation catalysts. It has also been reported that formaldehyde can be produced by reaction between carbon monoxide and hydrogen at elevated pressures but repeated attempts to carry out this synthesis of formaldehyde have invariably failed to yield any substantial quantity of the desired product. It is generally recognized that the previously disclosed processes for the synthesis of formaldehyde from carbon monoxide and hydrogen at high pressures are either completely inoperative or else give rise to insignificantly small quantities of formaldehyde.

In British Patent Specification No. 655,237, published July 11, 1951, there is disclosed the reaction between carbon monoxide and hydrogen at elevated pressures and temperatures, e.g., above 1500 atmospheres at temperatures up to 400°C., using certain hydrogenation catalysts as exemplified by cobalt-containing compounds. U.S. Patents No. 2,534,018, 2,570,792, and 2,636,046 are substantially similar in disclosure to the above said British patent. The only catalysts employed in the numbered examples of said U.S. 2,636,046 are those which contain cobalt.

It is also well-known that nickel is predominantly a catalyst for synthesis and for reforming methane according to the reaction

$$CO + 3H_2 \qquad CH_4 + H_2O$$

whose equilibrium favors the right hand side of the equation at temperatures below about 500°C. and the left hand side of the equation at higher temperatures; see Kirk-Othmer, Encyclopedia of Chemical Technology, Second Edition, Volume 4, pages 452-453, John Wiley and Sons, New York (1964).

Polyhydric alcohols are presently being produced synthetically by the oxidation of petroleum derived materials. Owing to the limited availability of petroleum sources, the cost of these petroleum derived materials has been steadily increasing. Many have raised the dire prediction of a significant oil shortage in the future. The consequence of this has been the recognition of the need for a new low cost source of chemicals which can be converted into such polyhydric alcohols.

This invention is directed to a process of making alkane polyols, for example containing 2, 3 or 4 carbon atoms. As byproducts of this invention there may be produced derivatives of the alkane polyols such as their ether and ester derivatives, oligomers of the alkane polyols and also monohydric alkanols such as methanol, ethanol and propanols, and their ether and ester derivatives.

The alkane polyols made according to the present invention include diols and triols, for example ethylene glycol.

The products of the process of this invention contain carbon, hydrogen and oxygen.

There is described in U.K. patent specifications Nos. 1,424,007 and 1,424,008 a process for reacting hydrogen and oxides of carbon in the presence of rhodium carbonyl complex catalysts. The conditions, broadly speaking, employed in that process involve reacting a mixture of an oxide of carbon and hydrogen with a catalytic amount of rhodium in complex combination with carbon monoxide, at a temperature of between about 100°C to about 375°C and a pressure of between about 500 p.s.i.a. to about 50,000 p.s.i.a. The patents discuss the use of catalyst complexes which have "ligands" as a component thereof. Illustrative of such "ligands" are oxygen and/or nitrogen organic compounds. A similar description can be found in British Patent Specification No. 1,477,391. These patents speak about the use of such "ligands" as well as a number of amines which can be used in the catalytic process.

It has been found that such "ligands" and amines enhance the glycol producing capacity of the rhodium carbonyl complex catalyst. In that sense, the "ligands" and amines can be considered to promote the activity of the catalyst. Since the filing of the applications which resulted in U.K. patent specifications Nos. 1,424,007 and 1,424,008, the mechanism of action of such "ligands" and amines with the rhodium carbonyl complex has not been clearly defined.

They may be functioning as ligands and/or forming counter-ions under the reaction conditions of the present process or they may be functioning just merely as Lewis bases and neutralizing or tying up a molecular species which if allowed to remain "free" or in its non-base-bound state would adversely affect the productivity of the present invention. Because of this, it is more favorable to look at their presence in this process in terms of the results they achieve; hence, for the purposes of this invention they are defined as catalyst promoters or rhodium carbonyl complex catalyst promoters.

Even though such promoters were recognized to be beneficial in such a process for making alkane polyols as the important product of manufacture, there was a lack of appreciation that if employed in certain concentrations the productivity of such polyols would be materially and unexpectedly enhanced. It has now been found that there is an amount for each such promoter which will provide the optimum rate of formation of alkane polyol that is obtainable under each selected condition of reaction and catalyst concentration. It follows from this that there now exists a recognition of a specific concentration of such promoter which creates the most favorable balance between the promoting and inhibiting effects of such promoters.

The process of this invention, as stated previously, involves the production of alkane polyols, for example of two to four carbon atoms. The primary product of the process is ethylene glycol mainly in terms of commercial value and secondly in terms of product efficiency. The process involves providing oxide of carbon (as herein defined), particularly carbon monoxide, and hydrogen in a homogeneous liquid phase reaction mixture containing a rhodium carbonyl complex and a nitrogen Lewis base promoter. The catalyst concentration, the temperature and the pressure during the reaction are correlated so as to result in the production of alkane polyol. The promoter provided to the mixture is present in an amount, which may be determined from the promoter's basicity, to achieve the optimum rate of formation of said alkane polyol at said correlated catalyst concentration, temperature and pressure of such reaction mixture.

Suitable nitrogen Lewis bases used as promoters generally contain hydrogen and nitrogen atoms. They may also contain carbon and/or oxygen atoms. They may be organic or inorganic compounds. With respect to the organic compounds, the carbon atoms can be part of an acyclic and/or cyclic radical such as aliphatic, cycloaliphatic, aromatic (including fused and bridged) carbon radicals and the like. Preferably, the organic Lewis bases contain from 2 to 60, most preferably 2 to 40 carbon atoms. The nitrogen atoms can be in the form of imino (-N=),

amino ($-\overset{|}{N}-$),

nitrilo (N≡), etc. Desirably, the Lewis base nitrogen atoms are in the form of imino nitrogen and/or amino nitrogen. The oxygen atoms can be in the form of groups such as hydroxyl (aliphatic or phenolic), carboxyl ($-\overset{\displaystyle O}{\overset{\|}{C}}OH$), carbonyloxy ($-\overset{\displaystyle O}{\overset{\|}{C}}O-$), oxy (-O-), carbonyl ($-\overset{\displaystyle O}{\overset{\|}{C}}-$), etc., all of said groups containing Lewis base oxygen atoms. In this respect, it is the "hydroxyl" oxygen in the

$-\overset{\displaystyle O}{\overset{\|}{C}}OH$ group and the "oxy" oxygen in the $-\overset{\displaystyle O}{\overset{\|}{C}}O-$

group that are acting as the Lewis base oxygen atoms. The organic nitrogen Lewis bases may also contain other atoms and/or groups, as substituents of the aforementioned radicals, such as alkyl, cycloalkyl, aryl, chloro, trialkylsilyl substituents.

