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HOMOGENEOUS CATALYSIS OF 1-BUTENE ISOMERIZATION WITH HYDRIDO NICKEL PHOSPHITE COMPLEXES

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INTRODUCTION

The use of nickel phosphite complexes as olefin isomerization catalysts has been investigated extensively by various groups of workers. The initial work in this area was conducted by Cramer and Lindsey [1], who noted that olefin isomerization could be initiated by $Ni[P(OEt)_3]_4$ in the presence of an acid co-catalyst. Later work by the Du Pont group [2] demonstrated that a $NiH[P(OEt)_3]_4^+$ species was produced in such catalyst mixtures. In a series of elegant experiments, Tolman delineated the mode of formation of the $HNiL_4^+$ species [3] in methanolic sulfuric acid solutions of $Ni[P(OEt)_3]_4$ and discussed its importance in the mechanism of olefin isomerization [4] via the equilibria shown in reaction (1). Tolman concluded that the coordinatively unsaturated

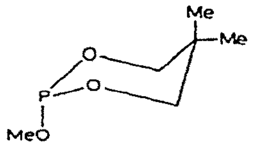
$$H^+ + NiL_4 \overset{K_1}{\rightleftharpoons} HNiL_4 \overset{K_2}{\rightleftharpoons} HNiL_3^+ + L \quad . \tag{1}$$

$HNiL_3^+$ moiety was the catalytically active intermediate. Related work by Wells [5] also showed a high catalytic activity for $Ni[P(OEt)_3]_4$—CF_3COOH—benzene solutions, but the results suggested that $HNiL_4^+$ was the active intermediate. More recent observations by Graziani [6] indicate that $Ni[P(OEt)_2Ph]_4$ *p*-toluenesulfonic acid—methanol mixtures also catalyze olefin isomerization and that excess free ligand suppresses the rate of isomerization in accord with Tolman's suggested mechanism.

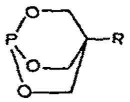
The work from Tolman's laboratories [7] and more recently from our own [8], has demonstrated that the extent of protonation of $Ni(phosphite)_4$ complexes depends upon the basicity of the phosphite ligand. Whereas Tolman showed this for acyclic $P(OR)_3$ systems wherein the alkyl group becomes substituted with an electronegative group, we found that the same was true when the acyclic phosphite is constrained to a caged phosphite ester, $P(OCH_2)_3CR$, where R = Me or *n*-hexyl. The primary aim of the present work was to investigate the influence of geometrical constraint of the phosphite on the effectiveness of the $HNiL_4^+$ [1] complexes in isomerizing 1-butene to *cis* and *trans* 2-butenes in the series of ligands:

$P(OEt)_3$

(I)



(II)



(III)

(IIIa) R = Me
(IIIb) R = *n*-hexyl

EXPERIMENTAL

NiL_4

The tetrakis(phosphite)nickel(0) complexes were prepared as described previously [8]. They were preserved under vacuum and handled under nitrogen. Tetrakis(triethylphosphite)nickel(0) was recrystallized from hot methanol under a nitrogen atmosphere and stored under vacuum at −70° C. The analogous complex of (II) was recrystallized from hot hexane in a nitrogen atmosphere.

Reagents

All solvents used were reagent grade. Methanol was refluxed over, and distilled from, $Mg(OMe)_2$. Benzene was distilled from CaH_2 and acetone was dried by allowing it to stand over molecular sieves for several days. All solvents were thoroughly saturated with prepurified nitrogen for 10—12 h prior to use since the $HNiL_4^+$ species are known to be oxygen sensitive in solution [3, 5, 8]. The concentrated H_2SO_4 used was Baker "analyzed" reagent. Trifluoroacetic acid (Aldrich) was used as supplied, while *p*-toluenesulfonic acid (Baker prac.) was dried under vacuum by pumping on the molten material at 90° C for 8 h. The 1-butene employed was Matheson C.P. Grade and was used without further purification.

Apparatus

The apparatus was assembled as shown in Fig. 1. The reaction vessel and all glassware used in the preparation of solutions were dried in an oven at 140° C and cooled in nitrogen prior to use. All solutions were prepared and maintained under nitrogen and transferred to the reaction vessel by syringe.

