adequately represented by arc plots, in which the values of the imaginary part of the dielectric constant are plotted as ordinates against those of the real part as abscissas. The critical wave lengths or relaxation times of the polar molecules tend to be longer in the pure polar liquids than in solutions of about the same viscosity and tend to increase with increasing viscosity of the solvent much less than is required by the Debye theory. They increase with molecular volume in, at least, qualitative conformity to the Debye theory.

PRINCETON, NEW JERSEY RECEIVED DECEMBER 9, 1949

[CONTRIBUTION NO. 63 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Influence of Certain Additives on the Rate of Catalytic Hydrogenation of Terpenes on Nickel

BY HILTON A. SMITH AND JOHN F. FUZEK

In a previous communication[1] it was shown that the rate of catalytic hydrogenation of some terpenes on Raney nickel catalyst was influenced by the presence of small amounts of palmitic acid. A thorough study of this phenomenon has been made, and the results are reported here.

Experimental

The terpenes were the same as those previously described.[1]

Raney nickel was prepared both by the method of Mozingo,[2] and by the method of Pavlic and Adkins[3] which is said to give a more active form.

Many of the materials tested as additives were Eastman Kodak Co. best grade chemicals, and were used without further purification. Pure formic acid was prepared by fractionation of 89% solution, giving the pure acid and maximum-boiling azeotrope. **Acetic, propionic, butyric and valeric acids** were purified by fractionation of reagent grade or Eastman Kodak Co. best grade acids. ***n*-Undecanoic acid** was prepared by hydrogenation of 10-undecenoic acid.[4] **Pentadecylic acid** was prepared by addition of carbon dioxide to the Grignard reagent prepared from myristyl bromide. **Nonadecylic** and **tricosanoic** acids were similarly prepared from octadecyl and *n*-docosyl bromides. **Behenic acid** was prepared by hydrogenation of Eastman erucic acid. Some of the behenic acid was converted to *n*-docosyl alcohol by reduction with hydrogen in the presence of copper chromite. This was then converted to the bromide by reaction with hydrobromic acid. **N-Tetracosanoic acid** and **arachidic acid** were prepared by a malonic ester synthesis using *n*-docosyl bromide and *n*-octadecyl bromide, respectively. **γ-Phenylbutyric acid and ε-phenyl-*n*-caproic acid** were prepared by carbonation of the Grignard reagents prepared from γ-phenylpropyl bromide and ε-phenylamyl bromide. **δ-Phenylvaleric acid and ζ-phenylheptanoic acid** were prepared from the same bromides through malonic ester syntheses. The ε-phenylamyl bromide was prepared from γ-phenylpropyl bromide by addition of ethylene oxide to the Grignard reagent, and reaction of the resulting alcohol and anhydrous hydrogen bromide.

The **cyclohexyl-substituted acids** were all prepared by catalytic hydrogenation of the corresponding phenyl-substituted acids using Adams platinum catalyst and acetic acid as solvent.

Laurylamine and stearylamine were obtained from Armour and Co., and were fractionated prior to use. Sodium oleate was Merck U.S.P. grade chemical. **Cetyldimethylethylammonium bromide and octadecyldimethylbenzylammonium chloride** were Eastman practical grade chemicals, and were used without purification. Sodium lauryl sulfate was obtained from the Fisher Scientific Company.

The runs were carried out in a small hydrogenation bomb of the type described by Adkins.[5] The bomb had a volume of 45 ml., while the volume of the pressure gage and connections was 11 ml. The bomb was equipped with a heating jacket of conventional design, and was agitated through an angle of 30° at a rate of 42 cycles per minute. This speed has been shown to be sufficient to maintain equilibrium conditions.[1] Reactions were carried out in the manner previously described,[1] with the exception of the fact that, after the catalyst and terpene were in the bomb, a weighed amount of the additive to be tested was added before connection to the gage was made. When runs were made at elevated temperatures, the bomb was heated to the desired temperature as quickly as possible (usually not longer than fifteen minutes were required), after which shaking was commenced. In general, no reaction took place during the preliminary heating period. During an individual hydrogenation, temperatures were maintained constant to ±0.5°. After the runs were completed, the catalyst was filtered out and weighed under carbon dioxide.[1] The catalyst weights were corrected for the amount of adsorbed additive.

