The Addition of Hydrogen Cyanide to α-Olefins Catalyzed by Nickel(0) Complexes

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The hydrocyanation of hexene-1 to a mixture of heptanenitrile and 2-methyl-hexanenitrile, using Lewis acid promoted Ni(0) phosphite complexes, has been studied. A reaction mechanism has been postulated, involving $(HNiL_3)^+$ (L = tri-p-tolyl phosphite) as the catalytic intermediate. The Lewis acid, in addition to significantly enhancing the reaction rate, has an effect on the ratio of heptanenitrile:2-methyl-hexanenitrile. An attempt was made to correlate the acceptor properties of a number of Lewis acids with the selectivity observed to heptanenitrile during hydrocyanation. The isomerization of hexene-1 to the equilibrium distribution of isomers was rapid compared with the rate of hydrocyanation under normal operating conditions. Using $AlCl_3$ as the promoter, it has been shown that about 85% of the 2-methyl-hexanenitrile produced, resulted from direct hydrocyanation of hexene-2, and only 15% from "Markownikoff" addition to hexene-1. Steric hindrance in the substrate had a marked effect in directing the –CN addition to the terminal rather than the internal position. Propylene gave only 60% of the terminal addition product, whereas isobutylene gave >99%. Phenolic solvents were found to have a promoting effect on the reaction rate compared to aromatic and nitrile solvents and also improved the selectivity to terminal addition products.

INTRODUCTION

The use of soluble transition metal complexes as catalysts for the synthesis of nitriles from nonactivated olefins and hydrogen cyanide has been known for several years (1–3). The scope and usefulness of this reaction has been limited by the short-lived activity of the catalysts. Recently, however, it has been discovered that certain zero valent phosphite complexes of palladium and nickel can act as efficient catalysts for the addition of hydrogen cyanide to olefins under controlled conditions (4). The reaction mechanism is complex and is not well understood. The presence of an excess of the phosphite ligand in solution is essential for good activity. Further, in the case of the nickel catalyst, a Lewis acid co-catalyst has a promoting effect on activity and a marked influence on selectivity to the straight chain product. The application of this catalysis to the synthesis of such

commercially important products as adiponitrile has stimulated much research activity in the field. We wish now to report the results of a study of the mechanism of hydrocyanation of hexene-1 using a catalyst comprising tetrakis-(tris-p-tolyl phosphite)nickel(0) promoted with a number of Lewis acids.

EXPERIMENTAL METHODS

Materials

The liquid olefins and solvents were dried over activated 5 Å sieves and distilled under nitrogen before use. Those olefins which were gases under ambient conditions were dried by passage over a column of the 5 Å sieves before entering the reactor. The hydrogen cyanide (American Cyanamid) was purged with nitrogen to remove any sulfur dioxide stabilizer and then distilled under nitrogen immediately

before use. Tri-*p*-tolyl phosphite (Eastman Kodak) was used as received. Anhydrous zinc chloride was prepared by treating the commercial product (Fisher Scientific) with thionyl chloride and then drying *in vacuo*. Aluminum trichloride (Fisher Scientific) was sublimed before use. Titanium trichloride and cobalt dichloride were used as received. Tetrakis-(tri-*p*-tolyl phosphite)nickel(0) was prepared by the method of Clark and Storrs (*5*).

Reaction Procedure

In order to avoid the presence of excess HCN in the reaction solution, the HCN was fed to the reactor at a rate similar to that at which it was consumed in the reaction. This was achieved by containing liquid HCN at 0°C in a calibrated trap, and feeding it to the reactor by bubbling a stream of dry nitrogen through the liquid. At any given N_2 flow rate the reproducibility of the HCN feed rate was ±5%. The experimental example described below is typical of the procedure used.

Tetrakis-(tri-*p*-tolyl phosphite) nickel (0) (1.4 g; 0.001 mole), zinc chloride (0.24 g; 0.002 mole) and tri-*p*-tolyl phosphite (1.75 g; 0.005 mole) were charged to the reaction flask under heavy nitrogen purge. Hexene-1 (25 ml; 0.2 mole) and acetonitrile (25 ml) were then added and the mixture heated with stirring to 60°C. When equilibrium temperature had been reached the HCN was continuously fed into the reaction mixture by passing a stream of dry nitrogen through a trap containing liquid HCN at 0°C. After 2.5 hr 1.90 ml (0.05 mole) of HCN had been added to the system. Gas–liquid chromatography analysis on a 10 ft column (10% SE-30 on chromosorb W) indicated that a total of 5.5 g of nitriles had been produced. These nitriles which were identified by nmr, IR and mass spectrometry, consisted of 79.4% heptanenitrile, and 20.6% 2-methyl-hexanenitrile.