Gas chromatographic analyses

GC analyses were conducted on a Varian 1700 chromatograph at 25° C with a He flow rate of about 40 ml/min using a $AgNO_3$/ethylene glycol column as described earlier [9].

Typical isomerization run

In a typical run about 40 mg (50 μmol) of NiL_4 complex was introduced into

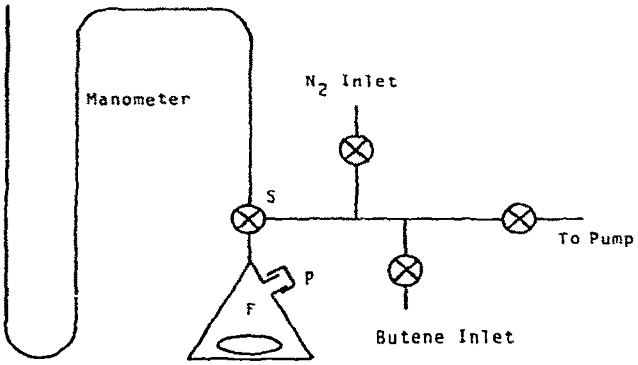


Fig. 1. The apparatus used in the isomerization experiments.

the reaction flask, F, which had an approximate volume of 170 ml. After evacuation of the system an atmosphere of 1-butene was admitted and isolated in the vessel by means of the three-way stopcock, S. One ml of solvent was syringed into the flask through septum, P, after which the mixture was rapidly stirred with a magnetic stirring bar until pressure equilibrium was established. One ml of solvent containing the desired amount of acid was then injected and a stopwatch started.

Data treatment

While Tolman [4] used the change in volume to record the progress of isomerization, we have monitored the change in pressure over a relatively small range. Thus we can define a "rate constant" κ as

$$\kappa = \frac{1}{\Delta p}\frac{dp}{dt}$$

where Δp is the total pressure change upon isomerization and dp/dt is the maximum rate of pressure change. It should be emphasized that the "rate constants" so obtained are dependent upon the volume of olefin to be isomerized. Figure 2 and Table 1 illustrate this result. Such a result is merely a consequence of the way in which κ is defined and measured. Under a given set of conditions the actual reaction rate in solution will be constant whatever the amount of butene to be isomerized. However, the smaller the volume of gaseous olefin, the sooner isomerization will be complete. The present work used 6.8 mmol of butene (approximately 170 ml) throughout.

RESULTS

As Tolman pointed out earlier [4], the higher solubilities of the *cis* and *trans* 2-butenes lead to a pressure drop as isomerization proceeds. Monitoring

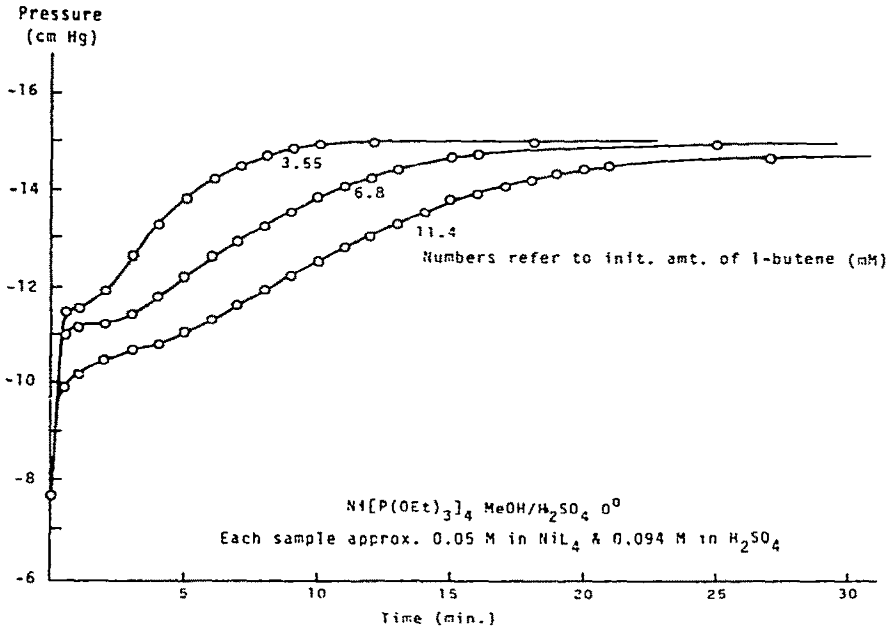


Fig 2. The dependence of the maximum isomerization rate on the amount of 1-butene present.

of the reaction was accomplished by noting pressure changes with time as well as GC analyses of 0.35 ml gas aliquots.