Illustrative of organic aza-oxa Lewis bases which may be used as the promoter are, for example, the alkanolamines, such as ethanolamine, diethanolamine, isopropanolamine and di-*n*-propanolamine; N,N-dimethylglycine, N,N-diethylglycine; iminodiacetic acid, N-methyliminodiacetic acid; N-methyldiethanolamine; 2-hydroxypyridine, 2,4-dihydroxypyridine, 2-methoxypyridine, 2,6-dimethoxypyridine, 2-ethoxypyridine; lower alkyl substituted hydroxypyridines, such as 4-methyl-2-hydroxypyridine and 4-methyl-2-6-dihydroxypyridine; morpholine, substituted morpholines, such as 4-methylmorpholine, 4-phenylmorpholine; picolinic acid, methyl-substituted picolinic acid; nitrilotriacetic acid, 2,5-dicarboxypiperazine, N-(2-hydroxyethyl)-iminodiacetic acid, ethylenediaminetetraacetic acid; 2,6-dicarboxypyridine; 8-hydroxyquinoline, 2-carboxyquinoline, cyclohexane-1,2-diamine-N,N,N′,N′-tetraacetic acid and the tetramethyl ester of ethylenediaminetetraacetic acid.

Illustrative of suitable inorganic amine promoters are, e.g., ammonia, hydroxylamine, and hydrazine. Any primary, secondary, or tertiary organic amine is suitable as a promoter in the practice of the present invention. This includes the mono- and polyamines (such as di-, tri-, tetraamines, etc.) and those compounds in which the Lewis base nitrogen forms part of a ring structure as in pyridine, quinoline, pyrimidine, morpholine and hexamethylenetetraamine. In addition any compound capable of yielding an amino nitrogen under the reaction conditions of the present invention is suitable, as in the case of an amide, such as formaldehyde, cyanamide, and urea, or an oxime. Further illustrative of these Lewis base nitrogen compounds are aliphatic amines such as methylamine, ethylamine, *n*-propylamine, isopropylamine, octylamine, dimethylamine, diethylamine, diisoamylamine, methylethylamine, diisobutylamine, trimethylamine, methyldiethylamine, triisobutylamine and tridecylamine; aliphatic and aromatic di- and polyamines such as 1,2-ethanediamine, 1,3-propanediamine, N,N,N′,N′-tetramethylenediamine, N,N,N′,N′-tetraethylethylenediamine, N,N,N′,N′-tetra-*n*-propylethylenediamine, N,N,N′,N′-tetrabutylethylenediamine, *o*-phenylenediamine, *m*-phenylenediamine, *p*-phenylenediamine, *p*-tolylenediamine, *o*-tolidene, N,N,N′,N′-tetramethyl-*1*-phenylenediamine and N,N,N′,N′-tetraethyl-4,4′-biphenyldiamine; aromatic amines such as aniline, 1-naphthylamine, 2-naphthylamine, *p*-toluidine, *o*-3-xylidine, *p*-2-xylidine, benzylamine, diphenylamine, dimethylaniline, diethylaniline, N-phenyl-1-naphthylamine and bis-(1,8)-dimethylaminonaphthalene; alicyclic amines such as cyclohexylamine and dicyclohexylamine; heterocyclic amines such as piperidine; substituted piperidines such as 2-methylpiperidine, 3-methylpiperidine, 4-ethylpiperidine, and 3-phenylpiperidine; pyridine; substituted pyridines such as 2-methylpyridine, 2-phenylpyridine, 2-methyl-4-ethylpyridine, 2,4,6-trimethylpyridine, 2-dodecylpyridine, 2-chloropyridine, and 2-(dimethylamino)pyridine; quinoline; substituted quinolines, such as 2-(dimethylamino)-6-methoxyquinoline; 4,5-phenanthroline; 1,8-phenanthroline; 1,5-phenanthroline; piperazine; substituted piperazines such as N-methylpiperazine, N-ethylpiperazine, 2-methyl-N-methylpiperazine; 2,2′-dipyridyl, methyl-substituted 2,2′-dipyridyl; ethyl-substituted 2,2′-dipyridyl; 4-triethylsilyl-2,2′-dipyridyl; 1,4-diazabicyclo[2.2.2]octane, methyl substituted 1,4-diazabicyclo[2.2.2]octane and purine.

As stated previously, the promoter is provided in the homogeneous reaction mixture in an amount, which may be determined from its basicity, to achieve the maximum rate of formation of the alkane polyols, such as ethylene glycol. For the purpose of discussion of the above provision of the promoter in the reaction, the promoter shall be characterized initially in terms of basicity as either a strong or weak base. However, it is important to bear in mind that this determination of promoter concentration predicated on basicity is not intended to mean that of necessity the promoter is or becomes a cation in the homogeneous mixture as noted in the previous discussion relative to the so-called "ligands" and amines, and their function in the catalytic reaction.

It has been found that the preferred concentration of a strongly basic nitrogen Lewis base promoter used in the process of this invention is a minimum concentration that provides the optimum results, i.e. the optimum rate of formation of alkane polyol. This means that a relatively small amount of such promoter achieves the optimum rate of formation obtainable with that promoter. On the other hand, it has been found that as the base becomes progressively weaker, a greater and greater amount of the base is needed to achieve the maximum rate of formation of the alkane polyol.

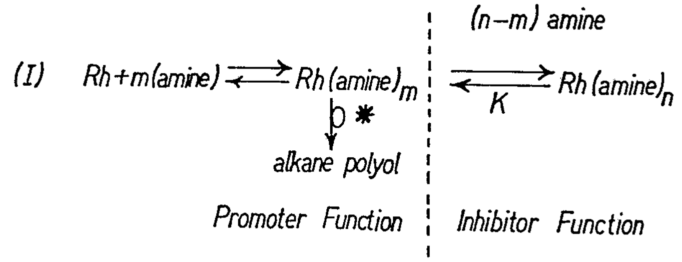
The following (defined in terms of an amine as representative of a nitrogen Lewis base) postulate possible mechanism which could result in the observed behavior discussed above:

a.) the inhibitor function of the amine is of higher kinetic order in amine than is the promoter function;

b.) the promoter function of the amine has a stoichiometric limit after which only the inhibitor function of the amine remains.

The term "inhibitor function" means that function of the amine which results in a decrease in rate of formation of alkane polyol as amine concentration increases.

Postulate a.) can be illustrated by the following reaction scheme:

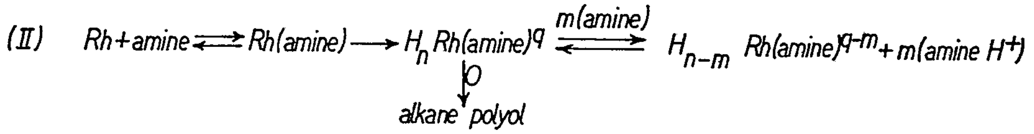


* The looped arrow employed herein denotes several undefined process steps.

[Note: In the above reaction scheme the charge of the rhodium carbonyl complex is not shown; *n* and *m* represent integers; *Rh* denotes a species with a fixed number of rhodiums with the option of a changing number of CO's and H's; the rate and equilibrium constants implicitly contain any appropriate CO and H_2 concentrations.]