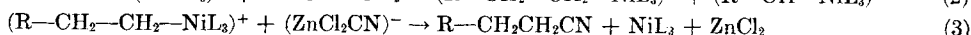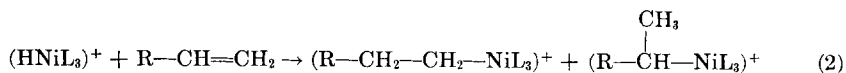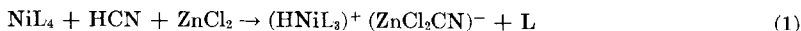The catalyst components and their ratios were changed as the experiment dictated, and with certain volatile liquid olefins the temperature was lowered, but the general procedure remained as above.
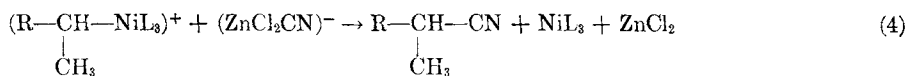
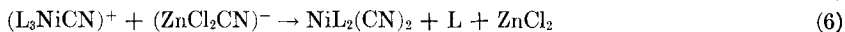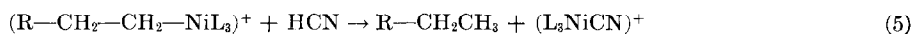### RESULTS AND DISCUSSION

The Catalyst and Reaction Mechanism

The catalyst consisted of essentially three components, the Ni(0) phosphite complex, NiL_4 (L = tri-*p*-tolyl phosphite) an excess of the ligand L, and a Lewis acid. In the presence of the Ni(0) complex alone, the rate of hydrocyanation was very slow, and the catalyst lifetime was short. The roles of the excess ligand and the Lewis acid therefore appear to be associated with activation of the Ni(0) complex, and stabilization of the catalytic intermediate. It has been speculated (*4*) that in the Pd catalyzed reaction, the role of the excess ligand was to prevent the formation of $PdL_2(CN)_2$, which was not active for olefin hydrocyanation. Similarly, we have shown that $NiL_2(CN)_2$ is inactive as a hydrocyanation catalyst, so that the increased activity which resulted from the presence of excess ligand L may be due to suppression of the reaction which converts the active form of the catalyst to the inactive $NiL_2(CN)_2$.

H^1 nmr (*6*) has been used to show that a Lewis acid, $ZnCl_2$, can increase the acidity of HCN with respect to its ability to protonate $Ni[P(OEt)_3]_4$ to give $HNi[P(OEt)_3]_4^+$. A similar result might be expected with the NiL_4 hydrocyanation catalyst. If this is so, the Lewis acid effectively acts as a cyanide ion acceptor or carrier in this reaction. The product distribution, in particular the ratio of normal/branched isomers produced (N/B), has been found to depend upon the nature of the Lewis acid promoter. This aspect will be fully discussed later. The above postulates can be summarized by the following scheme for the addition of HCN to an α-olefin:

$$NiL_4 + HCN + ZnCl_2 \rightarrow (HNiL_3)^+ (ZnCl_2CN)^- + L \qquad (1)$$

$$(HNiL_3)^+ + R\!-\!CH\!=\!CH_2 \rightarrow (R\!-\!CH_2\!-\!CH_2\!-\!NiL_3)^+ + (R\!-\!\overset{\overset{\displaystyle CH_3}{|}}{C}H\!-\!NiL_3)^+ \qquad (2)$$

$$(R\!-\!CH_2\!-\!CH_2\!-\!NiL_3)^+ + (ZnCl_2CN)^- \rightarrow R\!-\!CH_2CH_2CN + NiL_3 + ZnCl_2 \qquad (3)$$

$$(R—CH—NiL_3)^+ + (ZnCl_2CN)^- \rightarrow R—CH—CN + NiL_3 + ZnCl_2 \tag{4}$$
$$\quad\quad |\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad | $$
$$\quad\quad CH_3\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad CH_3$$