Four acid—solvent systems were chosen for study and experiments were conducted at both ambient temperature (24°) and, by immersing the entire reaction flask in a well stirred ice bath, at 0°. Tables 2 and 3 list the relative concentrations and the observed rates while the comparative results are graphically represented in Figs. 3 and 4.

TABLE 1

Variation in κ with change in volume in MeOH/H$_2$SO$_4$ at 0° [a]

Acid concn. (molar)	Ni[P(OEt)$_3$]$_4$ concn. (molar)	Vol. 1-butene (mMol)	dp/dt (cm Hg min^{-1})	κ (min^{-1})
0.094	0.066	3.55	0.68	0.20
0.094	0.044	6.8	0.39	0.10
0.094	0.048	11.4	0.29	0.064

[a] Final solution volume was 1 ml.

TABLE 2

Typical rate results with NiL_4 systems in various acids and solvents at 24° [a]

Solvent	Acid	Acid concn. (molar)	Ligand	NiL_4 concn. (molar)	dp/dt (cm Hg min^{-1})	κ (min^{-1})
MeOH	H_2SO_4	0.094	I	0.023	0.82	0.36
			II	0.018	0.45	0.20
			IIIa	0.032	0.062	0.027
			IIIb	0.023	0.079	0.034
Me_2CO	CF_3CO_2H	0.0675	I	0.022	1.04	0.37
			II	0.021	0.22	0.077
			IIIa or IIIb	0.025	[b]	[b]
C_6H_6	CF_3CO_2H	0.0675	I	0.030	1.50	0.50
			II	0.026	1.60	0.53
			IIIa or IIIb	0.025	[b]	[b]
MeOH	p-MeC_6H_4-SO_3H	0.031	I	0.021	0.34	0.15
			II	0.021	0.22	0.10
			IIIa	0.026	0.044	0.020
			IIIb	0.026	0.049	0.022

[a] Final solution volume was 2 ml.
[b] No catalysis observed.

In the case of $Ni(I)_4$ and $Ni(II)_4$ the addition of acid to the initially colorless NiL_4 solutions immediately produced a pale yellow solution which persisted throughout the isomerization. In contrast, the $Ni(IIIb)_4$ solution only developed a pale yellow solution slowly. In the case of the $Ni(IIIa)_4$ derivative,

