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Homogeneous Catalyzed Reduction of Nitrocompounds

II. Hydrogenation to Oximes

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Group IB metal salts solubilized in alkylpolyamine solvents have been found to catalyze the homogeneous hydrogenation of nitroalkanes to oximes in good yields. The selective synthesis of various linear, cyclic, and substituted oximes is described. The effectiveness of copper and silver salts is in the order, Cu(I) $\approx$ Cu(II) $>$ Ag(I), for constant anion, with specific activity being particularly sensitive to the structure and basicity of the amine solvent and to the addition of π-acceptor ligands. For the synthesis of cyclohexanone oxime from nitrocyclohexane, catalyzed by solutions of copper(I) chloride in ethylenediamine, the proposed mechanism involving initial formation of cuprous hydride by heterolytic splitting of molecular hydrogen, followed by deoxygenation of the coordinated nitroalkane anion as a rate-determining step, is consistent with observed kinetics, deuterium isotope effects, and the use of complex metal hydrides as the hydride source.

INTRODUCTION

While the ability to catalyze reactions of molecular hydrogen homogeneously in solution has been demonstrated for numerous transition and posttransition metal ions and complexes (*1*, *2*), published literature on the homogeneous catalyzed hydrogenation of organic substrates has been concerned primarily with the reduction of poly- and monoalkenes, alkynes, organic halides, and carbonyls (*3*). We report herein a technique for the selective hydrogen reduction of nitroalkanes to oximes, utilizing as catalyst, Group IB metal salts solubilized in alkylpolyamine solvents. This represents one of the first examples of the use of homogeneous hydrogenation catalysts for reducing nitroalkanes (*4*). The objective of this study included a general survey of the catalytic effectiveness of posttransition metal ions in various amine solvents for the selective hydrogenation of a variety of nitroalkane substrates. This, together with preliminary kinetic and deuterium isotope studies, should provide some understanding of the mechanism and stereochemistry of this reduction. Particular attention has been given to the synthesis of cyclohexanone oxime in view of its potential importance as a precursor of ϵ-caprolactam and the polyamide known as Nylon-6.

EXPERIMENTAL

Hydrogen (prepurified grade) and deuterium (technical grade) were from the Matheson Co. Ethylenediamine was distilled (117–118°C) and dried over molecular sieve. Other amine solvents were reagent grade quality and were flushed with nitrogen prior to use. The copper(I), copper(II), and silver salts, 1-nitropropane, nitrocyclohexane, α-nitrotoluene, methyl 4-nitropentanoate, 3-nitro-2-pentanol, and β-nitrostyrene were commercial products. Nitrododecane, a mixture of 2 through 6 isomers, was prepared by nitration of *n*-dodecane with nitrogen dioxide, 2-nitrocyclohexanone was prepared *via* the nitro-oxidation of cyclohexene (*5*).

Synthesis Procedure

The synthesis procedure for aliphatic oximes is exemplified here for cyclohexanone oxime, using solutions of copper(I) chloride in ethylenediamine as catalyst. A similar procedure was employed for the preparation of other aldoximes and ketoximes.

Synthesis of Cyclohexanone Oxime

Copper(I) chloride (0.99 g, 10 mmole) is dissolved, with stirring, in a degassed sample of ethylenediamine (100 ml), 12.9 g of N_2-saturated nitrocyclohexane (100 mmole) added, and the mixture charged to a glass-lined 300 ml "autoclave" pressure unit. Hydrogenation is carried out under a constant pressure of hydrogen (35 atm) while heating to 105°C for 1–6 hr. On cooling, the product liquid is concentrated *in vacuo*, diluted with water, and extracted with diethyl ether. The ethereal extracts are reconcentrated and the residual crude cyclohexanone oxime is recrystallized from aqueous ethanol. Cyclohexanone oxime yield 8.81 g (78%), mp 90°C (lit (*6*) mp 91°C). Identification is also by infrared (*7*) and NMR (*8*) spectroscopy, and elemental analysis.

Anal. Calcd for $C_6H_{10}NOH$: C, 63.7; H, 9.79; N, 12.4. Found: C, 63.6; H, 9.6; N, 12.3.

Kinetic Measurements

Kinetic studies were carried out under superatmospheric pressures of H_2 with the aid of a glass-lined "autoclave" pressure reactor of 300 ml rated capacity fitted with mechanical stirring and linked to a temperature controller and recorder and pressure gauge. Studies at atmospheric pressure were made in glass apparatus set in a constant temperature bath.

