12, as compared with our rates of 8.7, 15 and 4.9, respectively.

While the exact mechanism of chloromethylation of aromatic compounds is not known, and probably depends on the nature of the chloromethylation reagent which is employed, it can be safely assumed that the chloromethylation reaction falls into the broad class of substitution reactions brought about by electrophilic reagents.[6] Thus, the relative chloromethylation rates are in accord with those to be expected from the usual effect of substituent groups on the reactivity of the benzene ring in other substitution reactions involving an electrophilic reagent.

The initial slope of the curves depicting the change in ionic chlorine with time is directly related to the rate of chloromethylation; the actual shape of the curves, on the other hand, depends on the extent to which the competing reactions interfere with the principal chloromethylation process. Work is in progress to determine how the competing reactions are related to the chemical structure of the compound being chloromethylated. The effect of the competitive reactions on the shape of the chloromethylation curve is clearly demonstrated in the comparison of anisole and mesitylene (Fig. 2). Both compounds are very reactive in the principal chloromethylation reaction, but the initial chloromethylated product of anisole undergoes further reactions which restore ionic chlorine to the mixture. Since chloromethylmesitylene is capable of undergoing further substitution reactions[7] the lack of side-reactions in this case may be due to the relative inertness of chloromethylmesitylene as an aralkylating agent.

Acknowledgment.—The authors wish to express their appreciation to Mr. Joseph Anzenberger for his technical assistance in several of the experiments, and to Drs. T. H. Dunkelberger and O. Gawron for their interest in this work and helpful suggestions. Dr. Gawron originally suggested the kinetic approach to the chloromethylation study of diphenyl sulfide.

Summary

The relative chloromethylation rates of twelve aromatic compounds have been determined. The relative rates of six compounds have been critically compared with those previously reported, and the discrepancies between the new and old rates have been explained. The relative order of the chloromethylation rates was found to be in general agreement with that expected from the effect of the substituent on the substitution reactions of benzene involving an electrophilic reagent.

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[6] Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 90.

[7] Excellent yields of the dichloromethylated mesitylene can be obtained (ref. 3, p. 76).

PITTSBURGH 10, PENNSYLVANIA RECEIVED MAY 23, 1949

[CONTRIBUTION NO. 62 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Catalytic Hydrogenation of Terpenes

BY HILTON A. SMITH, JOHN F. FUZEK AND HENRY T. MERIWETHER

Introduction

While a number of studies dealing with the catalytic hydrogenation of terpenes have been reported, few investigations have been concerned with the kinetics of this process. Furthermore, much of the work has been done with mixtures of terpenes, rather than with pure compounds. The present work was undertaken in order to study the kinetics of the catalytic hydrogenation of certain terpenes which could be obtained in a reasonably pure state.

Experimental

Dipentene, terpinolene, α- and β-pinenes and camphene were all furnished in relatively pure form by the Hercules Powder Company of Wilmington, Delaware. Four of these terpenes were fractionated before use through an eight-foot Vigreux column in an atmosphere of carbon dioxide. The other, β-pinene, was fractionated in the same column under vacuum. Constant boiling cuts were obtained for each material. *d*-Limonene was purchased from the Eastman Kodak Company, and carefully fractionated in an atmosphere of carbon dioxide. The constant boiling fraction used had an optical rotation $\alpha^{20}\text{D}$ of 104°. Head temperatures and refractive indices of the terpenes used are given in Table I.

Tank hydrogen[1] was used without further purification. Methanol and acetic acid, which were used as solvents, were prepared by fractionation of du Pont methanol or C. P. glacial acetic acid in a five-foot helix-packed still. Sodium oleate and palmitic acid were Merck U.S.P. and Eastman Kodak Co. best grade materials, and were used without further purification. The nickel catalyst was prepared from Raney alloy and the platinum catalyst from platinic chloride in the standard manner.[2,3] The nickel was stored under ethanol.

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[1] Purchased from the National Cylinder Gas Co. of Chattanooga, Tenn.

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

[3] Adams, Voorhees and Shriner, "Organic Syntheses," Coll. Vol. I, 463 (1944).