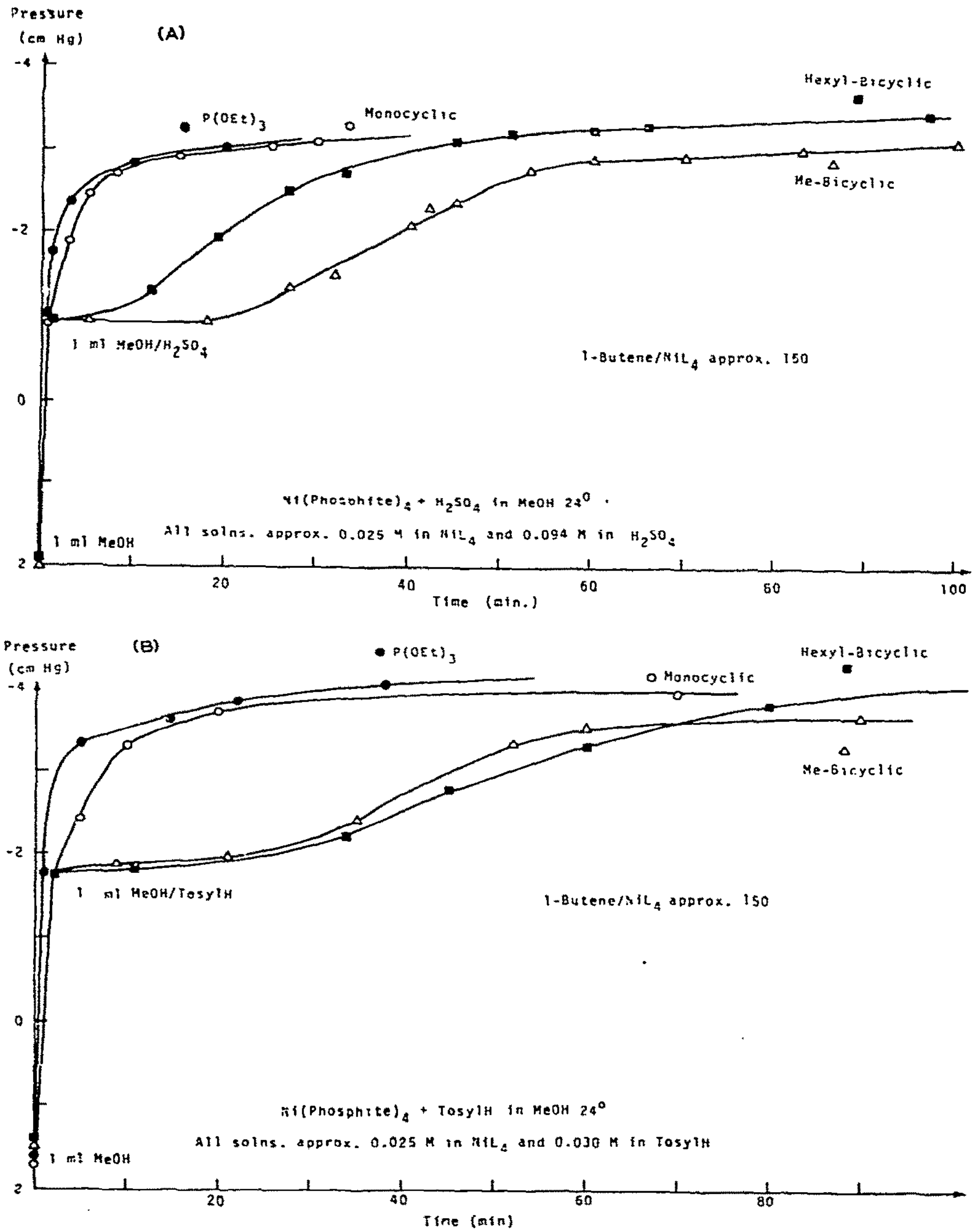
TABLE 3

Typical rate results realized with NiL_4 systems in various acids and solvents at 0° [a]

Solvent	Acid	Acid concn. (molar)	Ligand	NiL_4 concn. (molar)	dp/dt [b] (cm Hg min^{-1})	κ (min^{-1})
MeOH	H_2SO_4	0.094	I	0.050	0.37	0.10
		0.094	II	0.052	0.12	0.033
		0.47	II	0.079	0.32	0.080
		0.94	I	0.041	0.74	0.17
		0.94	II	0.055	0.34	0.085
		0.94	IIIb	0.037	0.071	0.018
C_6H_6	CF_3CO_2H	0.135	I	0.056	0.19	0.059
		0.135	II	0.046	0.45	0.12

[a] Final solution volume was 2 ml.
[b] Precision is ± 0.01.

which was only partially soluble in all the solvents chosen, the initial white suspension gradually became cream colored which, when isomerization was about 50% complete, produced a homogeneous pale yellow solution. Attention is drawn to four observations concerning Figs. 3—5:



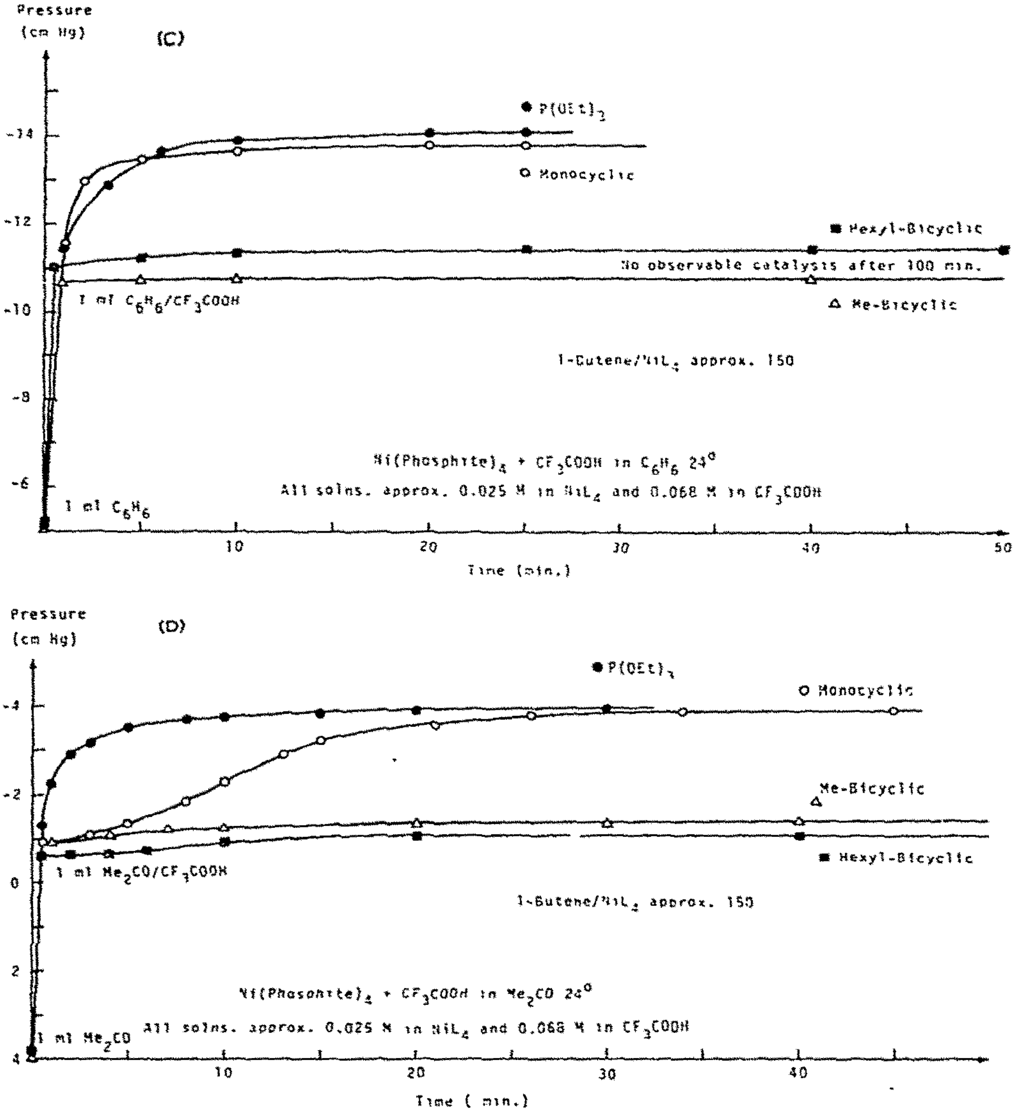


Fig. 3. The change in pressure due to the room temperature isomerization of 1-butene in the presence of NiL_4 as a function of time using (a) H_2SO_4 in MeOH; (b) *p*-$MeC_6H_4SO_3H$ in MeOH; (c) CF_3COOH in C_6H_6 and (d) CF_3COOH in Me_2CO as the medium.

(1) In all cases, the rates of isomerization follow the ligand order acyclic (I) $\gtrsim$ monocyclic (II) $\gg$ bicyclic (IIIa, IIIb)

(2) Induction periods precede catalysis in several instances

(3) The various solvent systems show differing abilities to differentiate the ligands regarding catalyst effectiveness.