Experimental Calculations and Results

It has already been shown that the rates of these hydrogenations follow the equation

$$\log p^0/p = k'T/2.303\,V$$

where p is the pressure at any time t, p^0 is the initial pressure, V is the volume of hydrogen in the system and k' is the reaction rate constant.[1] All rate constants which are recorded here are obtained by dividing k' by the weight of catalyst used, thus referring all constants to one gram of catalyst. Table I gives a list of such constants for the hydrogenation of *d*-limonene on Standard Raney nickel catalyst in the presence of a number of additives.

Figure 1 shows the effect of varying amounts of additive on the rate constant for hydrogenation of *d*-limonene. Figure 2 shows a similar effect for varying amounts of palmitic acid on the rate constant for the hydrogenation of several terpenes. Figure 3 shows similar curves for caproic and palmitic acid using *d*-limonene and standard Raney catalyst, as well as the effect of palmitic

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[1] Smith, Fuzek and Meriwether, THIS JOURNAL, **71**, 3765 (1949).

[2] Mozingo, *Org. Syn.*, **21**, 15 (1941).

[3] Pavlic and Adkins, THIS JOURNAL, **68**, 1471 (1946).

[4] Obtained from the Baker Castor Oil Company.

[5] Adkins, "Reactions of Hydrogen," The University of Wisconsin Press, Madison, Wisconsin, 1937, pp. 29-45.

TABLE I

RATE CONSTANTS FOR THE HYDROGENATION OF *d*-LIMONENE ON RANEY NICKEL CATALYST WITH VARIOUS ADDITIVES

Additive (0.0004 mole/g. Ni)		Rate constant $k \times 10^4$ liters min.$^{-1}$ g.$^{-1}$
Alcohols (normal)	Butyl	1.20
	Heptyl	0.46
	Myristyl	1.10
	Stearyl	1.48
	Ceryl	0.56
Acids	Palmitic	29.4
	Phenylethylacetic (see Figs. 4 and 5 for others)	4.7
Esters	Methyl stearate	1.75
	Ethylene distearate	1.01
	Tristearin	7.7
Amides	*n*-Caproamide	3.8
	Stearamide	4.0
Amines	Laurylamine	9.6
	Stearylamine	6.5
	Myristyldimethylamine	7.5
Quaternary ammonium salts	Cetyldimethylammonium bromide	8.7
	Octadecyldimethylbenzylammonium chloride	6.8
Sulfated alcohols:	Sodium lauryl sulfate	7.9
Soaps:	Sodium oleate	17.9
No additive	Standard catalyst	1.93
	Special catalyst	38.6

acid on a more active nickel. Figure 4 indicates the effect of the chain length of fatty acids when used as additives in the hydrogenation of terpenes. Figure 5 is a similar plot showing the effect of omega-substituted phenyl and cyclohexyl substituted acids on the hydrogenation of *d*-limonene on nickel. Figure 6 indicates the effect of small amounts of methanol on the rate of hydrogenation of *d*-limonene and terpinolene on standard catalyst. Figure 7 indicates the effect of agitation on the rate of hydrogenation of *d*-limonene on nickel with or without additive.

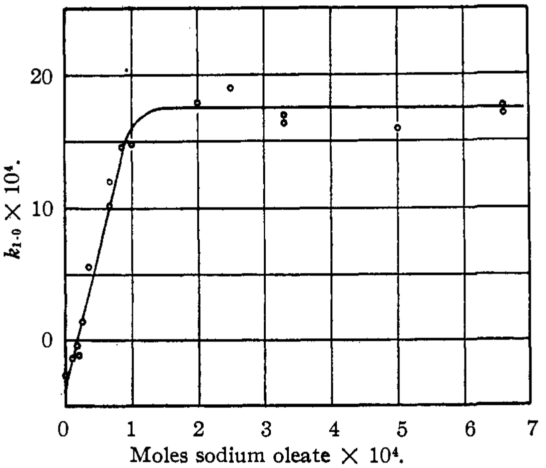

Fig. 1.—Hydrogenation of *d*-limonene on Raney nickel catalyst in the presence of sodium oleate.