Degassed amine solvent (50–100 ml) containing a weighed quantity of copper salt (0.50–12.0 mmole) and nitroalkane (12.5–250 mmole) is introduced into the reactor and flushed with N_2. The mixture is heated to temperature under a small pressure of N_2, and hydrogen then introduced into the reactor (3–100 atm). Rates of nitroalkane reduction are monitored by

TABLE 1

SYNTHESIS OF ALIPHATIC OXIMES FROM NITROALKANES CATALYZED BY COPPER(I) SALTS IN ALKYLPOLYAMINES SOLVENT[a]

Nitroalkane	Nitroalkane conversion (mole %)	Major product[b]	Oxime yield (mole %)[c]
1-Nitropropane	100	Propanal oxime	61
2-Nitropropane	100	Acetone oxime	75
Nitrocyclohexane	100	Cyclohexanone oxime	93
Nitrododecanes[d]	100	Dodecanone oximes	90
Nitrated *n*-dodecane[e]	100	Dodecanone oximes	80
α-Nitrotoluene	95	Benzaldoxime	69
Methyl 4-nitropentanoate	100	Methyl 4-(hydroxyimino)-pentanoate	60
α-(2-Cyanoethyl)-nitrododecanes[d]	95	α-(3-Aminopropyl)-nitrosododecanes	12
2-Nitrocyclohexanone	100	—[f]	—
3-Nitro-2-pentanol	100	—[f]	—
β-Nitrostyrene	100	—[g]	—

[a] Experimental conditions, 2.0–10 mmole CuCl; 25–50 mmole RNO_2; 80–95°; 35 atm H_2.

[b] Oximes identified by elemental analyses and comparison of melting points and spectral properties (infrared, NMR) with those reported in the literature.

[c] Based upon moles of nitroalkane charged.

[d] An isomeric mixture of 2- through 6-nitrododecanes.

[e] A mixture of 25.9% (v/v) nitrododecanes, 64.1% (v/v) *n*-dodecane, and 10% other materials including dodecanones, prepared by liquid/vapor phase nitration of *n*-dodecane.

[f] A mixture of products containing some oxime but with loss of carbonyl or hydroxyl functionality.

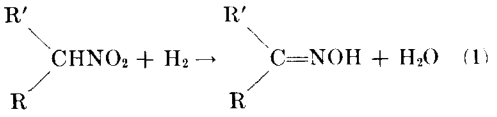
[g] Oligomers.

withdrawing liquid samples (0.2 ml) at regular time periods. The samples are rapidly cooled in ice water and analyzed by gas chromatography with the aid of standard calibration curves. Chromatographic analyses are used to follow both the rate of disappearance of nitroalkane and the formation of oxime.

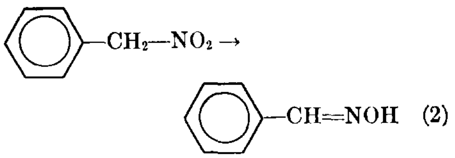
RESULTS

General Synthesis

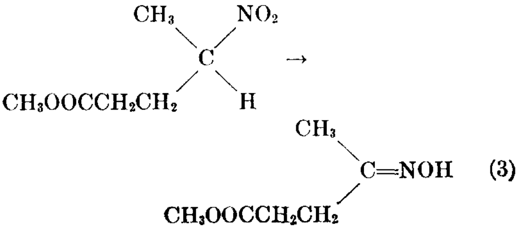
The synthesis of alkyl oximes from nitroalkanes may be conveniently carried out in alkylpolyamine solvents containing copper(I) salts under moderate pressures of hydrogen. Illustrated in Table 1 are typical syntheses from various primary and secondary nitroalkanes. While the technique most readily lends itself to the preparation of linear and cyclic aliphatic oximes, such as dodecanone oxime and cyclohexanone oxime [Eq. (1)], certain substituted nitroalkanes, exemplified here by α-nitrotoluene and methyl 4-nitropentanoate, may also be selectively reduced to the corresponding oximes in modest yields [Eqs. (2) and (3)]. The cyano group in α-(2-cyanoethyl)-nitrododecanes undergoes at least partial hydrogenation to amine during concomitant reduction of the nitro group, and a mixture of products, including α-(3-aminopropyl)-nitrosododecanes in low yields (Eq. 4), are obtained. Other substituted nitroalkanes, notably those containing carbonyl, alcohol, and olefinic linkages, suffer loss of functionality during hydrogenation in the copper(I)-amine media, due in part to solvent displacement of the functional group (*9*) as in the case of 2-nitrocyclohexanone and 3-nitro-2-pentanol, or because of competing oligomerization reactions, as in the case of β-nitrostyrene. The aliphatic oximes may also be prepared in good yields from paraffin-diluted nitroalkanes such as might be produced by paraffin nitration. This is illustrated in Table 1 for nitrated *n*-dodecane.