In the above scheme, the amine aids production of glycol by forming a more active catalyst and hinders it by inactivating the active catalyst through a mass law effect. Both of these functions of the amine involve it as a ligand on rhodium. A consequence of this reaction scheme is that, if the rate of glycol formation passes through a maximum as a function of the concentration of the amine, the amine concentration which corresponds to the maximum increases as K increases. [Note: K is the equilibrium constant for dissociation of an amine ligand from rhodium to yield the active catalyst.] Since K would be expected to be larger for weaker bases, this scheme is consistent with the aforementioned observed results.

A complementary or supplementary reaction scheme may be characterized as follows:



In this scheme the amine functions both as a rhodium- and as a proton base. It aids production of alkane polyol by forming a more active catalyst and hinders it by deprotonating the active catalyst.

The resulting kinetic equation for reaction scheme (II) is -

(III)

$$\text{(III)} \quad \text{rate is proportional to} \quad \frac{(Rh)\ (amine)}{1 + \left[\dfrac{K_b\ (amine)}{(amine\ H^+)}\right]^m \prod_{i=1}^{m} K_{ai}}$$

where the K_{ai}'s are successive acid dissociation constants of the active catalyst, K_b is the proton affinity of the amine.

Equation (III) supports the previously observed result by showing that if the reaction is treated as being specific base catalyzed [see: A.A. Frost & R.G. Pearson, "Kinetics & Mechanism", 2^d Ed., John Wiley & Sons (1961)], addition of increasing amounts of amine could eventually become counter-productive. The equation (III) predicts that if the nature of the amine effects K_b more than it does the K_{ai}'s, and this is submitted to be a plausible assumption, the amine concentration corresponding to any maximum in rate of formation of alkane polyol would be greater the less basic the amine.

A third reaction scheme, illustrative of postulate b.), is characterized as follows:

$$\begin{tikzcd}
(IV) \quad Rh + \text{amine} \arrow[r] & {[Rh^- \,\text{amine}H^+} \arrow[r, shift left, "K"] & Rh^- + \text{amine}H^+] \arrow[l, shift left] \arrow[d, "b"] \\
 & & \text{alkane polyol}
\end{tikzcd}$$

[Note: *Rh* is defined as above in the note to equation (I).]

In equation (IV) the amine acts as a promoter because it helps to produce the active catalyst and as an inhibitor because its conjugate acid has an adverse mass law effect on the equilibrium concentration of a direct precursor of the active catalyst.

In terms of reaction scheme (IV), with the use of a less basic amine, more amine would be necessary to ensure that the first step of the equation is quantitative. After enough of such an amine is provided, any further amine additions can have only negative effects in regards alkane polyol production because there is a consequent production of more amine H^+, which serves to decrease Rh^- concentration. A consequence of the reaction scheme (IV) is that the rate passes through a maximum as a function of amine concentration and that as basicity of the amine increases the optimum concentration of amine decreases to a limiting value corresponding to stoichiometric destruction of *Rh*.

Consistent with reaction scheme (IV) is the fact that the optimum concentration of an amine as sole promoter for *Rh* is less when the solvent employed has a high dielectric constant. For example, the optimum concentration of an amine as the sole promoter in sulfolane* [ε=43] is less than that in tetraglyme* [ε=7.5]. "Tetraglyme" is the dimethyl ether of tetraethylene glycol.

The concentration of the nitrogen Lewis base promoter in the homogeneous liquid phase mixture of the process of this invention has not been found to be critically dependent upon the temperature and pressure of the reaction, the rhodium concentration or the solvent employed.‡ Of these factors, the rhodium concentration will have the more significant impact upon the optimum promoter concentration while temperature, pressure and solvent choice have minimum effect. However, the effect of rhodium concentration on optimum promoter concentration is considered to be small and is hereafter discounted except for the purposes of giving numerical values to the selection of an amount of promoter for practicing this invention.

The terms strong or weak base are relative, and in view of the preceding discussion, such relative values are considered appropriate in defining this invention. However, for convenience and to provide a numerical base from which it may be considered desirable to discuss this invention, one may characterize a strong base as having a pK greater than about 5 and a weak base as having a pK less than 5, with the assumption that each is definitive in the region of a pK of 5. Of course one may give values more limiting in regards to such pK characterizations by stating that a strong base has a pK of 5 to about 15 and a weak base has a pK of 0 to about 5. pK refers to the acid dissociation constant of the conjugate acid of the nitrogen Lewis base in water at 25°C.

The optimum concentration of an untried promoter may be determined on a relative scale by comparing the pK of that promoter to those set forth in Table I below and selecting a concentration according to the pK relationships and trends indicated. Overall, the concentration of promoter one can employ will be within about 0.001 to about 10 molar. Obviously this range is definitive of the potential scatter of concentrations predicated on the varieties of promoter basicity available.

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*For a description of the use of sulfolane, see U.K. Patent Specification No. 1,523,131, and for a description of tetraglyme see U.K. Patent Specification No. 1,477,391.

‡This statement refers to normal operation, which in tetraglyme involves the use of a salt (see below) in addition to an amine as promoter, while the previous paragraph refers to use of amine as sole promoter in both solvents.

TABLE I

Optimum Concentration of Amine Promoter*

REACTION SYSTEM-See Examples (below)

Amine	pK‡	Solvent	Temp.	Other promoter present	Optimum* moles amine/ mole Rh
1,8-bis(dimethylamino)naphthalene	12.3	Sulfolane	240°	-	~0.1
Sparteine	12.0	"	"	-	0.2-0.3
"	"	"	260	-	0.4-0.7
Dibutylamine	11.3	"	240	-	0.3-0.5
Piperidine	11.1	"	220	-	0.3-0.5
Triethylamine	10.7	"	240	-	0.3
N-methylpiperidine	10.4	"	"	-	0.3-0.5
Piperazine	9.7	"	240	-	0.3-0.5
4-dimethylaminopyridine	9.6	"	220	-	~0.2
Ammonia	9.3	"	240	--	0.3
Amberlite IRA-93 ("Amberlite" is a Trade Mark)	9.0§	"	"	-	0.3-0.5
1,4-diazabicyclo[2.2.2]octane	8.8	"	220	--	0.1
" "	"	"	240	-	0.2-0.3
2,4,6-trimethylpyridine	7.4	"	240	-	0.2-0.3
N-methylmorpholine	7.4	"	"	-	0.3-0.4
Trimethylenedimorpholine	7.3	"	260	-	0.5
Pyridine	5.2	"	220	-	0.2-0.3
"	"	"	240	-	~0.1
"	"	"	"	$(Ph_3P)_2NOAc$	~0.1
"	"	tetraglyme	220	"	0.2-0.6
"	"	"	"	HCO_2Cs	0.2-0.4
"	"	"	230	$PhCO_2Cs$	0.3-0.6
1,10-phenanthroline	4.8	sulfolane	240	-	1.6
Aniline	4.6	"	"	-	2-3
2-hydroxypyridine	0.8	tetraglyme	220	Cs_2-pyridinolate	~1

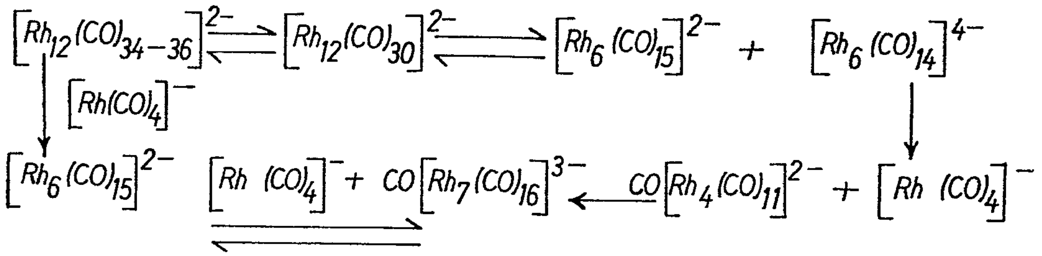
§ p^K of benzyldimethylamine; IRA-93 is an arylmethyl dimethyl amine ion exchange resin sold by Rohm & Haas Co., Phila., Pa.