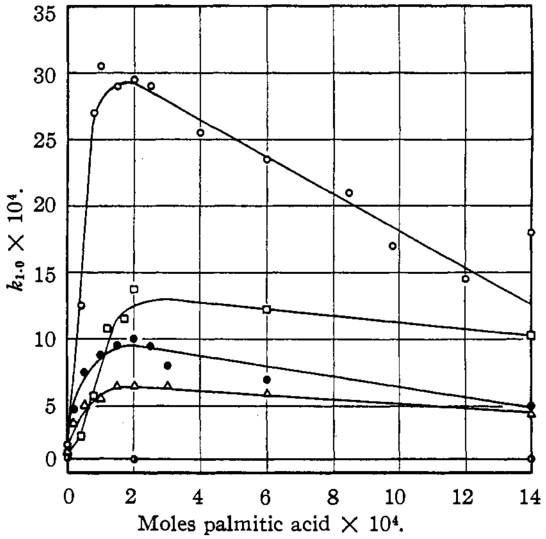

Fig. 2.—Hydrogenation of some terpenes on Raney nickel catalyst with palmitic acid as accelerator: ○, *d*-limonene; ◑, α-pinene; ●, β-pinene; △, terpinolene; □, camphene.

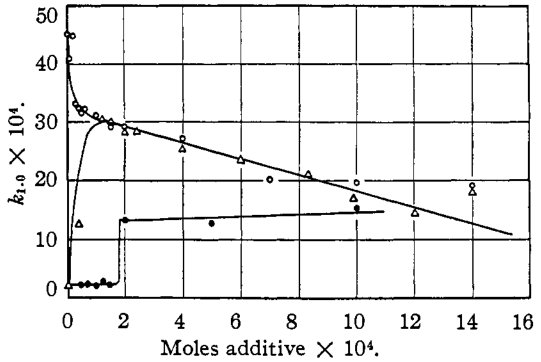

Fig. 3.—Hydrogenation of *d*-limonene: 1, on Pavlic and Adkins Raney nickel catalyst in the presence of palmitic acid (○); 2, on normal Raney nickel catalyst in the presence of (a) palmitic acid (△), (b) caproic acid (●).

The rate constants for hydrogenation of the terpenes at various temperatures were analyzed by means of the Arrhenius equation, and activation energies calculated for hydrogenations of the terpenes on nickel with or without additives. Figure 8 shows sample plots representing log *k* *vs.* the reciprocal of absolute temperature; Table II gives the activation energies for several of these reactions as calculated from such plots.

Discussion

As is plainly indicated in Table I, certain of the additives tried in the hydrogenation of *d*-limonene on Raney nickel catalyst caused an increase in the rate of hydrogenation of the terpene. The most effective of these tried was palmitic acid.

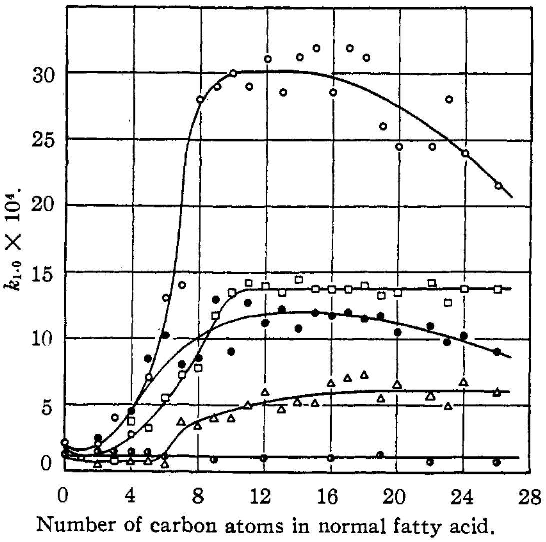

Fig. 4.—Hydrogenation of some terpenes on Raney nickel catalyst with normal fatty acids: O, *d*-limonene; ◑, *α*-pinene; △, terpinolene; □, camphene; ●, *β*-pinene.

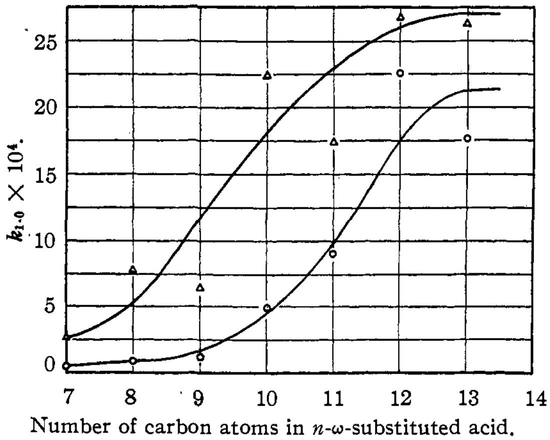

Fig. 5.—Hydrogenation of *d*-limonene on Raney nickel catalyst in the presence of *ω*-substituted fatty acids: ⊙, *ω*-phenyl acids; △, *ω*-cyclohexyl acids.