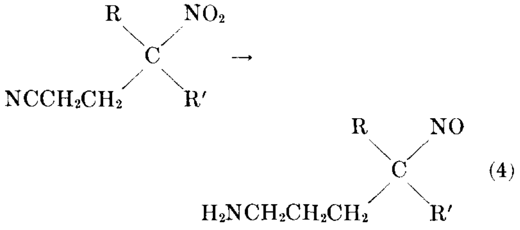
$$\mathrm{(R')(R)CHNO_2} + \mathrm{H_2} \rightarrow \mathrm{(R')(R)C{=}NOH} + \mathrm{H_2O} \qquad (1)$$



$$\mathrm{C_6H_5{-}CH_2{-}NO_2} \rightarrow \mathrm{C_6H_5{-}CH{=}NOH} \qquad (2)$$



$$\mathrm{(CH_3)(NO_2)(H)C{-}CH_2CH_2COOCH_3} \rightarrow \mathrm{(CH_3)C({=}NOH){-}CH_2CH_2COOCH_3} \qquad (3)$$



$$\mathrm{(R)(NO_2)(R')C{-}CH_2CH_2CN} \rightarrow \mathrm{(R)(NO)(R')C{-}CH_2CH_2CH_2NH_2} \qquad (4)$$

Of particular note is the truly catalytic character of this oxime synthesis. While initial nitrocyclohexane-to-copper(I) mole ratios normally range from 10 to 30, catalyst recycle has been demonstrated, and in a typical experimental series a total of 0.4 mole of nitrocyclohexane, in four 0.1-mole batches, was hydrogenated to cyclohexanone oxime with a sample of copper(I) chloride (0.013 mole) in ethylenediamine. Both the catalytic activity, as measured by the rate of consumption of nitrocyclohexane (see Fig. 1), and the yield of cyclo-

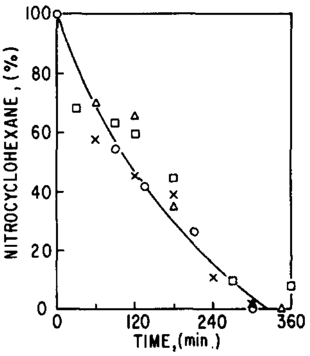


FIG. 1. Nitrocyclohexane hydrogenation, catalyst recycle. (×) cycle 1; (○) cycle 2; (□) cycle 3; (△) cycle 4.

hexanone oxime isolated by solvent extraction were maintained over the four cycles. The total cyclohexanone oxime yield was 27 moles/g atom of copper; the maximum productivity of the catalyst would certainly exceed this value. The major by-product is water [Eq. (1)] and there is no evidence for reduction of the copper salts to the metal, or hydrolysis to the oxide, except at high catalyst concentrations.

Catalyst Composition

The aldoxime and ketoxime syntheses shown in Table 1 were each carried out using copper(I) salts in alkylpolyamine as catalyst, primarily solutions of copper(I) chloride in ethylenediamine. Cyclohexanone oxime synthesis may also be demonstrated with solutions of silver(I) and copper(II) salts (see Table 2). The slower rates of reduction and low oxime yields obtained with silver(I) acetate and nitrate are due primarily to accompanying reduction of the silver ions to the metal *(10)*, which can only be avoided by operating at much lower temperatures (≈22°C) where oxime formation is extremely slow.