* The smallest which maximizes the rate of formation of glycol.

‡ H_2O, 25°.

The precise role of the rhodium carbonyl complexes, such as the rhodium carbonyl clusters, in the reaction of hydrogen with oxide of carbon to produce polyhydric alcohols is not fully appreciated at present. Under the reaction conditions of the present process the carbonyl complexes are believed to be anionic in their active forms. Rhodium carbonyl anions are known to be involved in the following set of reactions as indicated by S. Martinengo and P. Chini, in Gazz. Chim. Ital., *102*, 344 (1972) and the references cited therein.

(V)



*electron

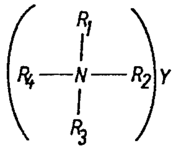
Infrared spectra under reaction conditions of the present process have shown both $Rh(CO)_4^-$ and $[Rh_{12}(CO)_{34-36}]^{2-}$ anions, and other rhodium clusters to be present at various concentrations at different times of the reaction. Therefore the set of reactions and equilibria shown in (V) above may represent the active rhodium carbonyl species responsible for polyhydric alcohol formation or may be merely symptomatic of some further intermediate transitory rhodium carbonyl structure which serves to convert the carbon monoxide and hydrogen to the polyhydric alcohol.

The novel process is suitably effected over a wide superatmospheric pressure range of from 800 psia to 50,000 psia. Pressures as high as 50,000 psia, and higher can be employed but with no apparent advantages attendant thereto which offset the unattractive plant investment outlay required for such high pressure equipment. Therefore, the upper pressure limitation is desirably approximately 16,000 psia. Effecting the present process below about 16,000 psia, especially below about 13,000 psia, and preferably at pressures below about 8000 psia, results in cost advantages which are associated with low pressure equipment requirements. In attempting to foresee a commercial operation of this process, pressures of from 4,000 psia to 16,000 psia appear to represent most realistic values.

In a preferred embodiment of the present invention the pressures referred to above represent the pressures of hydrogen and oxide of carbon in the reactor.

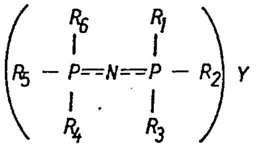
The process of this invention can also be carried out by providing salts in the homogeneous liquid phase reaction mixture. Suitable salts include any organic or inorganic salt which does not adversely affect the production of polyhydric alcohols. Experimental work suggest that any salt is beneficial as either a copromoter and/or in aiding in maintaining rhodium in solution during the reaction. Illustrative of the salts useful in the practice of the present invention are the ammonium salts and the salts of the metals of Group I and Group II of the Periodic Table (Handbook of Chemistry and Physics - 50th Edition) for instance the halide, hydroxide, alkoxide, phenoxide and carboxylate salts such as sodium fluoride, cesium fluoride, cesium pyridinolate, cesium formate, cesium acetate, cesium benzoate, cesium *p*-methylsulfonylbenzoate ($(CH_3SO_2C_6H_4COO)Cs$), rubidium acetate, magnesium acetate, strontium acetate, ammonium formate and ammonium benzoate. Preferred are the cesium and ammonium carboxylate salts, most preferably their formate, benzoate and *para*-lower alkyl sulfonyl benzoate salts.

Also useful in the practice of the present invention are organic salts of the following formula:



$$\left(R_4-\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{N}}-R_2\right)Y$$

quaternary ammonium salts



$$\left(R_5-\overset{\displaystyle R_6}{\underset{\displaystyle R_4}{P}}=N=\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{P}}-R_2\right)Y$$

bis(triorgano phosphine) iminium salts

wherein R_1 through R_6 in formulas (II) and (III) above are any organic radicals which do not adversely affect the production of polyhydric alcohols by reacting oxide of carbon with hydrogen in the present of the aforedefined rhodium carbonyl complex, such as a straight or branched chain alkyl group, having from 1 to 20 carbon atoms in the alkyl chain, such as methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, octyl, 2-ethylhexyl and dodecyl; or a cycloaliphatic group including the monocyclic and bicyclic groups cyclopentyl, cyclohexyl, and bicyclo[2.2.1] heptyl groups or an aryl, alkylaryl, or aralkyl group such as phenyl, naphthyl, xylyl, tolyl, *t*-butylphenyl, benzyl, *beta*-phenylethyl and 3-phenylpropyl; or a functionally subtituted alkyl such as *beta*-hydroxyethyl, ethoxymethyl, ethoxyethyl and phenoxyethyl; or a polyalkylene ether group of the formula $-\!\!(C_nH_{2n}O)_x$-OR wherein *n* has an average value from 1 to 4, *x* has an average value from 2 to about 150, and R may be hydrogen or alkyl of 1 to about 12 carbon atoms. Illustrative of such polyalkylene ether groups are poly(oxyethylene), poly(oxypropylene), poly(oxyethyleneoxypropylene) and poly(oxyethyleneoxybutylene). *Y* in formulas II and III above may be any anion which does not adversely effect the production of polyhydric alcohols in the practice of the present invention such as hydroxide; a halide, for instance fluoride, chloride, bromine and iodide; a carboxylate group, such as formate, acetate, propionate, and benzoate; an alkoxide group such as methoxide, ethoxide and phenoxide; a functionally substituted alkoxide or phenoxide group such as methoxyethoxide, ethoxyethoxide and phenoxyethoxide; a pyridinolate or quinolate group; and others. Preferably *Y* in formulas II and III, above, is a carboxylate, most preferably formate, acetate and benzoate.

A suitable method for preparing the bis(triorganophosphine) iminium salts is disclosed in an article by Appel, R. and Hanas, A. appearing in Z. Anorg. u. Allg. Chem., *311*, 290, (1961).

Other organic salts useful in the practice of the present invention include the quaternized heterocyclic amine salts such as the pyridinium, piperidinium, morpholinium and quinolinium salts, e.g., N-ethylpyridinium fluoride, N-methylmorpholinium benzoate, N-phenylpiperidinium hydroxide and N,N'-dimethyl-2,2-bipyridinium acetate.