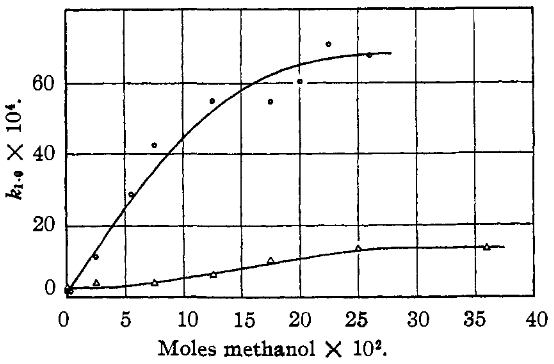

Fig. 6.—Hydrogenation of *d*-limonene (⊙) and terpinolene (△) on Raney nickel catalyst in the presence of methanol.

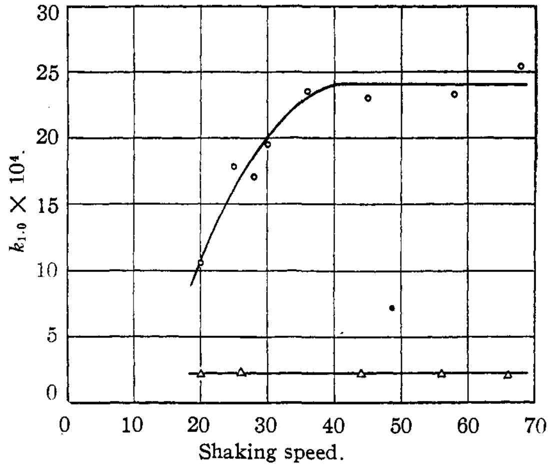

Fig. 7.—Effect of shaking speed on the rate constant for the hydrogenation of *d*-limonene on Raney nickel catalyst: (△) with no accelerator; (O) with palmitic acid as accelerator.

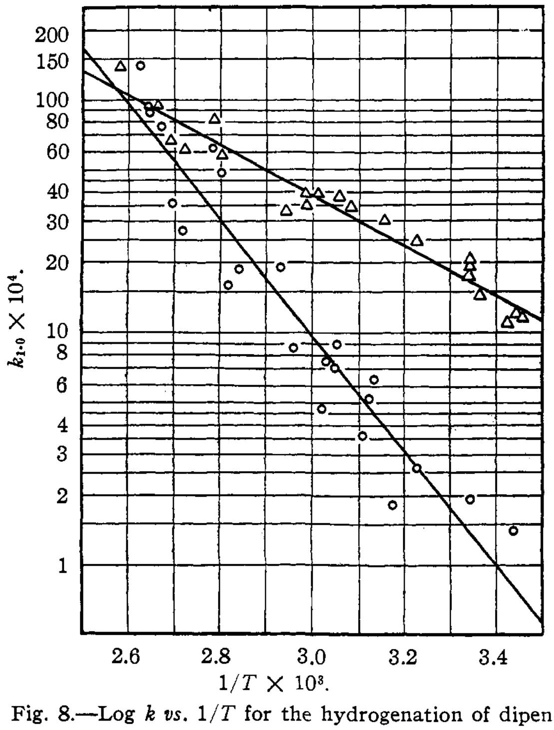

Fig. 8.—Log *k* *vs.* $1/T$ for the hydrogenation of dipentene on Raney nickel catalyst: (⊙) with no solvent or accelerator; (△) with palmitic acid as accelerator. (Lines were obtained by method of least squares.)

Soaps, amines, sulfated alcohols, quaternary ammonium salts and amides also increase the hydrogenation rate, while alcohols and some esters cause retardation, or have no effect.[6]

From Figs. 1 and 2 it appears that, up to a cer-

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(6) Tristearin appears to cause acceleration of the hydrogenation rate. However, further study of the tristearin indicated that a sufficient amount of free stearic acid might be present in the ester to account for the increase recorded.

tain point, the accelerating influence of fatty acids, soaps, etc., is approximately proportional to the amount of additive used, while larger amounts of these materials either caused no further rate increase, or were less effective. It has been previously shown that fatty acids are adsorbed on nickel catalyst in a unimolecular layer.[7] The point at which additional additive causes no further acceleration corresponds to that point at which sufficient fatty acid or soap is present to complete the unimolecular layer on the nickel, assuming that the hydrocarbon chain extends away from the metal surface in a manner similar to that found in a unimolecular film on water. As Fig. 2 shows, this point seems to be independent of the nature of the terpene although the magnitude of the acceleration is not. Also, this point appears to be independent of the chain length of the fatty acid used.