The deactivation of the catalyst to the inactive $NiL_2(CN)_2$ could occur as follows:

ratio of primary:secondary alkyl. If, however, reaction (2) is reversible then a num-

$$(R—CH_2—CH_2—NiL_3)^+ + HCN \rightarrow R—CH_2CH_3 + (L_3NiCN)^+ \tag{5}$$
$$(L_3NiCN)^+ + (ZnCl_2CN)^- \rightarrow NiL_2(CN)_2 + L + ZnCl_2 \tag{6}$$

The presence of excess ligand in the solution would set up the following equilibrium:

ber of complicating factors arise. The secondary alkyl can eliminate a hydrogen

$$(R—CH_2—CH_2NiL_3)^+ + L \rightleftarrows (RCH_2CH_2NiL_4)^+ \tag{7}$$

The latter complex is coordinatively saturated, and would not readily react according to Eq. (5); the net result being an increased catalyst lifetime.

The reaction scheme proposed above is based on both experimental observations and upon some well-known concepts of homogeneous catalysis. Equation (1) is an example of an oxidative addition reaction, while reaction (2) is an olefin insertion into a metal hydride bond. The catalytic cycle is completed by the cleavage of a metal–alkyl bond [Eq. (3)] which is a reductive elimination reaction. These classes of reactions are all common to the well studied homogeneous hydrogenation, hydroformylation, hydrosilation and olefin isomerization reactions. The model which has thus far been developed will be used to discuss and explain the chemistry of α-olefin hydrocyanation.

The Ratio of Normal:Branched Products

It is clear from Eq (2) that the olefin is able to insert into the Ni–H bond to form either a primary or secondary nickel alkyl. In the hydrocyanation of hexene-1, the primary alkyl is presumed to lead to heptanenitrile and the secondary to 2-methyl-hexanenitrile. If reaction (2) is irreversible then the ratio of N/B will be equal to the

atom from the adjacent $-CH_2-$ rather than the $-CH_3$, which will lead to olefin isomerization. The isomerized olefin can then undergo hydrocyanation to give products which may be the same or different from those obtained from the α-olefin. Analysis by glc of the reaction mixture showed that the isomerization of hexene-1 to the equilibrium mixture of isomers was a very rapid reaction compared to hydrocyanation. This is in good agreement with the observations of Tolman (7) and others (8), that the cationic nickel hydrides are extremely active olefin isomerization catalysts. Table 1 shows the products which can be expected from hydrocyanation of hexene-1 as a result of the rapid isomerization which occurs.

In no experiment was the formation of 2-ethyl-pentanenitrile observed, which effectively means that the direct hydrocyanation of hexene-3 and the formation of this product from hexene-2 can be ignored. Thus the ratio of N/B products will depend only on the relative concentrations of primary and secondary alkyls in solution, and the relative rates of reactions (3) and (4). The secondary alkyl can be formed by insertion of either hexene-1 or hexene-2 into the Ni–H bond, whereas the primary alkyl can result only from hexene-1. Figure 1 shows

TABLE 1
THEORETICAL PRODUCTS FROM THE HYDROCYANATION OF HEXENE ISOMERS

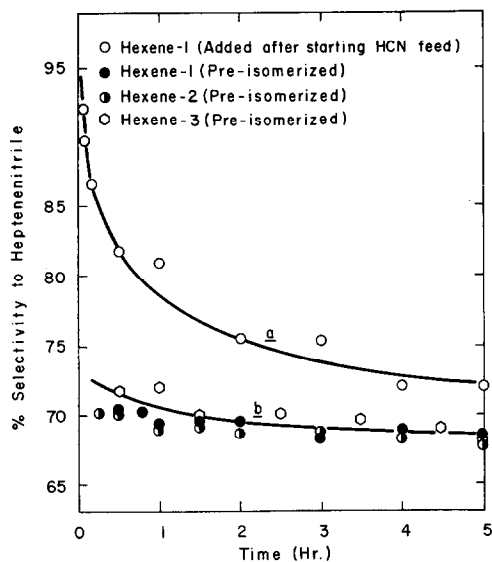| Hexene-1 | Heptanenitrile | 2-Methylhexanenitrile | |
| Hexene-2 | | 2-Methylhexanenitrile | 2-Ethylpentanenitrile |
| Hexene-3 | | | 2-Ethylpentanenitrile |

FIG. 1. Selectivity to heptanenitrile as a function of feed and reaction conditions. Catalyst–NiL$_4$:L:AlCl$_3$ = 1:5:2 in acetonitrile at 60°C.

data in which an attempt was made to determine the amount of 2-methyl-hexanenitrile which resulted from each isomer, using AlCl$_3$ as the co-catalyst.