TABLE 2

CYCLOHEXANONE OXIME SYNTHESIS CATALYZED BY GROUP IB AND IIB METAL SALTS[a]

Metal salts	Nitrocyclohexane Conversion (%)	Nitrocyclohexane Rate (M hr^{-1})	Cyclohexanone oxime yield (mole %)[b]
Copper(I) chloride	100	1.10	93
Copper(I) acetate	100	0.41	80
Copper(II) acetate monohydrate	100	0.40	78
Silver(I) acetate	8.9	≈0.01[c]	6.7
Silver(I) nitrate	71	0.06[c]	43
Silver(I) nitrate[d]	<1	<0.01	Trace
Mercury(II) chloride	None	—	—

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[a] Experimental conditions: 0.47 M [RNO_2]; 57 mM [Cu] or [Ag]; solvent, ethylenediamine; 95°C; 50 atm H_2.

[b] Cyclohexanone oxime yield based on nitrocyclohexane charged.

[c] Extensive precipitation of silver metal during this run.

[d] Reaction temperature 22°C.

Rates of nitrocyclohexane reduction for comparable solutions of copper(I) and copper(II) acetates in ethylenediamine are essentially equivalent. This result is somewhat surprising since copper(I) salts in basic media are reported to be significantly more active for hydrogen activation than those of copper(II) *(11)*. Furthermore, reduction of copper(II) by hydrogen is itself copper(I) catalyzed in solvents like quinoline *(12)*. These latter reactions are evidently not rate determining under the conditions of nitroalkane reduction described in Table 2, with ethylenediamine as solvent and superatmospheric pressures of hydrogen, since reduction rates with copper(I) and copper(II) acetate are so similar. The apparent order of activity for the Group IB and IIB metal salts, for constant anion, is then:

$$\mathrm{Cu(I)} \approx \mathrm{Cu(II)} > \mathrm{Ag(I)} \gg \mathrm{Hg(II)}. \qquad (5)$$

Selective reduction of nitroalkanes to oximes is normally favored by strongly basic reaction conditions *(13)*. In this work, solvent studies were concerned with the effect of the amine solvent structure upon the rate and yield of cyclohexanone oxime formation (see Table 3). The trends are similar to those noted previously for the CO reduction of nitroalkanes by copper(I)-amine solutions *(13)* and for the hydrogenation of silver salts in amines *(14)*. Reaction rates, as measured by the formation of cyclohexanone oxime, are maximized with highly basic alkylpolyamine solvents such as ethylenediamine and 1,3-propylenediamine, although the high solubility of the cyclohexanone oxime in certain of these solvents (e.g., diethylenetriamine) precludes ease of separation of this oxime from the crude hydrogenation product. Less effective are highly basic monoamines like piperidine and other liquid amines of base strength less than about 9 pK_a units. An earlier, more exhaustive study of solvent effects for the Cu(I)-CO system *(13)* served to demonstrate that here too catalyst activity is favored by alkylpolyamine solvents, with no nitroalkane reduction being detected with amine solvent of pK_a < 9.2 *(13)*.

TABLE 3
CYCLOHEXANONE OXIME SYNTHESIS IN VARIOUS AMINE SOLVENTS[a]

Solvent		Nitrocyclohexane conversion	Yield of isolated cyclohexanone oxime
Composition	pK_a[b]	(%)	(mole %)[c]
Pyridine	5.45	<5	None
Triethanolamine	8.02	50	Trace
Morpholine	8.70	35	20
Diethanolamine	9.00	80	22
Diethylenetriamine	9.94	98	50
Ethylenediamine	10.18	100	78
n-Hexylamine	10.4	100	14
3,3′-Iminobispropylamine	10.65	100	74
Piperidine	11.28	100	20

[a] Typical run conditions: 0.1 *M* [CuCl], 1.0 *M* [$C_6H_{11}NO_2$], 95°C, 50 atm H_2.

[b] Data taken from "Stability Constants of Metal-Ion Complexes," Section II: Organic Ligands, Chem. Soc. Spec. Publ. No. 17, 1964, and Supplement No. 1, Spec. Publ. No. 25, 1971.

[c] Cyclohexanone oxime yield based on nitrocyclohexane charged.

