

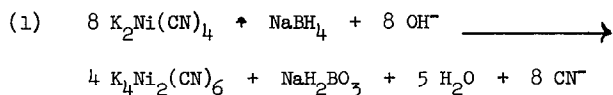
REDUCTION OF ORGANIC COMPOUNDS BY POTASSIUM
HEXACYANODINICKELATE (I) IN HOMOGENEOUS SOLUTION

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Potassium hexacyanodnickelate (I), $K_4Ni_2(CN)_6$, has been previously synthesized by several methods (1,2,3,4) and the structure and reactions of this material reviewed (5). It has been reported (6) that aqueous solutions of $K_4Ni_2(CN)_6$ can be prepared by the action of sodium borohydride upon aqueous potassium tetracyanonickelate (II), $K_2Ni(CN)_4$. We found the stoichiometric equation of this reaction to be:



Solutions of $K_4Ni_2(CN)_6$ generated with borohydride were found to reduce α,β -unsaturated acids rapidly in high yield, to reduce benzonitrile much more slowly, and to slowly hydrogenolyze triethylbenzylammonium chloride in water or water-alcohol solutions at 25°.

Reductions were carried out in homogeneous solution in a single step. Table 1 shows these reductions using 0.005 mole of $NiCl_2 \cdot 6 H_2O$, 0.025 mole of KCN, 0.10 mole of substrate, and 0.10 mole of $NaBH_4$ in 500 ml of solvent. Since a stoichiometric amount of $Ni(CN)_4^{-2}$ is not required for reduction, a catalytic process must be in operation. The reduction of α,β -unsaturated acids proceeded quickly at pH 8 - 11 with only mild evolution of hydrogen. There was a considerable evolution of hydrogen due to hydrolysis of the borohydride ion if the pH was below 7. Manometric measurements made on solutions of sodium borohydride containing $Ni(CN)_4^{-2}$ at pH 8.4 showed that the nickel ion did not accelerate the normal hydrolysis rate of the borohydride ion. It must be noted that nickel ion complexed by cyanide is unique in its interaction with sodium borohydride, in that aqueous solutions of other nickel salts react with the borohydride ion to form nickel boride, Ni_2B , a powerful catalyst for the hydrolysis of BH_4^- .

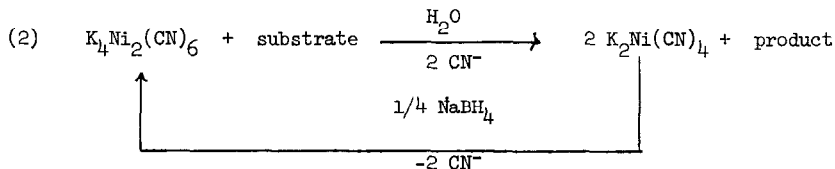
In order to determine whether $Ni_2(CN)_6^{-4}$ is the actual reducing species or if the ion catalytically activates the reduction by borohydride ion, reductions were carried out in the absence of borohydride by employing $K_4Ni_2(CN)_6$ prepared by the method of Eastes and Burgess (3). Reduction of crotonic acid was found to proceed in the absence of BH_4^- when pure $K_4Ni_2(CN)_6$ with excess CN^- was employed. Unlike the $Ni(CN)_4^{-2} - BH_4^-$ reduction system, stoichiometric quantities of $K_4Ni_2(CN)_6$ were necessary for complete reduction. Therefore, the hydrogen source for this reduction must be the aqueous solvent. This was

TABLE I
 Reductions with Tetracyanonickelate (II) - Borohydride
 System in Aqueous Solution at 25°