The points on curve "b" were obtained under the experimental conditions described previously. They demonstrate that under the usual hydrocyanation conditions the olefin exists as an equilibrium mixture of isomers, and regardless of which hexene is used as the reactant the ratio N/B is the same. The curve "a" was obtained in the following way. The solvent and catalyst were preheated to reaction temperature, and the HCN feed started. After allowing time for a significant build-up of HCN in the reactor, preheated hexene-1 was added to the mixture. Under these conditions it was anticipated that the initial rate of hydrocyanation would be comparable to that of isomerization. This means that the initial value of N/B would be close to the value for hexene-1 hydrocyanation as opposed to that for the equilibrium mixture of isomers. The nature of curve "a" indicates that the hypothesis was correct since the initial selectivity was much higher (92% vs 71%) that was normally observed.

Confirmation that this was due to the

large initial concentration of hexene-1 as compared to that in the equilibrium mixture was obtained from glc, which showed <20% isomerization of hexene-1 during the early part of the reaction. By extrapolating curve "a" to zero time, the N/B ratio can be obtained for the hydrocyanation of pure hexene-1, the value being at least 19/1 compared to 2.3/1 for the isomeric mixture. Therefore, approximately 85% of the branched nitrile product results from direct hydrocyanation of hexene-2 and only 15% from "Markownikoff" addition of HCN to hexene-1. An attempt was made to confirm these results by studying the hydrocyanation of propylene, which can only exist as an α-olefin, so that all of the branched product must result from "Markownikoff" addition to the terminal olefin. The results which are shown as part of Table 2 indicate that propylene and hexene-1 are very different in their behavior since the N/B ratio for propylene was only 1.5/1.

This difference raised the question of the importance of steric effects in directing the course of the reaction, and led to the hydrocyanation of a number of sterically hindered olefins, the results of which are shown in Table 2. It is clear that the N/B ratio is very sensitive to steric effects, for in going from propylene to isobutylene, i.e., substitution of a methyl group for hydrogen at the 2-position, N/B changed from 1.5 to >99. A similar result was obtained with 2,3-dimethyl-1-butene. It was also noted that in the latter case the CH$_3$– substituents had a marked effect on the rate of isomerization to the internal olefin. After 5 hr

TABLE 2

THE RATIO OF NORMAL/BRANCHED PRODUCTS IN THE HYDROCYANATION OF OLEFINS WITH DIFFERING DEGREES OF STERIC HINDRANCE[a]

Olefin	N/B
Propylene	1.5
Isobutylene	>99
2,3-Dimethyl-1-butene	>99
3,3-Dimethyl-1-butene	>99
1-Hexene	19

[a] Catalyst—NiL$_4$:L:AlCl$_3$ = 1:5:2.

reaction only 37% of the 1-olefin had isomerized, which compared to complete equilibration of hexene-1 in minutes. Another sterically hindered olefin studied was 3,3-dimethyl-1-butene. Because of its structure it cannot isomerize to an internal olefin, although it can be hydrocyanated to give products with the –CN group attached to either C_1 or C_2. The presence of the CH_3– substituents, even in the 3-position, have a strong steric effect since again the N/B ratio was >99.

If the active catalytic intermediate is assumed to be $(IINiL_3)^+$, then the pronounced steric directing effect of the methyl group probably results from the bulky nature of L, tri-p-tolyl phosphite. Since $(HNiL_3)^+$ is a sterically crowded complex, the manner in which an olefin first coordinates to it, and then inserts into the Ni–H bond, will be very sensitive to the structure of the olefin. Insertion of an olefin into the Ni–H bond to give a primary Ni–alkyl represents a path of lower steric resistance than insertion to give a secondary Ni–alkyl. Thus in substrates which already possess branched chain structures the driving force to form a primary alkyl, and thus a nitrile with the –CN group attached to C_1, will be considerably enhanced. This results in the formation of products with a very high N/B ratio for sterically hindered substrates.