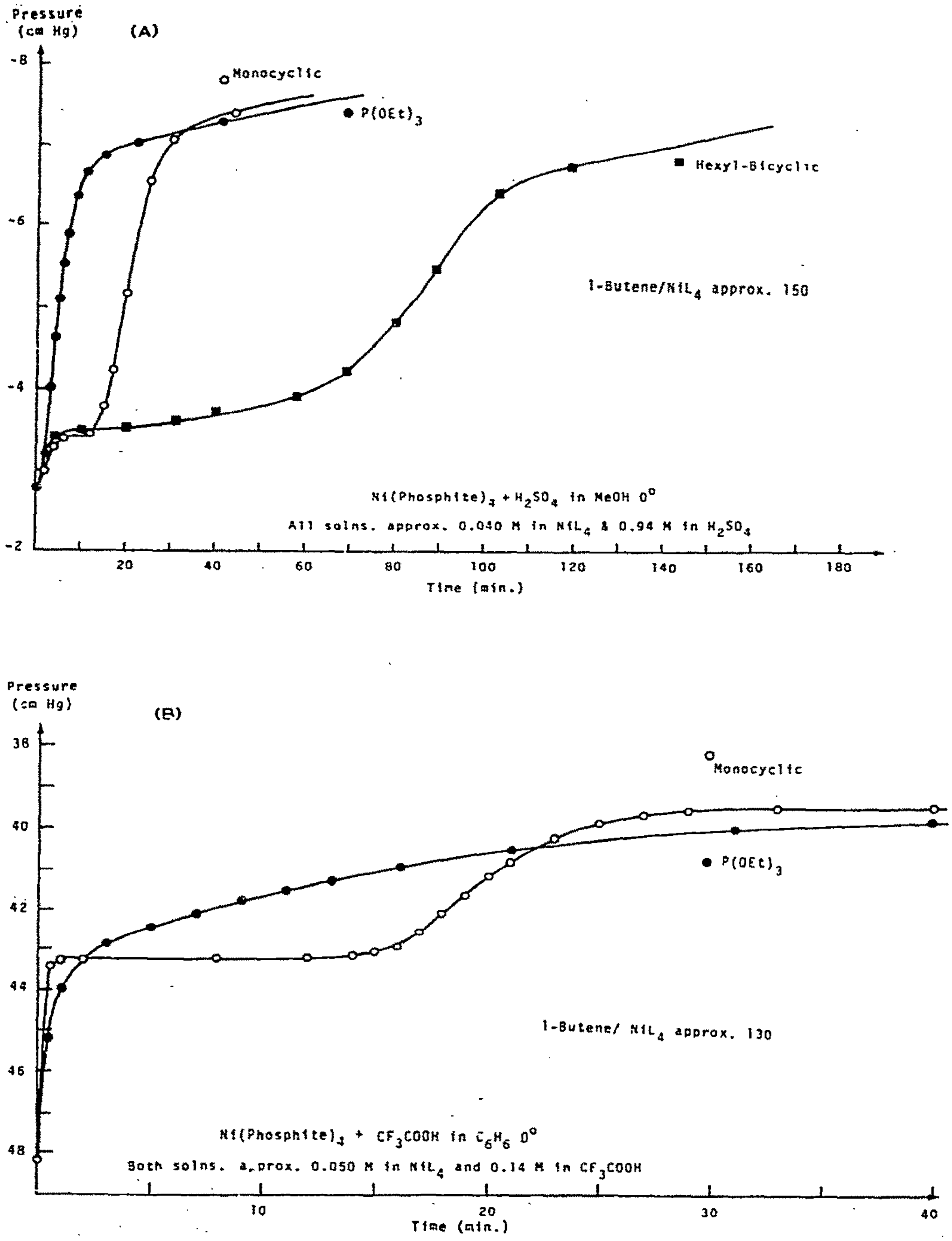


Fig. 4. The change in pressure due to the ice temperature isomerization of 1-butene in the presence of NiL_4 as a function of time using (a) H_2SO_4 in MeOH and (b) CF_3COOH in C_6H_6.