TABLE I

PROPERTIES OF THE TERPENES AND HYDROGENATED PRODUCTS CONSIDERED IN THIS INVESTIGATION

Compound	B. p., °C.	Mm.	n^{20}D
Diphentene	176.9	745	1.4729
d-Limonene	176.9	745	1.4729[a]
α-Pinene	155.3	740	1.4659
β-Pinene	166.1	744	1.4758
Terpinolene	102.5	50	1.4898
	119.2	95	
Camphene	91.5	100[b]	
d-Carvomenthene (from *d*-limonene)	179.0	737	1.4572[c]
p-Menthane (from dipentane or terpinolene)	168.0	745	1.4395
Pinane (from α-pinene)	166.0	745	1.4624
Pinane (from β-pinene)	165.7	735	1.4625
iso-Camphane (from camphene)	166.5	740[d]	....
p-Menthene-3 (from terpinolene)	169.0	745	1.4501
	85.0	50	

[a] α^{20}D 104°. [b] M. p. 48.7°. [c] α^{20}D 96°. [d] M. p. 63.5°.

High pressure hydrogenation experiments were carried out in bombs of 45-ml. capacity. These were constructed according to the directions of Adkins.[4] They were equipped with gages of 0–1000 p. s. i. range in 10 p. s. i. subdivisions, or of 0–2000 p. s. i. range in 20 p. s. i. subdivisions. Room temperatures were used except for camphene where the bomb was heated to 65° so as to have the terpene in the liquid state.

For most of the rate work a conventional shaker was used. This shaker completed 42 cycles per minute through an angle of 30° per stroke. For experiments with varying shaking speeds, a similar shaker was constructed having a Mixmaster motor for driving power. With this instrument, any shaking speed between 20 and 70 cycles per minute could be obtained. The shakers were equipped with conventional heating jackets.

In making rate studies, the nickel catalyst was placed in the hydrogenation bomb along with a small amount of the ethanol under which it was stored. This alcohol was removed by evaporation under vacuum. While the bomb was still under vacuum, the terpene was admitted in such a way that it covered the catalyst before any air entered the bomb. The bomb was then sealed, hydrogen admitted to the desired pressure, and the reaction started by shaking the bomb.

After the hydrogenation, the bomb was opened and the contents transferred to a beaker. Any catalyst remaining in the bomb was washed out by acetone. The catalyst was then filtered from the liquid and from the washings in an atmosphere of carbon dioxide, dried in a vacuum desiccator and weighed under carbon dioxide.

Low pressure hydrogenations using either nickel or platinum catalysts were carried out in a standard Parr low-pressure catalytic reduction apparatus. Platinum catalyst was weighed as platinic oxide before use. The nickel catalyst was weighed after each run in the same manner as that described for high-pressure experiments.

Reaction Mechanisms

α-Pinene, β-pinene and camphene each absorbed one mole of hydrogen per mole of terpene to form pinane from the pinenes, and isocamphane from the camphene. Each of these products distilled through an efficient fractionating column at a constant head temperature. Their physical constants are given in Table I.

Dipentene and terpinolene each absorbed two moles of hydrogen per mole of terpene. The hydrogenation of one double bond proceeds quite readily. That of the second bond takes place more slowly. The dipentene hydrogenation proceeded first to carvomenthene and then to *p*-menthane. This was shown by use of the optically active isomer of dipentene, *d*-limonene. If the hydrogenation proceeds by the path *d*-limonene → dihydrodipentene → *p*-menthane, the absorption of one mole of hydrogen will lead to an optically inactive product. If the hydrogenation proceeds by the path *d*-limonene→carvomenthene →*p*-menthane, the absorption of one mole of hydrogen will form carvomenthene, the asymmetric carbon will not be affected, and the intermediate product, *d*-carvomenthene, should have an optical activity comparable to that of the unhydrogenated material. If both bonds are saturated simultaneously, the activity of the half-hydrogenated material should be one-half of that of the starting terpene. Figure 1 indicates that the product formed by the absorption of one mole of hydrogen per mole of terpene is definitely *d*-carvomenthene.[5]

When one equivalent of hydrogen is absorbed by terpinolene, the product would presumably be either carvomenthene or dihydroterpinolene. The half-hydrogenated terpinolene contains no carvomenthene, and it appears that the product is actually an equimolecular mixture of two *p*-menthenes. This mixture was separated by fractionation in an eight foot Vigreux column. The lower-boiling fraction was identified as 3-*p*-menthene by its physical properties, and by the formation of its nitroso derivative. The higher boiling fraction was not positively identified. It forms a low-melting solid nitroso derivative, and its physical properties conform more closely to those published for 2-*p*-menthene than for any other known *p*-menthene. A summary of such data is given in Table II. Apparently the 1,2 bond in terpinolene is first saturated, and the 4-8 bond shifts, partly to the 3-4 position, and partly in some other manner.