In addition, the anion of the above salt may be any of the rhodium carbonyl anions. Suitable rhodium carbonyl anions include $[Rh_6(CO)_{15}]^{2-}$; $[Rh_6(CO)_{15}Y]^-$ wherein *Y* may be halogen, such as chlorine, bromine, or iodine, $[Rh_6(CO)_{15}(COOR'')]^-$ wherein R″ is lower alkyl or aryl such as methyl, ethyl, or phenyl; $[Rh_6(CO)_{14}]^{2-}$; $[Rh_7(CO)_{16}]^{3-}$; $[Rh_{12}(CO)_{30}]^{2-}$; $Rh_{13}(CO)_{24}H_3^-$; and $Rh_{13}(CO)_{24}H_2^{2-}$.

Under reaction conditions where a salt is employed the salt is desirably added with the intial charge of reactants in amounts of from 0.5 to 2.0 moles, preferably from 0.8 to 1.6 moles, and most preferably from 0.9 to 1.4 moles of salt for every five atoms of rhodium present in the reaction mixture.

Illustrative solvents which are generally suitable in making the homogeneous mixture include, for example, ethers such as tetrahydrofuran, tetrahydropyran, diethyl ether, 1,2-dimethoxybenzene, 1,2-diethoxybenzene, the mono- and dialkyl ethers of ethylene glycol, of propylene glycol, of butylene glycol, of diethylene glycol, of dipropylene glycol, of triethylene glycol, of tetraethylene glycol, of dibutylene glycol, of oxyethylenepropylene glycol, etc; alkanols such as methanol, ethanol, propanol, isobutanol and 2-ethylhexanol; ketones such as acetone, methyl ethyl ketone, cyclohexane and cyclopentanone; esters such as methyl acetate, ethyl acetate, propyl acetate, butyl acetate, methyl propionate, ethyl butyrate and methyl laurate; water; gamma-butyrolactone, delta-valerolactone; substituted and unsubstituted tetrahydrothiophene-1,1-dioxides (sulfolanes) as disclosed in British Patent Specification No. 1,537,850. The mono and dialkyl ethers of tetraethylene glycol, gamma-butyrolactone, particularly sulfolane and 3,4-bis(2-methoxyethoxy)sulfolane, are the preferred solvents.

The temperature which may be employed can vary over a wide range of elevated temperatures. In general, the process can be conducted at a temperature in the range of from 100°C and upwards to approximately 375°C, and higher. Temperatures outside this stated range are not excluded from the scope of the invention. At the lower end of the temperature range, and lower, the rate of reaction to desired product becomes markedly slow. At the upper temperature range, and beyond, signs of some catalyst instability are noted. Notwithstanding this factor, reaction continues and alkane polyols and/or their derivatives are produced. Additionally, one should take notice of the equilibrium reaction for forming ethylene glycol

$$2\,CO + 3H_2 \qquad\qquad HOCH_2CH_2OH$$

At relatively high temperatures the equilibrium increasingly favors the left hand side of the equation. To drive the reaction to the formation of increased quantities of ethylene glycol, higher partial pressures of carbon monoxide and hydrogen are required. Processes based on correspondingly higher pressures, however, do not represent preferred embodiments of the invention in view of the high investment costs associated with erecting chemical plants which utilize high pressure utilities and the necessity of fabricating equipment capable of withstanding such enormous pressures. Suitable temperatures are from 150°C to 320°C, and desirably from 210°C to 300°C.

The novel process is effected for a period of time sufficient to produce the alkane polyols. In general, the residence time can vary from minutes to several hours, e.g., from a few minutes to approximately 24 hours, and longer. It is readily appreciated that the residence period will be influenced to a significant extent by the reaction temperature, the concentration and choice of the catalyst, the total gas pressure and the partial pressures exerted by its components, the concentration and choice of diluent, and other factors. The synthesis of the desired product(s) by the reaction of hydrogen with an oxide of carbon is suitably conducted under operative conditions which give reasonable reaction rates and/or conversions.

The relative amounts of oxide of carbon and hydrogen which are initially present in the reaction mixture can be varied over a wide range. In general, the mole ratio of $CO:H_2$ is in the range of from 20:1 to 1:20, suitably from 10:1 to 1:10, and preferably from 5:1 to 1:5.

It is to be understood, however, that molar ratios outside the aforestated broad range may be employed. Substances or reaction mixtures which give rise to the formation of carbon monoxide and hydrogen under the reaction conditions may be employed instead of mixtures comprising carbon monoxide and hydrogen which are used in preferred embodiments in the practice of the invention. For instance, polyhydric alcohols are obtained by using mixtures containing carbon dioxide and hydrogen. Mixtures of carbon dioxide, carbon monoxide and hydrogen can also be employed. If desired, the reaction mixture can comprise steam and carbon monoxide.

The novel process can be executed in a batch, semi-continuous, or continuous fashion. The reaction can be conducted in a single reaction zone or a plurality of reaction zones, in series or in parallel, or it may be conducted intermittently or continuously in an elongated tubular zone or series of such zones. The material of construction should be such that it is inert during the reaction and the fabrication of the equipment should be able to withstand the reaction temperature and pressure. The reaction zone can be fitted with internal and/or external heat exchanger(s) to thus control undue temperatue fluctuations, or to prevent any possible "run-away" reaction temperatures due to the exothermic nature of the reaction. In preferred embodiments of the invention, agitation means to vary the degree of mixing of the reaction mixture can be suitably employed. Mixing induced by vibration, shaker, stirrer, rotation, oscillation, ultrasonics, etc., are all illustrative of the types of agitation means which are contemplated. Such means are available and well-known to the art. The catalyst may be initially introduced into the reaction zone batchwise, or it may be continuously or intermittently introduced into such zone during the course of the synthesis reaction. Means to introduce and/or adjust the reactants, either intermittently or continuously, into the reaction zone during the course of the reaction can be conveniently utilized in the novel process especially to maintain the desired molar ratios of and the partial pressures exerted by the reactants.

As intimated previously, the operative conditions can be adjusted to optimize the conversion of the desired product and/or the economics of the novel process. In a continuous process, for instance, when it is preferred to operate at relatively low conversions, it is generally desirable to recirculate unreacted synthesis gas with/without make-up carbon monoxide and hydrogen to the reaction. Recovery of the desired product can be achieved by methods well-known in the art such as by distillation, fractionation, extraction, and the like. A fraction comprising rhodium catalyst, generally contained in byproducts and/or normally liquid organic diluent, can be recycled to the reaction zone, if desired. All or a portion of such fraction can be removed for recovery of the rhodium values or regeneration to the active catalyst and intermittently added to the recycle stream or directly to the reaction zone.

The active forms of the rhodium carbonyl clusters may be prepared by various techniques. They can be preformed and then introduced into the reaction zone or they can be formed in situ.

The equipment arrangement and procedure which provides the capability for determining the existence of anionic rhodium carbonyl complexes or clusters having defined infrared spectrum characteristics, during the course of the manufacture of polyhydric alcohols from carbon monoxide and hydrogen, pursuant to this invention is disclosed and schematically depicted in British Patent Specification No. 1,477,391.