The Effect of Lewis Acids

A. On reactivity. The role of the Lewis acid as a promoter for increasing the rate of hydrocyanation is readily apparent from the data in Fig. 2. The percentage conversion of hexene-1 to C_7 nitriles under standard reaction conditions is plotted as a function of the mole ratio of Lewis acid/NiL_4. The very rapid increase in reaction rate as the ratio increased from 0 to 1, followed by a constant rate once the ratio reached unity, implied some type of 1:1 complex formation between NiL_4 and the Lewis acid. Although it has not proved possible to isolate this particular compound, nmr and infrared results indicate the existence of similar complexes (7), e.g., $HNi[P(OEt)_3]_4^+$ $(ZnCl_2CN)^-$. Further, the compound $(HNiL_2')^+(AlCl_4)^-$, where
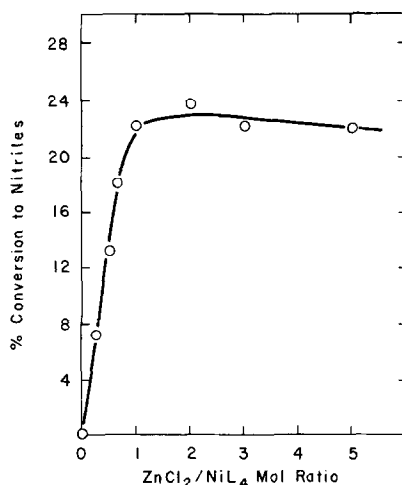
$$L' = (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2,$$

has been prepared (7) and was quite stable. Based on these results, the 1:1 complex shown in Eq. (1) was proposed as the active catalyst.

B. On selectivity. The nature of the Lewis acid used to promote the reaction, has been found to have a significant effect on the N/B product ratio for hexene hydrocyanation. The results for three Lewis acids are shown in Fig. 3, in which % selectivity to the normal product is plotted as a function of time. It was mentioned earlier that the N/B ratio depended upon the relative concentrations of primary and secondary Ni–alkyls in solution, and upon the relative rates of reactions (3) and (4). In all cases studied, the equilibration of hexene isomers was essentially instantaneous, so that for a given nickel catalyst and solvent, the relative amounts of primary and secondary Ni–alkyl should be independent of the nature of the Lewis acid. Thus any effect of the Lewis acid on selectivity, i.e., the N/B ratio, must result from changes in the relative rates of reactions (3) and (4). If the rate constants for these reactions are designated k_3 and k_4, the larger the ratio k_3/k_4 then the greater the
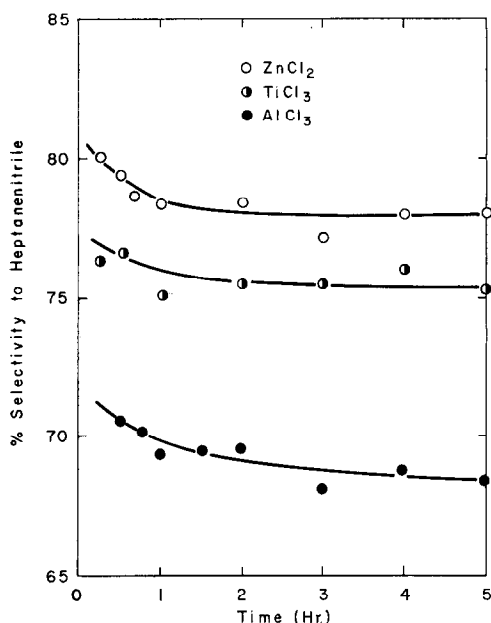
FIG. 3. Variation of selectivity to heptanenitrile with different Lewis acids. Catalyst—NiL₄:L:Lewis acid = 1:5:2 in acetonitrile at 60°C.

any particular property of the series of Lewis acids studied. Figure 4 shows one attempt which was made at such a correlation. The function, which is plotted as the ordinate, is intended to be a qualitative measure of the acceptor strength of the particular Lewis acid. The ionic charge of the central metal, divided by the surface area of the sphere carrying that charge, should provide some measure of the relative positive charge density of the acceptor site. The latter will be important in determining the degree of interaction with the $-CN^-$ ion. It appears from Fig. 4 that there is some correlation between Lewis acidity and the selectivity obtained in hydrocyanation, but the nature of the interaction from which this correlation results is not clear at the present time. Attempts to broaden the relationship were not successful, since many of the other Lewis acids tested were either completely inactive as co-catalysts, insoluble in the reaction media, or unstable under hydrocyanation conditions.

Solvent Effects

selectivity to normal product, i.e., the greater the value of N/B.