Also considered briefly was the effect upon the hydrogenation activity of the copper catalyst of certain Lewis bases capable of π back bonding. Copper(I) is known to form series of stable complexes with both triaryl and trialkylphosphines (*15*), the trialkylphosphines, in particular, stabilizing copper(I) against oxidation to the +2 state (*16*). In a series of experiments, rates of nitrocyclohexane reduction were measured using standard catalyst solutions (0.1 *M* copper(I) chloride in ethylenediamine) containing added triphenylphosphine, triphenylphosphite, and tri-*n*-butylphosphine (P:Cu = 3.3). In all three cases the added ligands resulted in slower rates of reduction and lower oxime yields. The order of increasing inhibition was

$$P(OC_6H_5)_3 < P(C_6H_5)_3 < P(n\text{-}C_4H_9)_3, \qquad (6)$$

with the more weakly complexing triphenylphosphite (*16b*) showing the smallest effect.

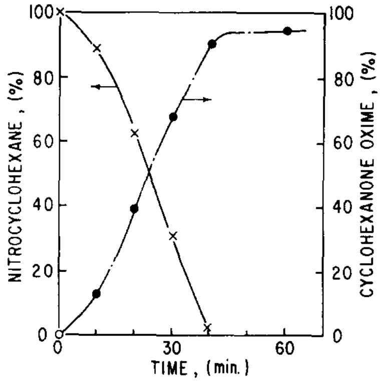

FIG. 2. Synthesis of cyclohexanone oxime from nitrocyclohexane, typical rate plot with 50 mmole $C_6H_{11}NO_2$; 6.4 mmole CuCl; 50 ml ethylenediamine; 100°C; 48 atm H_2.

Kinetic Studies

Kinetic studies included the measurement of rates of nitrocyclohexane reduction with variance of temperature, H_2 pressure, nitrocyclohexane, and catalyst concentrations. Typical rate curves for the conversion of nitrocyclohexane to cyclohexanone oxime catalyzed by solutions of copper(I) chloride in ethylenediamine are shown in Fig. 2. The essential features of the ki-

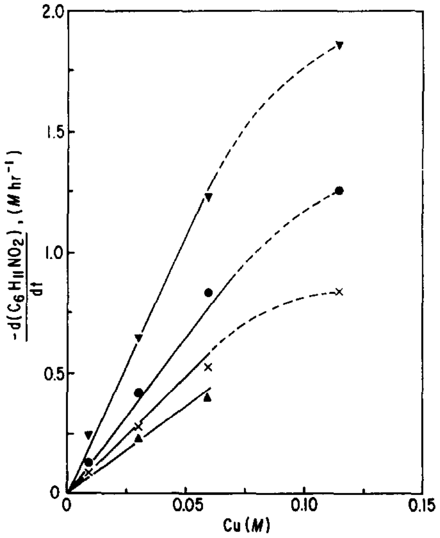

FIG. 3. Nitrocyclohexane reduction as a function of copper concentration. Nitrocyclohexane concentrations: (▲) 0.47 *M*; (×) 0.65 *M*; (●) 0.89 *M*; (▼) 1.61 *M*. Solid lines represent calculated best fit of data basis Eq. (8).

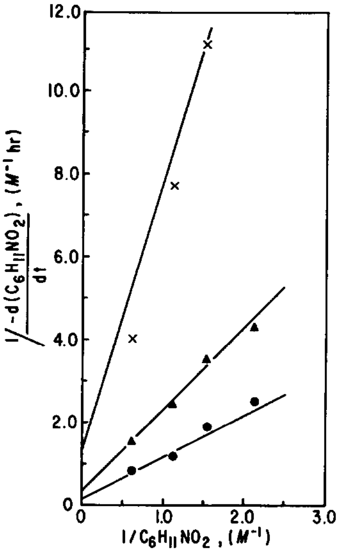

FIG. 4. Nitrocyclohexane reduction as a function of nitrocyclohexane concentration. Copper concentrations: (●) 0.059 M; (▲) 0.030 M; (×) 0.0089 M. Solid lines represent calculated best fit of data basis Eq. (8).

netics are illustrated in Figs. 3 and 4. All measurements were made under hydrogen pressures of 25–50 atm, where the rate is unaffected by changes in pressure. The dependence of the rate upon copper(I) chloride concentration is linear over the concentration range 0–0.06 M (see Fig. 3), the data being consistent with pseudo first-order kinetics. There is, however, considerable deviation from linearity at concentrations above 0.06 M that is likely the result of dimerization of the copper(I) in the amine solvent (*10*), while reproducibility of the measurements at catalyst concentrations below 0.005 M is poor. For constant [Cu], the rate approaches an asymptotic value with increasing nitrocyclohexane concentration, and plots of the reciprocal of the rate *versus* the reciprocal of the initial nitrocyclohexane concentration are linear. The data in Fig. 4 may be accommodated by the relationship,

$$\frac{1}{-d[\mathrm{RNO_2}]/dt} = C \cdot \frac{1}{[\mathrm{RNO_2}]} + C', \quad (7)$$

where C and C' are constants; the reciprocal of the positive intercept on the y axis gives the maximum rate under the specified conditions.