The mechanisms for the hydrogenation of both dipentene and terpinolene were the same whether the catalyst was platinum or nickel, whether or not

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(4) Adkins, "Reactions of Hydrogen," The University of Wisconsin Press, Madison, Wisconsin, 1937, pp. 29–45.

(5) *Cf.* Vavon, *Compt. rend.*, **152**, 1675 (1911); **158**, 409 (1914).

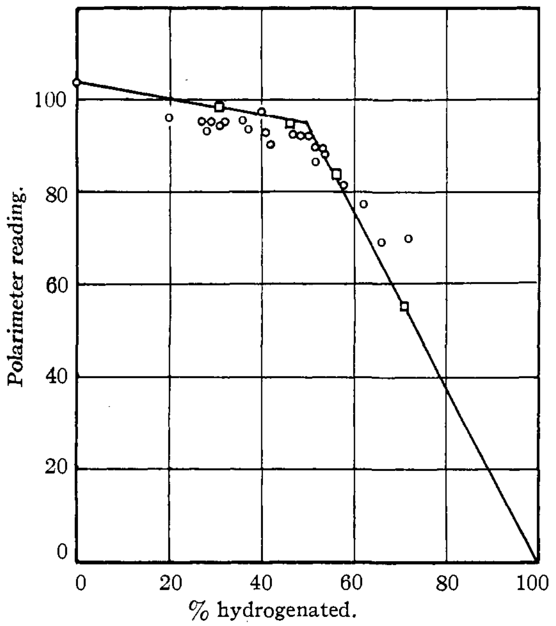

Fig. 1.—Per cent. hydrogenation of *d*-limonene on Raney nickel catalyst as a function of optical rotation ($\alpha^{20}D$ in 10-cm. tube): ○, hydrogenation at high pressures; □, hydrogenation at low pressures.

a solvent was present, and whether low or high hydrogen pressures were used. However, when nickel was used as a catalyst (with methanol as a solvent at low pressures, or with no solvent at high pressures) the hydrogenations of dipentene and terpinolene virtually ceased after one mole of hydrogen had been absorbed per mole of terpene.

TABLE II

PROPERTIES OF THE *p*-MENTHENES

Compound	$n^{20}D$	B. p., °C.	M. p. of nitrosochloride derivative, °C.
1-*p*-Methene[a] (carvomenthene)	1.4563	177	95–96
2-*p*-Menthene[a]	1.461	56 (12 mm.)	.....
3-*p*-Menthene[b]	1.4532	168.0	127
Dihydroterpinolene[a]	1.4568	174	101–103
Dihydrodipentene[a]	1.4523	170	.....
Fractions of the one-half hydrogenated terpinolene			
Fraction 1	1.4501	169 85 (50 mm.)	122–123
Fraction 2	1.4640	177 92 (50 mm.) 58 (12 mm.)[c]	22–23

[a] I. M. Heilbron, "Dictionary of Organic Compounds," Vols. I-III, Oxford University Press, London, 1934. [b] J. Zelikow, *Ber.*, **37**, 1374 (1904). [c] This value was obtained by extrapolation from a plot of log *p* *versus* 1/*T*.

Experimental Calculations and Results

Preliminary experiments indicated that the high pressure hydrogenation reactions were independent of the amount of terpene used, and that the low pressure hydrogenations did not depend on the concentration of the hydrogen acceptor. They also showed that, for all of the reactions studied, the rate was directly proportional to the pressure of hydrogen gas, and also directly proportional to the weight of catalyst used, provided shaking equilibrium was maintained. This was true whether the hydrogenation was carried out without solvent, with methanol or acetic acid as solvent, or in the presence of certain additives. The latter are such materials as fatty acids and soaps, which greatly influenced the rate of reduction. This being true, a plot of log p_0/p against time should result in a straight line.