Since the fatty acids seemed to have the greatest influence of the additives tested, a more thorough study was made of their use. It was shown that fatty acids of very low molecular weights had, if anything, a decelerating influence, while fatty acids with from 10 to 25 carbon atoms all caused acceleration to much the same degree. Acids with from 4 to 9 carbon atoms had intermediate effects. This is shown in Fig. 4. In this connection it is interesting to note the different character of the curve for caproic acid in Fig. 3 when compared with that for palmitic acid. The latter is characteristic of the behavior of acids with 10 or more carbon atoms.

In order to determine whether the fatty acids had to be of minimum chain length or of minimum weight, some omega-phenyl and omega-cyclohexyl substituted acids were run. The results, as shown in Fig. 5, indicate that the number of carbon atoms in the chain rather than its straight chain character is of importance.

From the foregoing discussion it appears that Raney nickel catalyst is active for causing the hydrogenation of certain terpenes when its surface is covered with a unimolecular layer of fatty acid; in fact, it may be even more active than when no fatty acid is present. It is well known that low molecular weight alcohols such as methanol and ethanol are effective solvents for hydrogenations using nickel and platinum catalysts.[1] As is indicated in Table I, the higher alcohols do not act as accelerators. It was thought that the lower alcohols might be good media for the hydrogenation of terpenes because of adsorption of the alcohols on the catalyst. Figure 6 shows that, while enough alcohol is present to cover the surface of one gram of catalyst when less than 2×10^{-4} mole are present, the rate of hydrogenation of *d*-limonene increases with the amount of methanol added up to 0.2 mole of alcohol per gram of nickel. Therefore, the influence of the alcohol must be of somewhat different nature than the influence of the additives discussed here.

The obvious explanation of the experimental data is that the surface of Raney nickel catalyst may be covered with a unimolecular film of some inactive material, and still remain a good catalyst. Since valence forces are known to extend over a distance of only a few ångström units, this obvious picture is extremely difficult to accept, and it is necessary to examine any other possibility which might explain the data. Either the adsorbed fatty acid must have actual holes in the surface film which allow the hydrogenation to proceed, or the entire film must be of a sufficiently loose structure as to allow diffusion of the terpene and hydrogen to the nickel surface. The character of the absorption isotherms of the fatty acid on Raney nickel taken in conjunction with the surface areas measured by the B.E.T. method are rather strong evidence for a continuous, close-packed film, and it is rather improbable that large holes are present. It is also improbable that a molecule as large as a terpene could diffuse through such a film.

It will be noted that most of the materials which accelerate the hydrogenation of these terpenes are wetting agents, and one might well raise the question as to whether this is not primarily the result of wetting action which causes more effective dispersion of the catalyst than is usually obtained. However, the best wetting agents do not appear to be the best additives and, further, one would predict that the active spots are covered most readily by the wetting agents so that the higher effective surface area would be one of greatly decreased activity.

In this connection, it is of interest to study the effect of temperature on the rates of reaction with and without added fatty acid. Figure 8 shows that these reactions follow the Arrhenius equation reasonably well, and that the activation energy of the reaction is lowered by the addition of the fatty acid. This is characteristic of a true catalytic action. Table II gives the values of the activation energies for the catalytic hydrogenation of some terpenes on Raney nickel with and without added palmitic acid. In all cases the activation energies are lowered when the fatty acid is added to the standard catalyst.

In addition to the above points, one would probably expect that, were the influence of those agents which accelerate the hydrogenation purely that of a wetting agent, the rate of hydrogenation of all of the terpenes would be approximately equally affected. Not only are the rates affected in varying degrees, but in the case of one terpene, α-pinene, no acceleration at all is observed when palmitic acid is added. This is the only terpene used which does not possess an exocyclic double bond, and it has been previously shown that the exocyclic bonds are more readily hydrogenated than are those within the ring.[1] This structural

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[7] Smith and Fuzek, THIS JOURNAL, **68**, 229 (1946).

difference is apparently the cause of the behavior of α-pinene.