Subject them to the limitations described *supra*, the rate of nitrocyclohexane reduction may be described by the expression,

$$\frac{-d[\mathrm{RNO_2}]}{dt} = k \cdot \frac{[\mathrm{Cu}][\mathrm{RNO_2}]}{1 + K[\mathrm{RNO_2}]}, \quad (8)$$

where the effective rate constant, k, has been estimated at 17 M^{-1}, hr^{-1}, and the equilibrium constant, K, the physical significance of which is discussed later, is approximately 0.17 M^{-1}. The apparent activation energy, E_a, calculated from Arrhenius plots over the temperature range 70–105°C, is 16 kcal mole^{-1}. Measurements over a wider range of hydrogen pressures

TABLE 4

NITROCYCLOHEXANE DEUTERATION EXPERIMENTS[a]

Catalyst solution	Nitroalkane	Reaction time (min)	Nitroalkane		Product gas analysis (mole %)[b]		
			Conversion (%)	Rate (moles/hr)	D_2	HD	H_2
CuCl + en[c,d]	$C_6H_{11}NO_2$	180	100	0.24	—	—	100
CuCl + en	$C_6H_{11}NO_2$	210	100	0.20	92.6	4.8	2.6
CuCl + en	$C_6H_{11}NO_2$	90	70	—[e]	82.2	15.3	2.5
CuCl + en	None	210	—	—	50.5	31.3	18.2
en	None	210	—	—	56.3	25.8	18.0

[a] Run conditions: 0.47 M [RNO_2]; 28 mM [CuCl]; 105°C, 27 atm D_2.

[b] Corrected for HD (0.7%) and H_2 (0.6%) originally present in deuterium gas.

[c] A control experiment using H_2 only.

[d] en = ethylenediamine.

[e] Not determined.

indicate that below 5 atm, the rate of nitrocyclohexane reduction is sensitive to p_{H_2}, the rate increasing with increased applied pressure. No detailed studies have been made at these lower pressures.

Deuterium Studies

A comparison of the rates of nitrocyclohexane reduction by pure deuterium, and by hydrogen, under comparable conditions (Table 4) shows the rate of deuteration to be slower by a factor of about 1.2. In view of this rather small, but significant, isotope effect, the possibility of competing isotopic exchange was investigated also. In a series of experiments using pure deuterium, the extent of exchange, as measured by the relative concentrations of HD and H_2 in the gas phase, was determined for various combinations of reactants (see Table 4). It was concluded from the data that competing exchange reactions are significant, and since they occur in the absence of the RNO_2 and copper salts, with ethylenediamine alone as the hydrogen donor (*10*), they could very well account for the small isotope factor.

The fate of the deuterium during nitroalkane reduction [Eq. (1)] was also considered. No deuterium could be detected in the cyclohexanone oxime product after work-up (basis infrared and mass spectra analyses).

Discussion of Mechanism

For a wide variety of transition and posttransition metal ions in solution, activation of molecular hydrogen leads to the formation of reactive metal–hydride complexes (2). Generally hydride formation proceeds by one of two mechanisms involving homolytic or heterolytic cleavage of the H_2 molecule. Copper(I) and silver(I) ions are known to activate molecular hydrogen by both paths [e.g., Eqs. (9) and (10), Ref. (*11*)].

$$Cu^+ + H_2 \rightarrow CuH + H^+, \qquad (9)$$

$$2Cu^+ + H_2 \rightarrow 2CuH^+. \qquad (10)$$

Generally though, the path involving heterolytic cleavage [Eq. (9)] will be favored wherever the metal ion is surrounded by basic ligands, or solvents of high polarity, due in part to (a) stabilization of the released proton, and (b) suppression of the reverse reaction. This effect can be seen quantitatively in the activation energy data for heterolytic splitting of H_2 by silver(I) in the presence of various complexing agents of increasing base strength (Table 5).