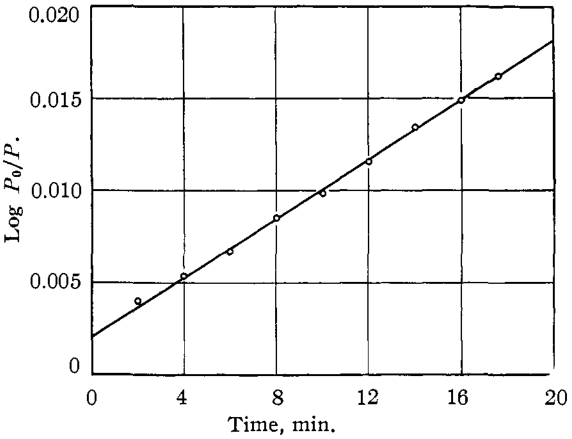

Fig. 2.—Sample hydrogenation curve for *d*-limonene on Raney nickel catalyst.

Figure 2 gives such a plot for the high pressure hydrogenation of *d*-limonene on nickel while Figs. 3 and 4 show similar plots for low pressure hydrogenations using Adams platinum catalyst and acetic acid or methanol as solvents. Since straight lines are obtained, rate constants for these hydrogenations can be calculated from the equation

$$\log p^0/p = kt/2.303\ V$$

where p is the pressure at any time t, p^0 is the initial pressure, V is the volume of the system, and k is the reaction rate constant.[6] Since k is directly proportional to the amount of catalyst used, it is divided by the weight of catalyst to give a k which represents the rate constant referred to one gram of catalyst.

Figure 5 demonstrates the necessity of maintaining shaking equilibrium. In all high pressure experiments for which rate constants are reported here, the shaking speed was maintained at 42 cycles per minute for catalyst weights of 0.3 to 0.5 g. The rate of shaking for the low pressure experiments was 180 cycles per minute, which was shown to be fast enough to maintain equilibrium conditions.

[6] Fuzek and Smith, THIS JOURNAL, **70**, 3743 (1948).

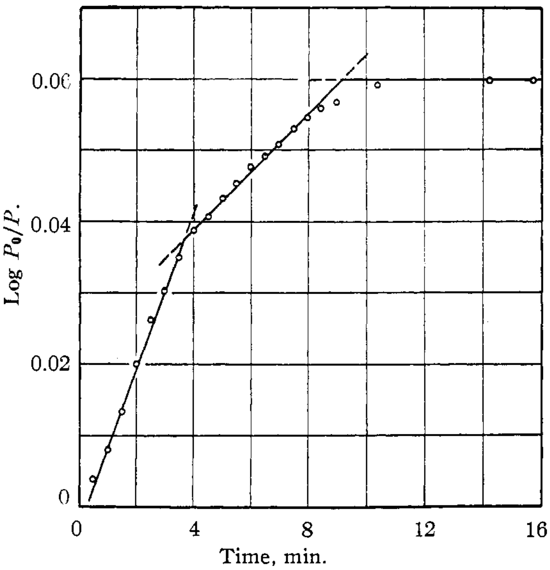

Fig. 3.—Sample hydrogenation curve for dipentene on Adams platinum catalyst in acetic acid at 64.3 p. s. i. a., *t*, 25°.

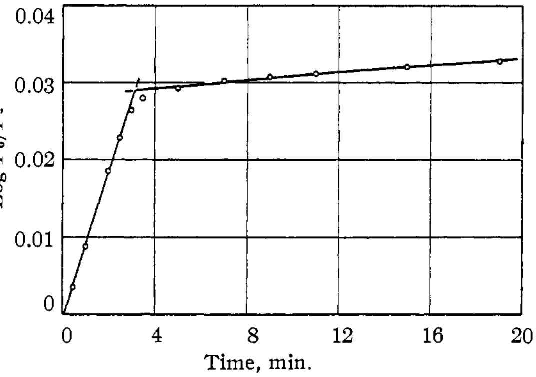

Fig. 4.—Sample hydrogenation curve for *d*-limonene on Adams platinum catalyst in ethanol at 64.2 p. s. i. a., *t*, 28°.