SUBSTRATE	PRODUCT ^a	YIELD (percent)	REACTION TIME (hours)
Sorbic acid	Caproic acid	95	3
Crotonic acid	Butyric acid	95	3
Tiglic acid	2-Methylbutyric acid	89	4
Methacrylic acid	Isobutyric acid	90	2
Maleic acid	Succinic acid	95	1/2
Citraconic acid	Methylsuccinic acid	68	1/2
Itaconic acid	Methylsuccinic acid	70	1/2
2,3-Dimethylmaleic acid	No reaction		16
Oleic acid ^b	Stearic acid	trace	16
Cyclohexene ^b	No reaction		16
Isoprene ^b	No reaction		16
α -Methylstyrene ^b	Cumene	8	16
Triethylbenzyl- ammonium chloride	Toluene	10	16
Benzonitrile ^b	Dibenzylamine Monobenzylamine	24 trace	16
Benzyl cyanide ^{b,c}	Diphenethylamine	trace	1

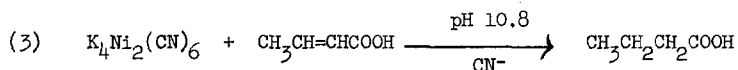
- a. All products with the exception of succinic acid and diphenethylamine were analyzed by gas chromatography.
- b. Run in 50 percent ethanol to effect homogeneity.
- c. Carried out at reflux temperature.

further corroborated when a $\text{Ni}(\text{CN})_4^{-2}$ catalyzed borohydride reduction of maleic acid was carried out in deuterium oxide and 2,3-dideuterio-succinic acid isolated as the product.* Reductions by the $\text{Ni}(\text{CN})_4^{-2}$ - BH_4^- system must be dependent upon the formation of the $\text{Ni}(\text{I})$ ion which is most likely the active component of this reduction. This cyclic process may be outlined as follows:

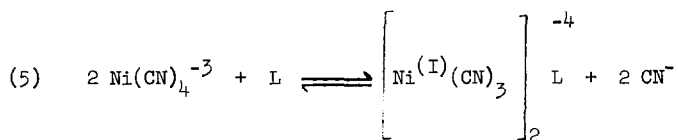
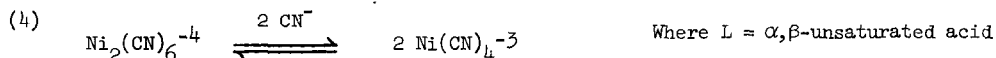


Relative reaction rates were obtained for solutions of pure $\text{Ni}_2(\text{CN})_6^{-4}$, allowed to react in the absence of BH_4^- with crotonic acid under various conditions of pH and CN^- concentration. The reaction was followed by measurement of product concentration gas chromatographically, using a 6 foot 10 percent DEGS column at 130° .

From this investigation it was established that the rate of butyric acid formation increased with decreasing pH and with increasing cyanide concentration. (In the absence of added cyanide, crotonic acid failed to react appreciably). The stoichiometry of this reduction was determined:

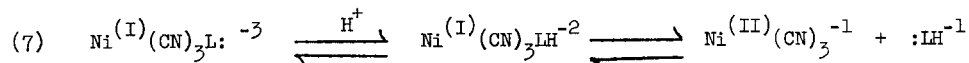
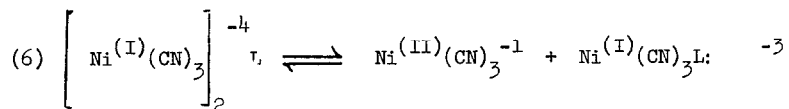


The above facts indicate that paramagnetic $\text{Ni}(\text{CN})_4^{-3}$ is the reactive species in these reductions. This species has been observed (2) in solutions of $\text{Ni}_2(\text{CN})_6^{-4}$ containing excess cyanide. Diamagnetic complexes between alkynes and $\text{Ni}(\text{I})$ compounds have been isolated previously (8,9) and suggest that a variety of unsaturated substrates might react with $\text{K}_4\text{Ni}_2(\text{CN})_6$ to form complexes. Indeed, the pH dependency observed in the reaction of $\text{K}_4\text{Ni}_2(\text{CN})_6$ with crotonic acid may be connected with the break-up of such complexes. We advance the following reduction scheme as a plausible explanation of our observations:**



* No exchange occurs between D_2O and NaBH_4 (7).

** For an excellent review by M. Anbar on oxidation and reduction of ligands by metal ions in unstable oxidation states, see ref. (10).



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