Although it is possible to see how the Lewis acid can cause changes in this ratio, it is not easy to correlate the changes with
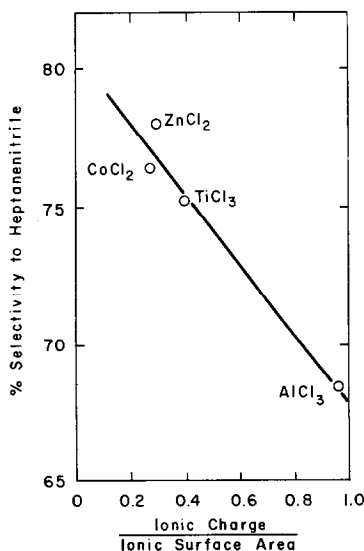
The nature of the solvent also has a significant effect on both the selectivity to

FIG. 4. Selectivity to heptanenitrile as a function of Lewis acid acceptor strength. Catalyst—NiL₄:L:Lewis acid = 1:5:2 in acetonitrile at 60°C.
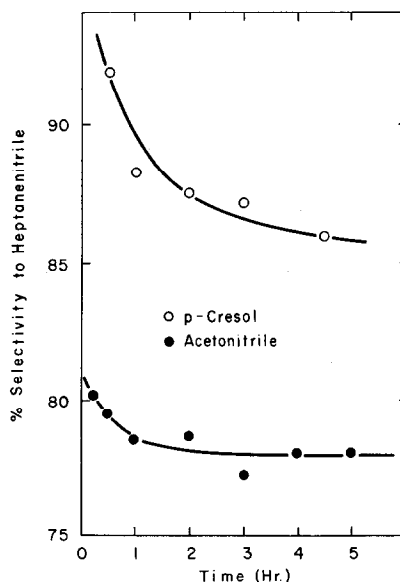

FIG. 5. Selectivity to heptanenitrile as a function of solvent. Catalyst—NiL₄:L:ZnCl₂ = 1:5:2 at 60°C.

normal nitriles, and upon the reaction rate. It is not easy to explain either of these effects. Figure 5 shows a plot of selectivity against time for two solvents. Higher N/B ratios were obtained with p-cresol as solvent compared with acetonitrile. It is possible that this could be a dielectric effect, with the less polar solvent giving higher N/B ratios. Using p-cresol as solvent the selectivity was high initially, but then tended to decrease steadily with time. This is most likely due to the increasing amounts of nitrile products in the reaction mixture, which will increase the dielectric constant of the medium. Based on the results with acetonitrile, this will tend to lower the selectivity. In a continuous operation in which the ratio of p-cresol:nitriles would be constant, the selectivity should also remain constant, and be considerably above that for acetonitrile. High selectivities were also obtained with other aromatic solvents, such as toluene, but catalyst lifetimes were short in these media.

Because it was necessary to feed the HCN to the reactor at a rate similar to that at which it was consumed, it proved difficult to obtain any quantitative rate information. An attempt was made to compare the rate of reaction in acetonitrile and p-cresol, the results of which are shown in Fig. 6. The HCN feed rate is plotted against the rate of product formation in acetonitrile and p-cresol. For the acetonitrile, once the HCN feed rate exceeded about 2 mmole/hr/mmole NiL_4, the rate of product formation became significantly less than the feed rate. In contrast, for p-cresol the rate of product formation was equal to the feed rate up to at least 20 mmole/hr/mmole NiL_4. Similar measurements were also made with toluene, and although the results were somewhat irreproducible, it was clear that toluene was similar to acetonitrile in rate rather than p-cresol. In experiments with other phenolic compounds, it became apparent that the rate increase was associated
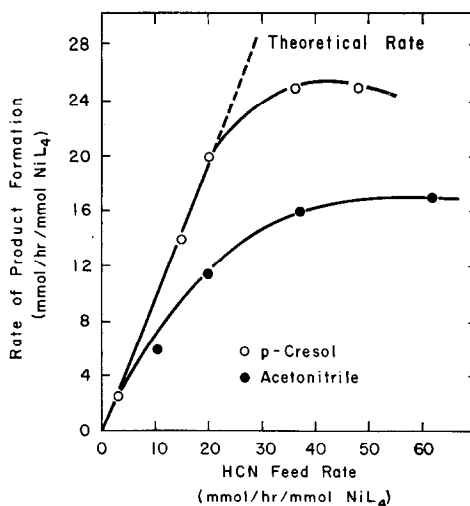

FIG. 6. Rate of product formation as a function of solvent at various HCN feed rates. Catalyst—NiL_4:L:$ZnCl_2$ = 1:5:2 at 60°C.

in some way with the phenolic –OH function. At this time the mechanism by which such a rate promotion operates is not understood.

ACKNOWLEDGMENT

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