Tables III and IV show that the rate constants calculated from such plots are constant over a wide range of conditions. Table V gives the rate constants for the terpenes studied when they are hydrogenated over Raney nickel or Adams platinum catalyst. For the monocyclic terpenes, the rate constants are for the hydrogenation of the first bond only. Hydrogenation of the second bond over nickel is negligible under the experimental conditions employed.

TABLE III

INFLUENCE OF THE AMOUNT OF *d*-LIMONENE ON ITS RATE OF HYDROGENATION ON NICKEL AT 100 P. S. I. PRESSURE AND AT ROOM TEMPERATURE

Moles *d*-limonene used	$k \times 10^4$ (liters min.$^{-1}$ g.$^{-1}$) No solvent or additive	With 0.0004 mole palmitic acid per g. of catalyst	With 10 ml. methanol as solvent
0.025	1.93	31.2	123.5
.050	1.84	32.2	127.0
.075	1.84	32.6	127.3
.100	1.93	33.1	126.8

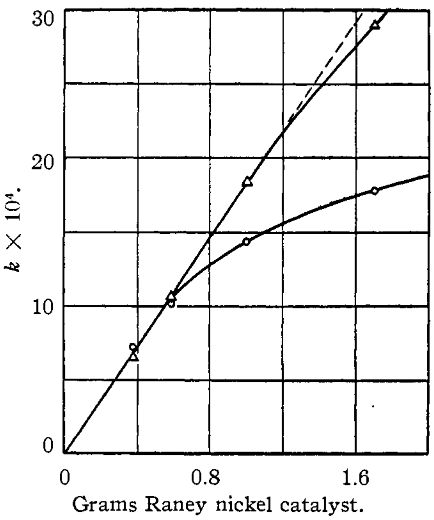

Fig. 5.—Hydrogenation of *d*-limonene on Raney nickel with 0.100 g. of sodium oleate: shaking speed, (⊙), 41 cycles/min.; (△), 96 cycles/min.

TABLE IV

INFLUENCE OF PRESSURE ON THE RATE OF HYDROGENATION OF *d*-LIMONENE ON NICKEL USING 0.05 MOLE OF TERPENE AT ROOM TEMPERATURE

Initial pressure, p. s. i.	$k \times 10^4$ (liters min.$^{-1}$ g.$^{-1}$) No solvent or additive	With 0.0004 mole palmitic acid per g. of catalyst	With 10 ml. methanol as solvent
300	1.93	..	127.9
360	..	32.6	..
945	1.84	..	..
980	1.93	..	126.8
1100	..	31.3	..
1720	1.84	30.4	128.9

TABLE V

RATE CONSTANTS FOR HYDROGENATION OF TERPENES AT ROOM TEMPERATURE

Terpene	Rate constant (liters min.$^{-1}$ g.$^{-1}$) On platinum with 50 ml. acetic acid solvent and 64 p. s. i. hydrogen pressure k	On nickel with no solvent and 100 p. s. i. hydrogen pressure $k \times 10^4$	On nickel with 0.0004 mole palmitic acid per g. nickel and 1000 p. s. i. hydrogen $k \times 10^4$
d-Limonene[a]	5.7	1.84	29.4
Dipentene[a]	5.7	1.84	29.4
Terpinolene[a]	1.3	1.47	6.1
Camphene	8.8	1.93[b]	12.7[b]
α-Pinene	2.7	1.10	0.9
β-Pinene	4.3	1.01	9.1

[a] For hydrogenation to the *p*-menthene only. [b] These runs were made at 65°.

Discussion

Not very much can be said concerning the effect of the structure of the terpene on its rate of hydrogenation, other than the fact that in general those containing an exocyclic double bond undergo hydrogenation more readily than do those where all of the unsaturation is in the ring. Whether or not the terpene is monocyclic or bicyclic appears to be unimportant since there is no apparent difference in the rates of hydrogenation of the *p*-menthadienes, dipentene and terpinolene, when compared with the pinenes and camphene which are bicyclic terpenes.