Group IB hydride species are generally labile and, in the absence of a suitable substrate, will tend to dissociate to the metal, or undergo the reverse reaction to regenerate hydrogen. In the presence of certain oxidizing agents, however, catalytic reduction by hydrogen has been observed. Examples include the reduction of dichromate (*18*) and permanganate (*19*) by hydrogen with aqueous solutions of silver (I) salts, and the reduction of *p*-benzoquinone (*20*) and carboxylic acids (*21*) by hydrogen and solutions of copper(I). For the reduction of aliphatic nitro compounds to the corresponding oximes, the involvement of intermediate copper(I) and silver(I) hydride complexes in the alkylpolyamine solvents would be consistent with these, and related studies, on H_2 activation by Group IB ions in quinoline (*22*, *23*) and other amine bases (*11*, *14*). Further evidence comes from the isotopic exchange and rate studies. A kinetic isotope effect of at least 1.2 for nitrocyclohexane reduction is of the same order as that for the cuprous-catalyzed hydrogenation of quinone in quinoline (*20*), and other solvents (*24*, $k_H/k_D \approx 1.4$), although there activation of the hydrogen by heterolytic splitting [Eq. (9)] is the rate-determining step. The activation energy for reaction (9) in quinoline (14.3 kcal $mole^{-1}$, *20*) is also

TABLE 5

Ligand Effects upon the Activation Energies for Reaction: $Ag^+ + H_2 \rightarrow AgH + H^+$

Silver salt	Solvent	E(kcal $mole^{-1}$)[a]
Silver acetate	Water	24
Silver heptanoate	Heptanoic acid	19
Silver acetate	Pyridine	13–16

[a] Data taken from Ref. (*17*).

comparable with calculated here for the oxime synthesis (16 kcal $mole^{-1}$), but in this case, by operating under superatmospheric pressures of hydrogen with ethylenediamine as solvent, reaction of the nitroalkane with the cuprous hydride species becomes rate determining (*v.s.* Kinetic Data). The function of the CuH is apparently to effect deoxygenation of the RNO_2 molecule, since no deuterium could be detected in the cyclohexanone oxime after work-up.

The critical role played by the amine solvent, particularly regarding its basicity and chelation properties, is evident from the data in Table 3. The function of the preferred alkylpolyamine solvents, like ethylenediamine, may be at least threefold. First, the more basic solvents will favor both the formation of CuH species by stabilizing the released hydrogen ion [Eq. (9)], and as better σ-donors to the copper(I), the electron transfer steps involved in subsequent RNO_2 reduction to oxime. Weller and Mills, for example, have reported the activation of molecular hydrogen by cuprous salts in organic bases to vary significantly with the base strength of the solvent (*23*) [see also Table 5 for silver(I) complexes]. The fact that in this work, however, no nitrocyclohexane reduction was detected with pyridine as solvent, even though activation of H_2 by copper(I) salts in pyridine is well established (*10*), implies that solvent basicity is a *critical* factor in some step other than the initial metal hydride formation. Possibly this step is proton abstraction from the nitroalkane to give the more reactive nitroalkane anion [Eq. (11)].

$$RR'CHNO_2 + B: \rightleftharpoons (RR'CNO_2)^- + BH^+. \quad (11)$$

Generally, the selective reduction of nitroalkanes to alkyl oximes proceeds most readily *via* the prior formation of the nitroalkane anion (*25*). While the p*K* values for short chain primary and secondary nitroalkanes in aqueous media are of the order 8–10 (*26*) in highly basic alkylamine solvents the nitroalkane molecule will be extensively deprotonated to the anionic form (*27*). This has been confirmed spectroscopically (*13*). A second function of the amine solvent then is to ensure the formation of the nitroalkane anion by shifting the equilibrium of Eq. (11) further to the right. A third function will be to stabilize the cuprous ion against disproportionation to the metal (*28*), although it is evident from the generally negative effect upon catalyst activity of adding strongly coordinating phosphines capable of π back-bonding that, as with numerous other homogeneous catalysts (*2*) there is a rather delicate balance here between stability and catalytic activity of the copper complexes.