A particularly desirable infrared cell construction is described in U.S. Patent No. 3,886,364, issued May 27, 1975.

The "oxide of carbon" as covered by the claims and as used herein is intended to mean carbon monoxide and mixtures of carbon dioxide and carbon monoxide, either introduced as such or formed in the reaction. Preferably, the oxide of carbon is carbon monoxide.

The present invention will now be further illustrated by way of the following examples which are merely illustrative and are not presented as a definition of the limits of the invention.

Procedure employed in examples:

A 150 ml. capacity stainless steel reactor capable of withstanding pressures up to 7,000 atmospheres was charged with a premix of 75 cubic centimeters (cc) of solvent, 3.0 millimoles (mmol), 0.77 grams, of rhodium dicarbonylacetylacetonate, and promoter(s). The reactor was sealed and charged with a gaseous mixture, containing equal molar amounts of carbon monoxide and hydrogen, to a pressure of 8,000 pounds per square inch (psig). Heat was applied to the reactor and its contents; when the temperature of the mixture inside the reactor reached 190°C, as measured by a suitably placed thermocouple, an additional adjustment of carbon monoxide and hydrogen (H_2:CO=1:1 mole ratio) was made to bring the pressure back to 8000 psig. The temperature (in °C.) was maintained at the desired value for 4 hours. During this period of time additional carbon monoxide and hydrogen was added whenever the pressure inside the reactor dropped below about 7500 psig. With these added repressurizations the pressure inside the reactor was maintained at 8000 psig ± 400 psig over the entire 4 hour period.

After the 4 hour period, the vessel and its contents were cooled to room temperature, the excess gas vented and the reaction product mixture was removed. Analysis of the reaction product mixture was made by gas chromatographic analysis using a Hewlett Packard FM model 810 Research Chromatograph ("Hewlett Packard" is a Trade Mark).

Rhodium recovery was determined by atomic absorption analysis of the contents of the reactor after the venting of the unreacted gases at the end of the reaction. A further analysis was run on a "wash" of the reactor. The wash of the reactor consisted of charging to the reactor 100 cc of the solvent used for that experiment, and bringing the reactor and its contents to a temperature of 160°C and a pressure of 14,000 to 15,000 psig (using carbon monoxide/hydrogen) and maintaining these conditions for a period of 30 minutes. The reactor was then cooled and the unreacted gases vented and an atomic absorption analysis for rhodium was run on the reactor's contents. The rhodium recovery values recited below are the percent rhodium based on the total rhodium charged to the reactor that is soluble or suspended in the reaction mixture plus the wash after the specified reaction time.

The same equipment and procedure were used in all the examples in Tables A-V except for the reactants and conditions specified. The product weights in the Tables are reported in grams.

EXAMPLES

Table A. 1,8-Bis(dimethylamino)naphthalene as Promoter

Conditions and other Reactants	millimoles of Amine Promoter	Weight of Product Methanol	Glycol	Rh Recovery, %
Sulfolane, 240°	0.20	2.4	0.8	34 + 5
"	0.31	2.9	6.0	78 + 3
"	0.63	2.7	5.1	67 + 4
"	0.94	2.8	5.0	66 + 3
"	1.25	3.7	5.5	69 + 5
"	2.5	2.7	4.6	72 + 4
"	5.0	3.7	4.3	85 + 2
"	7.0	4.4	4.8	83 + 7

Table B. Sparteine as Promoter

Conditions and other reactants	milli-moles of Amine Promoter	Weight of Product		Rh recovery, %
		Methanol	Glycol	
Sulfolane, 240°	0.31	2.9	0.3	65 + 6
"	0.63	3.3	5.7	79 + 8
"	1.25	3.9	4.8	80 + 8
"	5.0	0.9	0.6	94 + 6
Sulfolane, 260°	0.6	4.9	5.0	66 + 4
"	1.25	5.1	6.3	84 + 5
"	2.0	6.4	6.9	71 + 5
"	3.0	5.4	4.8	83 + 5

Table C. Dibutylamine as Promoter

Conditions and other reactants	milli-moles of Amine Promoter	Weight of Product		Rh Recovery, %
		Methanol	Glycol	
Sulfolane, 240°	0.65	2.7	5.4	77 + 5
"	1.25	3.5	6.2	77 + 6
"	2.5	4.3	4.9	86 + 5
"	5.0	4.7	4.0	77 + 6

Table D. Piperidine as Promoter

Conditions and other reactants	milli-moles of Amine Promoter	Weight of Product		Rh Recovery, %
		Methanol	Glycol	
Sulfolane, 220°	0	0.4	0.0	11 + 21
"	0.63	1.2	1.5	74 + 7
"	1.25	2.7	2.5	89 + 8
"	2.5	3.4	2.2	94 + 6

Table E. Triethylamine as Promoter

Conditions and other reactants	milli-moles of Amine Promoter	Weight of Product		Rh Recovery, %
		Methanol	Glycol	
Sulfolane, 240°	0.65	3.3	2.2	71 + 7
"	0.8	2.8	5.5	80 + 7
"	1.25	3.5	5.1	79 + 5
"	2.5	5.0	4.0	81 + 8
"	7.0	4.0	2.2	80 + 8

Table F. N-Methylpiperidine as Promoter

Conditions and other reactants	millimoles of Amine Promoter	Weight of Product		Rh Recovery, %
		Methanol	Glycol	
Sulfolane, 240°	0.63	3.0	3.0	66 + 3
"	0.94	2.6	5.0	Σ≈65
"	1.25	3.5	4.9	69 + 7
"	2.5	4.5	3.8	86 + 7

Table G. Piperazine as Promoter

Conditions and other reactants	millimoles of Amine Promoter	Weight of Product		Rh Recovery, %
		Methanol	Glycol	
Sulfolane, 240°	0.65	2.5	4.6	60 + 14
"	1.25	3.8	6.1	71 + 6
"	2.5	4.6	5.1	83 + 4

Table H. 4-Dimethylaminopyridine as Promoter

Conditions and other reactants	millimoles of Amine Promoter	Weight of Product		Rh Recovery, %
		Methanol	Glycol	
Sulfolane, 220°	0	0.4	0.0	11 + 21
"	0.31	1.6	1.3	74 + 4
"	0.63	2.6	2.3	90 + 9
"	1.25	3.3	1.6	92 + 8

Table I. Ammonia as Promoter

Conditions and other reactants	mmoles of Amine Promoter	Weight of Product		Rh Recovery, %
		Methanol	Glycol	
Sulfolane, 240°	0.50	2.7	4.3	63 + 15
"	0.65	2.2	4.7	79 + 5
"	0.80	2.3, 2.4	4.9, 5.2	81 + 6, 86 + 5
"	1.0	3.2, 3.6, 2.8	6.6, 5.3, 5.2	84+6, 77+9, 83+7
"	1.25	2.7, 3.3, 3.1	5.2, 5.0, 5.1	69+4, 80+4, 84+5
"	1.5	3.6	4.8	81 + 5
"	2.0	4.6	4.6	83 + 8
"	2.5	4.6	4.8	78 + 5
"	10.	2.3	1.6	84 + 5

Table J. Amberlite IRA-93 as Promoter

Conditions and other reactants	mmoles of Amine Promoter*	Weight of Product		Rh Recovery**, %
		Methanol	Glycol	
Sulfolane, 240°	0.62	1.8	3.9	51
"	1.25	3.0	5.8	82
"	2.5	3.0	5.0	63
"	10.	2.7	3.2	64

* mmoles of nitrogen.
** Wash not analyzed for rhodium.