It is interesting to note that the *p*-menthadienes undergo hydrogenation on either platinum or nickel more readily than do the *p*-menthenes, since it has already been shown that cyclohexene adds hydrogen much more quickly than does either the conjugated or unconjugated cyclohexadiene.[7] In this connection it would be interesting to study one of the *p*-menthadienes which has both double bonds in the ring.

As would be expected, the rates of hydrogenation of dipentene and the optically active *d*-limonene are identical in all cases.

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

Summary

Dipentene, *d*-limonene, terpinolene, α- and β-pinenes and camphene have been hydrogenated over Adams platinum or Raney nickel catalyst, and the results subjected to kinetic analysis. It has been shown that carvomenthene is an intermediate in the hydrogenation of dipentene or *d*-limonene, while terpinolene yields a mixture of 3-*p*-menthene and another *p*-menthene (perhaps 2-*p*-menthene) as intermediates. The factors influencing the rates of hydrogenation of these terpenes have been discussed.

KNOXVILLE, TENNESSEE RECEIVED APRIL 25, 1949

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[7] Smith and Meriwether, THIS JOURNAL, **71**, 413 (1949).

[CONTRIBUTION NO. 64 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Preparation and Aging of Raney Nickel Catalysts

BY HILTON A. SMITH, WILLIAM C. BEDOIT, JR., AND JOHN F. FUZEK

Several different methods for the preparation of Raney nickel catalyst from the standard alloy have been described. Mozingo[1] describes a preparation from the nickel–aluminum alloy according to which the aluminum is dissolved in sodium hydroxide leaving the active catalyst. It is stated that the temperature during the reaction should not rise above 25°. The catalyst is then digested on a hot-plate for twelve hours, and washed by decantation. Pavlic and Adkins[2] have indicated a revision of this method, according to which the alloy is treated with caustic at 50°, and washing is accomplished by a continuous process. The catalyst is claimed to be much more active than that prepared by the method of Mozingo. In a still more recent paper, Adkins and Billica[3] described a further modification in which the washing process was carried out under about 1.5 atmospheres hydrogen pressure. This catalyst (designated as W-6) is described as the most active catalyst known to the authors.

In connection with Mozingo's preparation, it is stated that the catalyst may lose much of its activity if it is kept too long. The purpose of the research reported here was to study the activity of various Raney nickel catalysts, considering both their method of preparation and the length of time which they had been kept.

Experimental

Raney nickel catalyst was prepared by the methods of Mozingo,[1] Pavlic and Adkins[2] and Adkins and Billica.[3] Special care was taken to follow the directions explicitly as given by the authors. In addition, several modifications were introduced. The alloy was taken from a single drum of commercial product furnished by Mr. Raney of the Gilman Paint and Varnish Company, Chattanooga, Tennessee.[4]

The activity of the catalyst was determined by measuring the rate of hydrogenation of freshly distilled *d*-limonene at a hydrogen pressure of 1000 p. s. i. by the method previously described.[5] The latter material was prepared by fractionation under carbon dioxide of Eastman Kodak Co. technical grade product. In addition, the surface areas of a number of these preparations were measured by the adsorption of palmitic acid from benzene solution as previously described.[6]

Experimental Calculations and Results

The rate of hydrogenation of the *d*-limonene has been shown to follow the equation

$$\log p_0/p = k't/2.303\ V$$

where p is the hydrogen pressure at any time, t, p_0 is the initial pressure, V is the volume of hydrogen gas in the system, *i.e.*, the total void which is constant for any system, and k' is the reaction rate constant.[5] (By dividing the value of k' by the weight of catalyst employed rate constants (k) referred to one gram of catalyst

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[1] Mozingo, *Org. Syntheses*, **21**, 15 (1941).

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

[3] Adkins and Billica, *ibid.*, **70**, 695 (1948).

[4] According to Mr. Raney, this alloy had the following analysis: Ni, 51.06; Al, 48.19; Si, Fe, and Cu combined, 0.75. It was further stated that these latter three elements have percentages approximately as follows: Fe, 0.5; Si, 0.15; and Cu, 0.1.

[5] Smith, Fuzek and Meriwether, *ibid.*, **71**, 3765 (1949).

[6] Smith and Fuzek, *ibid.*, **68**, 229 (1946).