Figure 7 illustrates the fact that the bomb must be agitated more rapidly to maintain equilibrium when palmitic acid is present in the hydrogenation of terpenes on Raney nickel than when no fatty acid is present. Unfortunately the lower limit of agitation was twenty cycles per minute at which rate equilibrium was still maintained when no acid was present.

After most of this experimental work had been completed, a revised method for preparation of Raney catalyst was published by Pavlic and Adkins.[3] This method was reported to yield a catalyst of considerably greater activity than that prepared by the method of Mozingo.[2] During the course of this work, eight different preparations of catalyst had been made from the same alloy. For each of these, the rate constant for the hydrogenation of *d*-limonene with no additive was within five per cent. of the figure 1.93×10^{-4} liter min.$^{-1}$ g.$^{-1}$ when the catalyst was freshly prepared. Unfortunately all of this alloy was exhausted; therefore, alloy from a different batch was used to prepare catalyst by the new method. The rate constant for the hydrogenation of *d*-limonene on the resulting catalyst was 38.7×10^{-4} liter min.$^{-1}$ g.$^{-1}$, thus indicating considerably increased activity. However, when catalyst was later prepared by Mozingo's method from the new batch of alloy, the activity was found to be essentially the same as that prepared by the method of Pavlic and Adkins.

TABLE II

ACTIVATION ENERGIES FOR THE HYDROGENATION OF SEVERAL TERPENES ON RANEY NICKEL CATALYSTS

Terpene hydrogenated	Activation energy, cal./mole With palmitic acid[a]	With no additive
d-Limonene[b]	6600	12,400
d-Limonene[c]	6000	5,600
Camphene[b]	8900	17,500
β-Pinene[b]	5600	8,500
Terpinolene[b]	10,900	12,900

[a] 0.0004 mole of palmitic acid added per gram of nickel. [b] Standard nickel catalyst prepared by the method of Mozingo, ref. 2. [c] Nickel catalyst prepared by the method of Pavlic and Adkins, ref. 3.

Whatever the cause for increased catalytic activity may have been, a few studies were made to find the influence of additives on the activity of this nickel. The results, shown in Table III, indicate that the activity of the catalyst in the presence of the additives tested is the same regardless of the original activity of the catalyst. In the case of the more active nickel, the result is a retardation rather than an acceleration. Again, this indicates that the influence of the additive is not simply that of a wetting agent, since this would result in increased rates on either catalyst.

Figure 3 includes points indicating the effect of increasing amounts of palmitic acid on the rates of hydrogenation of *d*-limonene using the more active nickel as well as using the standard catalyst. It is interesting to note that the decelerating influence of the fatty acid is approximately proportional to the amount of acid added up to the amount necessary to cover the catalytic surface with a unimolecular film, after which the curve is essentially identical with that for the standard catalyst.

TABLE III

EFFECT OF ADDITIVES ON THE RATE OF HYDROGENATION OF *d*-LIMONENE USING NICKEL CATALYSTS OF DIFFERENT ACTIVITIES

Additive[a]	$k \times 10^4$ (liters min.$^{-1}$ g.$^{-1}$) Normal catalyst[b]	Active catalyst[c]
None	1.93	38.6
Palmitic acid	26.7	24.8
Tristearin	8.9	9.4
Laurylamine	9.6	9.8
Cetyldimethylethylammonium bromide	8.7	8.9
Sodium lauryl sulfate	8.2	10.7

[a] 0.0004 mole additive per gram of nickel. [b] Prepared by the method of Mozingo, ref. 2. [c] Prepared by the method of Pavlic and Adkins, ref. 3.

Acknowledgment.—The authors are indebted to the Hercules Powder Company for a fellowship which made this research possible.

Summary

The influence of certain additives on the rate of hydrogenation of some terpenes on Raney nickel catalyst has been investigated. It has been shown that the nickel is an active catalyst for hydrogenations under conditions such that the metallic surface appears to be covered with a unimolecular layer of adsorbed material which takes no apparent part in the reaction. Certain fatty acids, soaps, amines, amides, sulfated alcohols and quaternary ammonium salts all influence the catalytic action. It is shown that this is not simply a wetting action. Possible explanations of this phenomenon are discussed.

KNOXVILLE, TENN.

RECEIVED MAY 2, 1949