Table K. 1,4-Diazabicyclo[2.2.2]octane as Promoter

Conditions and other reactants	mmoles of Amine Promoter	Weight of Product		Rh Recovery, %
		Methanol	Glycol	
Sulfolane, 220°	0	0.4	0.0	11 + 21
"	0.31	1.4	0.9	71 + 3
"	0.63	1.2	3.5	81 + 7
"	1.25	2.9	2.6	87 + 6
"	2.50	2.8	1.5	90 + 3
Sulfolane, 240°	0.31	2.8	0.5	41 + 11
"	0.63	3.1	6.5	75 + 6
"	1.25	4.4	6.1	76 + 4
"	2.5	4.3	4.5	74 + 6
"	5.0	4.4	3.7	75 + 7

Table L. 2,4,6-Trimethylpyridine as Promoter

Conditions and other reactants	mmoles of Amine Promoter	Weight of Product		Rh Recovery, %
		Methanol	Glycol	
Sulfolane, 240°	0.31	2.6	1.0	60 + 3
"	0.63	2.5	5.0	77 + 6
"	1.25	3.6	4.3	71 + 4
"	2.5	4.5	3.3	77 + 4
"	5.0	4.9	2.5	76 + 3

Table M. N-Methylmorpholine as Promoter

Conditions and other reactants	mmoles of Amine Promoter	Weight of Product		Rh Recovery, %
		Methanol	Glycol	
Sulfolane, 240°	0.63	3.2	4.2	66 + 5
″	1.25	3.2	5.8	64 + 4
″	2.5	4.5	5.4	74 + 4
″	5.0	3.6	5.3	80 + 4
″	7.0	4.1	5.4	82 + 2
Tetraglyme, 240°, 0.65 mmoles cesium benzoate	0	2.2	2.9	27 + 52
″	5.0	2.4	4.1	46 + 32
″	10.0	1.7	3.0	12 + 64
Sulfolane, 250°C	7.0	3.6	6.4	64 + 3
″	11.0	4.6	6.0	67 + 7
″	20.	5.4	5.4	69 + 6

Table N. Trimethylenedimorpholine as Promoter

Conditions and other reactants	mmoles of Amine Promoter	Weight of Product		Rh Recovery, %
		Methanol	Glycol	
Sulfolane, 260°	0.65	3.3	3.2	49 + 4
″	1.25	4.0	5.6	67 + 6
″	7.0	4.9	6.1	78 + 6
″	12.0	5.1	6.0	77 + 5

Table O. Pyridine as Promoter

Conditions and other reactants	mmoles of Amine Promoter	Weight of Product		Rh Recovery, %
		Methanol	Gylcol	
Sulfolane, 220°	0	0.4	0.0	11 + 21
″	0.31	1.9	0.5	66 + 6
″	0.63	2.2	3.8	91 + 8
″	1.25	3.3	2.1	87 + 7
″	2.50	3.4	1.2	97 + 7
Sulfolane, 240°	0.31	2.4, 2.6	2.1, 5.7	74 + 4, 82 + 2
″	0.63	2.7	5.7	76 + 4
″	0.94	3.0	5.2	73 + 6
″	1.25	3.4	4.7	76 + 3
″	2.5	3.5	3.4	79 + 2
″	5.0	2.6	2.0	87 + 3
Sulfolane, 240°, 0.75 mmoles bis(triphenylphosphine) iminium acetate, i.e. $(Ph_3P)_2NOAc$	0	3.2	5.2	79 + 4
″	0.15	3.9	5.6	80 042 2
″	0.30	4.1	5.9	91 + 7
″	0.60	4.7	5.2	84 + 5
″	1.25	4.4	4.3	73 + 7
Tetraglyme, 220°, 0.63 mmoles $(Ph_3P)_2NOAc$	0.63	1.4	5.3	91 + 7
″	1.25	1.4	5.0	85 + 8
″	2.5	1.5	4.5	82 + 7
Tetraglyme, 220°, 0.5 mmoles HCO_2Cs	0	1.2	2.8	69 + 3
″	0.63	2.0	3.1	74 + 13
″	1.25	2.2	3.1	78 + 12
″	2.5	2.8, 2.8	2.4, 2.5	74 + 9, 77 + 15
″	5.0	2.6	2.8	74 + 7
″	10.0	3.2	2.2	78 + 6
″	20.0	3.1	1.6	72 + 7
Tetraglyme, 230°, 0.65 mmole cesium benzoate	0	2.2	3.5	63 + 24
″	1.25	2.2	4.6	50 + 31
″	2.5	3.3	5.2	65 + 22
″	5.0	3.5	4.6	66 + 5

Tetraglyme, 240°, 0.65 mmole cesium benzoate	0	2.2	2.9	27 + 52
"	1.25	2.6	3.6	42 + 38
"	5.0	1.4	2.1	10 + 72
Sulfolane, 250°	0.63	3.8	6.4	68 + 9
"	2.5	6.3	5.5	93 + 11

Table P. 1,10-Phenanthroline as Promoter

Conditions and other reactants	mmoles of Amine Promoter	Weight of Product		Rh Recovery, %
		Methanol	Glycol	
Sulfolane, 240°	0.50	3.4	1.7	61 + 6
"	1.0	3.3	2.4	76 + 6
"	2.0	3.6	4.0	76 + 6
"	3.0	3.4	4.4	73 + 4
"	5.0	3.4	5.3	77 + 5
"	7.0	1.7, 2.6, 2.6	3.0, 3.9, 3.9	56+3, 69+4, 74+4
"	10.0	3.0, 2.7	4.7, 4.8	77+3, 77+4
"	15.	3.2	4.9	74 + 5
"	20.	2.5	4.3	77 + 5

Table Q. Aniline as Promoter

Conditions and other reactants	mmoles of Amine Promoter	Weight of Product		Rh Recovery, %
		Methanol	Glycol	
Sulfolane, 240°	5.0	3.1	2.5	70 + 5
"	10.0	2.9	3.3	64 + 10
"	20.	2.2	3.1	61 + 9

Table R. 2-Hydroxypyridine as Promoter

Conditions and other reactants	mmoles of Amine Promoter	Weight of Product		Rh Recovery, %
		Methanol	Glycol	
Tetraglyme, 220°, 0.5 mmole Cs 2-pyridinolate, 6 mmoles $Rh(CO)_2$ acetylacetonate	3.0	2.9	5.7	78 + 6
"	6.0	2.8	6.1	78 + 6
"	10.0	2.8	5.4	74 + 6
"	20.	4.3	4.5	83 + 8