A rationale for the nitroalkane reduction

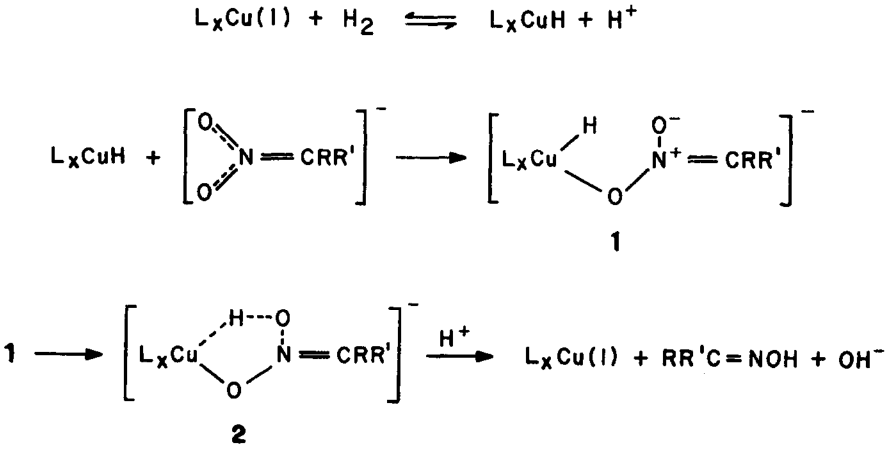

FIG. 5. L_x refers to coordinated solvent.

of oxime, consistent with the available data, is presented in Fig. 5. The initial reaction, heterolytic splitting of H_2 by solvated copper(I) to form a hydride complex, is followed by nucleophilic displacement, or addition, to the coordination sphere of the copper complex (*29*), by the nitroalkane anion, to give the labile intermediate **1**. Partial deoxygenation of the coordinated nitroalkane anion by hydride attack through the quasi-cyclic transition state **2** would yield the product oxime without the need to involve the nitroso tautomer (*27*). Consistent with the deuterium isotope effects described above, and the kinetic data summarized by Eq. (8), at moderate hydrogen pressures, where the rate is insensitive to H_2 pressure, deoxygenation of the nitroalkane anion is regarded as the slow, rate determining step, K is the formation constant then for the intermediate nitroalkane complex **1**.

Structure **1** is shown in Fig. 5 as involving metal–oxygen rather than metal–carbon bonding by analogy with known nitroalkane complexes (*30*). Subsequent deoxygenation of the coordinated nitroalkane has been invoked earlier in studies of nitrocompounds reduced by iron and ruthenium carbonyls (*4a*, *31*), although there reductions were believed to proceed via complete deoxygenation of the $-NO_2$ group, with the formation of nitrene-like intermediates stabilized by bonding to the metal. The lack of evidence for alkylamine reduction products and dimeric derivatives in this work, particularly azo and azoxy compounds, mitigates against the involvement of nitrenes here (*4a*) and is consistent with only partial deoxygenation of the nitro anion.

Consistent also with the mechanism of Fig. 5 is the finding that the hydride source required for nitroalkane reduction to oxime need not come from molecular hydrogen. Certain other hydride sources are also effective, although only under noncatalytic, near-stoichiometric, conditions (see Table 6). Sodium borohydride, which does not normally reduce nitroalkanes (*32*), and hydrazine both yield significant quantities of cyclohexanone oxime in the presence of ethylenediamine solutions of copper(I). Lithium aluminium hydride, which is reported to reduce nitroalkanes to the corresponding amines in ethereal solution (*33*, *34*) and ketoximes in basic media (*35*), is not effective. Control experiments under nitrogen, in the absence of either molecular hydrogen, or an alternate hydride source, also failed to show the formation of oxime.

TABLE 6

NITROCYCLOHEXANE REDUCTION BY VARIOUS REDUCING AGENTS[a]

Reducing agent	$[RNO_2]/[H]$	Reaction time (min)	Nitrocyclohexane conversion (%)	Cyclohexanone oxime yield (mole %)[b]
$NaBH_4$	0.42	210	59	17
N_2H_4	0.31	180	57	49
$LiAlH_4$	0.31	180	<1[c]	<1
None[d]	—	150	10.3	<1

[a] All experiments run under 1 atm nitrogen, 57 mmole [CuCl]; 0.47 mole $[RNO_2]$; 85°C.

[b] Yield based upon nitrocyclohexane charged.

[c] Extensive precipitation of solids during this run.

[d] A control experiment with no added reducing agent.

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