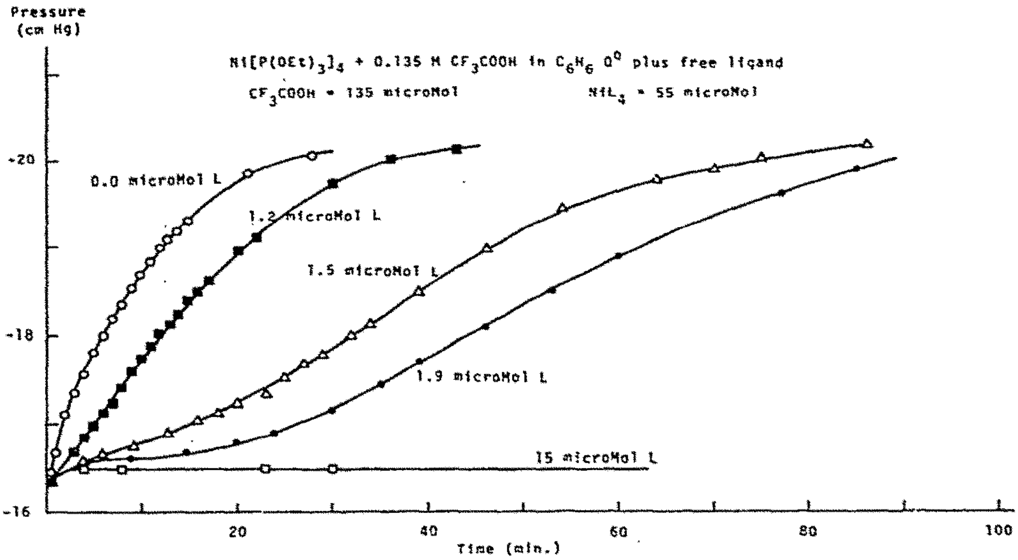


Fig. 5. The dependance of the isomerization commencement and maximum rate on the presence of free ligand.

(4) The addition of excess ligand (Fig. 5 and Table 4) drastically reduces the isomerization rate.

DISCUSSION

The appearance of sigmoid pressure—time relationships is in accord with the previous observations of Tolman [4]. Since protonation of NiL_4 is known to occur within milliseconds of mixing [3], the induction periods can be attrib-

TABLE 4

Variation in κ with added free ligand, $P(OEt)_3$, in CF_3COOH/C_6H_6 at 0°C [a]

Acid concn. (molar)	$Ni[P(OEt)_3]_4$ concn. (molar)	$P(OEt)_3$ concn. (molar)	dp/dt (cm Hg min^{-1})	κ (min^{-1})
0.135	0.055		0.20	0.054
		0.0012	0.14	0.036
		0.0015	0.070	0.019
		0.0019	0.060	0.016
		0.015	[b]	[b]

[a] Final solution volume was 1 ml.

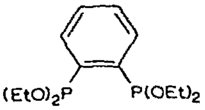
[b] No catalysis observed.

uted to a second, slower step which Tolman suggested involved ligand dissociation:

$$HNiL_4^+ \rightleftharpoons HNiL_3^+ + L \qquad (2)$$

Although spectroscopic evidence for the existence of $HNiL_3^+$ is presently lacking, the fact that a ligand-dependent induction period and isomerization rate (Fig. 5) is observed, strongly supports such an equilibrium. In sharp contrast, Wells [5] observed no such ligand dependence although he did note that isomerization terminated with excess ligand after about 40% of the 1-pentene had reacted. The discord in the results may be due to the fact that at the higher temperatures employed by Wells (35°) there appears to be little rate differentiation and, in addition, trifluoroacetic acid would react with excess $P(OEt)_3$ very rapidly at 35°C and hence, tend to nullify its effect. The induction periods can be attributed to a slow build up in catalyst concentration (presumably $HNiL_3^+$) until isomerization proceeds at a measureable rate.

Additional evidence supporting the idea that $HNiL_3^+$ is the catalytically active species is the lack of any observable isomerization of 1-butene after 108 min using NiL_2 in a methanol—sulfuric acid solution at 0° where L is the new



(IV)

chelate (IV) [11]. Here ligand dissociation is expected to be even more difficult than in the monodentate systems.

The trend of decreasing catalyst effectiveness upon increased cyclization of the ligand follows the previously established trend in ligand basicities [10] and NiL_4 basicities [8]:

acyclic (I) $\geq$ monocyclic (II) $\gg$ bicyclic (IIIa, IIIb)

The least basic phosphite (IIIa, IIIb) would give rise to the lowest concentration of $HNiL_4^+$ which in turn is expected to produce the lowest $HNiL_3^+$ concentration and hence, the slowest isomerization rates. While this rationale is consistent with the data, there may well be effects owing to changing metal—phosphorus bond strength and ligand labilities among these ligands but these influences cannot be evaluated presently. The longer induction periods associated with the $Ni(IIIc)_4$ and $Ni(IIIb)_4$ complexes may arise from a greater reluctance of the corresponding $HNiL_4^+$ species to dissociate a phosphite ligand.

While the ambient temperature data do not favor $Ni(I)_4$ over $Ni(II)_4$ as an olefin isomerization catalyst, we point out that the monocyclic phosphite complex displays better stability with respect to decomposition on storage and to aerial oxidation. Moreover, it has very comparable solubility properties to the acyclic phosphite complex and, in fact, is quite soluble in all common solvents.

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