Table S. Quinuclidine as Promoter

Conditions and other reactants	mmoles of Amine Promoter	Weight of Product Methanol	 Glycol	Rh Recovery, %
Sulfolane, 220°	0	0.4	0.0	11 + 21
"	0.63	2.5	3.5	76 + 7
"	1.25	4.1	1.7	90 + 9

Table T. Ethylenedimorpholine as Promoter

Conditions and other reactants	mmoles of Amine Promoter	Weight of Product Methanol	 Glycol	Rh Recovery, %
Sulfolane, 240°	0.65	3.0	6.3	89 + 5
"	1.25	3.5	6.3	78 + 5
"	7.0	4.6	4.9	78 + 5

Table U. Tetramethylenedimorpholine as Promoter

Conditions and other reactants	mmoles of Amine Promoter	Weight of Product Methanol	 Glycol	Rh Recovery, %
Sulfolane, 260°	0.65	3.8	4.2	68 + 5
"	1.25	4.5	5.3	73 + 5
"	7.0	3.6	3.2	72 + 3

Table V. Hydroxypyridines as Promoter

Conditions and other reactants	mmoles of Amine Promoter	Weight of Product		Rh Recovery, %
		Methanol	Glycol	
Mixture of Dihydroxypyridine (pK .046 5.2) and 2-Hydroxypyridine (see also Table R) (pK = 0.8)				
Tetraglyme, 220°, 0.75 mmole $(Ph_3P)_2$ NOAc	1.25	1.6	3.7	82 + 6
Tetraglyme, 220°	10.0	1.9	1.0	70 + 19
Tetraglyme, 220°, 0.5 mmole Cs 2-pyridinolate	10.0	1.7	4.3	82 + 15
3-Hydroxypyridine (pK = 4.8)				
Tetraglyme, 220°	10.0	3.2	0.4	99 + 15
Tetraglyme, 220°, 0.5 mmole Cs 2-pyridinolate	10.0	2.5	2.3	85 + 13
Tetraglyme, 220°, 0.75 mmole $(Ph_3P)_2NOAc$	1.25	1.2	5.1	85 + 8
" "	-	1.5	2.9	76 + 11
4-Hydroxypyridine (pK = 3.2)				
Tetraglyme, 220°	10.0	2.4	0.6	88 + 17
Tetraglyme, 220°, 0.5 mmole Cs 2-pyridinolate	10.0	2.6	1.5	78 + 10
Tetraglyme, 220° 0.75 mmole $(Ph_3P)_2NOAc$	3.0	1.3	4.6	87 + 9
"	-	1.5	2.9	76 + 11

Materials used in the examples possessed the following characteristics: cesium benzoate (recrystallized from H_2O. Analysis - Found: C, 32.62; H, 1.90. Calcd. for $C_7H_5O_2Cs$: C, 33.10; H, 1.98); sparteine ($b_{0.2}$88-90°); quinuclidine (sublimed, mp 161-2°); trimethylenedimorpholine [$b_{0.5}$ ~ 100°, nmr ($CDCl_3$) : τ = 6.2-6.5 (m, 8.0H), 7.4-7.8 (m, 12H), 8.1-8.6 (m, 2.0H)] tetramethylenedimorpholine [mp 51-4°, nmr (CCl_4) : τ = 6.3-6.6 (m, 8.0H), 7.5-7.9 (m, 12H), 8.4-8.7 (m, 4.0H)]

In our co-pending British Patent Application No. 40356/76 (Serial No. 1565979) there is described and claimed a process for producing alkane polyols having from 2 to 4 carbon atoms which comprises reacting carbon monoxide and hydrogen in a homogeneous liquid phase mixture containing a rhodium carbonyl complex catalyst and a nitrogen Lewis base promoter; the catalyst concentration, the temperature and the pressure being correlated so as to produce such alkane polyol; the promoter being provided in combination with the catalyst in an amount to achieve not less than 50% of the optimum rate of formation of the alkane polyol at said correlated catalyst concentration, temperatures and pressure of said mixture, and in which the amount of the promoter is greater than the amount which is sufficient to produce such optimum rate of formation.

WHAT WE CLAIM IS:-

1. A process for producing alkane polyol which comprises reacting oxide of carbon (as herein defined) and hydrogen in a homogeneous liquid phase mixture containing a rhodium carbonyl complex catalyst and a nitrogen Lewis base promoter; the catalyst concentration, the temperature and the pressure being correlated so as to produce such alkane polyol; and the promoter, provided with the catalyst, being present in an amount to achieve the optimum rate of formation of the alkane polyol at said correlated catalyst concentration, temperature and pressure of said mixture.

2. A process as claimed in claim 1 wherein the temperature is from 100°C to 375°C.

3. A process as claimed in claim 2 wherein the temperature is from 150°C to 320°C.

4. A process as claimed in claim 3 wherein the temperature is from 210°C to 300°C.

5. A process as claimed in any of claims 1 to 4 wherein the pressure is from 800 psia to 50,000 psia.

6. A process as claimed in any of claims 1 to 5 wherein the pressure is not more than 16,000 psia.

7. A process as claimed in claim 6 wherein the pressure is not more than 13,000 psia.

8. A process as claimed in claim 7 wherein the pressure is not more than 8,000 psia.

9. A process as claimed in claim 6 wherein the pressure is from 4,000 psia to 16,000 psia.

10. A process as claimed in any one of claims 1 to 9 wherein the concentration of the promoter is the minimum concentration that provides the optimum rate of formation of the alkane polyol.

11. A process as claimed in any one of claims 1 to 10 wherein the mixture contains a solvent.

12. A process as claimed in claim 11 wherein the solvent is tetraglyme (as herein defined).

13. A process as claimed in claim 11 wherein the solvent is sulfolane.

14. A process as claimed in any one of claims 1 to 13 wherein the mixture contains a salt therein.

15. A process as claimed in claim 14 wherein the salt is added with the initial charge of reactants in an amount of from 0.5 to 2.0 moles for every five atoms of rhodium present in the reaction mixture.

16. A process as claimed in claim 15 wherein the salt is added in an amount of from 0.8 to 1.6 moles for every five atoms of rhodium present in the reaction mixture.

17. A process as claimed in claim 16 wherein the salt is added in an amount of from 0.9 to 1.4 moles for every five atoms of rhodium present in the reaction mixture.

18. A process as claimed in any one of claims 1 to 17 wherein the oxide of carbon is carbon monoxide.

19. A process as claimed in any one of claims 1 to 18 wherein the mole ratio of carbon monoxide to hydrogen initially present in the reaction mixture is from 20:1 to 1:20.

20. A process as claimed in claim 19 wherein the mole ratio of carbon monoxide to hydrogen is from 10:1 to 1:10.

21. A process as claimed in claim 20 wherein the mole ratio of carbon monoxide to hydrogen is from 5:1 to 1:5.

22. A process for producing alkane polyol as claimed in claim 1 and substantially as hereinbefore described with reference to the examples.

23. Alkane polyol whenever produced by a process as claimed in any one of claims 1 to 22.

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