constant for the decomposition of free carbamic acid was about 80 at 0°, thus corresponding to a half-life of about 0.009 sec. The ionization constant of the carboxyl group was calculated roughly by the method used above for K_1 and found to be about 1.8×10^{-6} at 0°. No indication was found either of combination of a second H^+ ion with the $-NH_2$ group in very acid solution, or of zwitterion formation by the NH_2COOH molecule like that found in glycine or other amino acids. Further discussion must be postponed until fuller data are available, but owing to present conditions the writer will be unable to undertake such work for some time.

Summary

The rate of heat evolution when hydrochloric acid is mixed with sodium bicarbonate has been studied by the thermal method of measuring the velocity of rapid chemical reactions. The heat was found to be evolved in two stages, of which the first was practically instantaneous, being due to the combination of H^+ and HCO_3^- ions to form H_2CO_3, whereas the second slower stage lasting up to one second was due to the dissociation of H_2CO_3 into CO_2 and H_2O.

The data gave values for the dissociation velocity constant of H_2CO_3, and for the separate heats of the two reactions over the range 0–40° instead of the *sum* of the two heats as hitherto measured by the ordinary calorimetric methods. The heat of the reaction $H^+ + HCO_3^-$ was found to vary with temperature in the manner characteristic of weak acids, as studied by Harned.

The "true" first ionization constant of carbonic acid was calculated independently from the present data and checked fairly well with certain previous values.

Preliminary measurements were also made of the rate of dissociation of free carbamic acid, and of the ionization constant of its carboxyl group.

CAMBRIDGE, ENG. RECEIVED AUGUST 6, 1941

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

Alkali and Alkaline Earth Metals as Catalysts in the Hydrogenation of Organic Compounds

BY F. W. BERGSTROM AND JOHN F. CARSON

Hugel and Friess[1] and Hugel and Gidaley[2] have hydrogenated a number of organic compounds with sodium hydride and high pressure hydrogen. Thus, stilbene and 1,4-diphenylbutadiene were hydrogenated to dibenzyl and 1,4-diphenylbutane, respectively, while anthracene was hydrogenated successively to 9,10-dihydroanthracene, 1,2,3,4-tetrahydroanthracene and finally to octahydroanthracene.

As a result of this work, Hugel and Gidaley[2] showed that only those compounds capable of adding sodium metal could be reduced by sodium hydride and hydrogen. This suggests several possibilities for the mechanism of the reaction. The sodium hydride may dissociate reversibly into sodium and hydrogen, the former may add to the double bond and then be split off and replaced by hydrogen by a process that has been termed hydrogenolysis.[3] The sodium hydride may itself add to the double bond, the sodium then being replaced as above by hydrogen or, finally, the sodium hydride may simply act as a contact catalyst in the usual sense.

In the present work we have attempted to answer the question of the mechanism of this reaction by reducing organic compounds with high pressure hydrogen in the presence of alkali metals as catalysts. In order to see whether the alkali metals are specific catalysts for the reaction, we also have examined the activity of calcium.

Experimental

All hydrogenations were carried out in a high pressure rocking autoclave manufactured by the American Instrument Company. A stainless steel liner was used, the capacity of the bomb containing the liner being about 950 cc. In general, the initial hydrogen pressures were from 1000 to 2000 lb./sq. in. and the temperatures varied between 130 and 270°. Below 200° the catalysts were relatively inactive, except toward pyridine. Sodium, potassium and lithium, of the highest commercial purity, were cut and weighed under benzene before being transferred to the bomb. Calcium was activated by two methods: (1) the metal was pulverized under benzene in a stainless steel ball mill with stainless steel balls. This treatment produces a

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(1) Hugel and Friess, *Bull. soc. chim.*, **49**, 1042 (1931).

(2) Hugel and Gidaley, *ibid.*, **51**, 639-644 (1932).

(3) Gilman, "Organic Chemistry," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 416.

Table I

Hydrogenations with Alkali Metals or Calcium as Catalyst

Compound (moles)	Catalyst, g.	Temp., °C.	Time of hydrogenation, hr.	Product (%)
Naphthalene (0.55)	Na, 3	172–215	7.5	Tetrahydronaphthalene (40)
Naphthalene (1)	Li, 5	250–300	33	Tetralin (2)
Naphthalene (0.55)	Ca,[d] 10	250–265	11	Tetralin (56)
Anthracene (1)	Na, 10	230–254	1	9,10-Dihydroanthracene (yield not detd.)
9,10-Dihydroanthracene (0.33)	Na, 6	260–280	21	Octahydroanthracene
Stilbene[a] (0.083)	Na, 3	230–260	8.5	Diphenylethane (59)
Stilbene (0.061)	Ca,[c] 4	220–270	8	Diphenylethane (67)
Diphenylbutadiene (0.15)	Na, 3	220–250	11	Diphenylbutane (16)
Pyridine (1.25)	Na, 6	130–150	4.5	Piperidine[e] (30)
Pyridine (1.25)	Na, 1.5	137–147	4	Piperidine (17)
Pyridine (1.25)	K, 6	145–170	3.5	Piperidine[e] (30)
Pyridine (2.5)	Li, 6	200–220	3	Piperidine (7)
Pyridine (1.25)	Ca,[d] 7	140–170	11	Piperidine (5)
Pyridine (1.25)	Ca,[c] 5	205–250	14	Piperidine (18)
Quinoline (1)	Na, 5	180–204	3.7	Tar
Quinoline (0.5)	Ca,[c] 10	230–260	6	Tetrahydroquinoline (34)
Sodium cinnamate[b] (0.35)	Ca,[d] 10	260–280	30	Dihydrocinnamic acid less than 10%

[a] Hydrogenation carried out in benzene. [b] Hydrogenation carried out in toluene suspension. [c] Calcium metal pulverized in a steel ball mill under benzene. [d] Calcium metal precipitated by adding its liquid ammonia solution to toluene. [e] No dipyridyls or hydrogenated dipyridyls were isolated.

fine suspension of calcium, which was introduced directly into the bomb. (2) A solution of the metal in liquid ammonia was poured slowly into a large volume of toluene. The ammonia boiled off, leaving a very spongy porous metal suspended in the toluene. Catalysts prepared by both methods showed approximately the same activity in the hydrogenation of naphthalene.

To determine if the walls of the liner exerted a catalytic effect, a blank experiment was made with naphthalene alone. One-half mole of naphthalene was subjected to a pressure of 3200 lb./sq. in. of hydrogen at 225–250° for ten hours with no observable pressure drop. The product was unaltered naphthalene.

With the exception of the reactions carried out in benzene or toluene, no solvents were used. In one case (anthracene hydrogenation) the reaction product was removed from the liner by repeated extractions with ethanol; otherwise, water was cautiously added to destroy metallic salts and the water-insoluble liquid was distilled *in vacuo.* The highly colored (blue, red or bluish-green) mixture resulting from the hydrogenation of pyridine was treated with water and distilled at atmospheric pressure. The water solution of the mixture from the hydrolysis of sodium cinnamate was acidified and the slowly solidifying oil crystallized from ligroin to give hydrocinnamic acid.

Identification

All reaction products were identified by physical characteristics (m. p., b. p.) as well as by the following.[4]

Tetrahydronaphthalene.—Refractive index, $n^{18}\text{D}$ 1.5480, literature $n^{20}\text{D}$ 1.5461. Bromine did not react with the product in the cold, showing absence of dihydronaphthalenes.

Hydrogenated Anthracenes.—9,10-Dihydroanthracene was identified by mixed m. p. with authentic material prepared by reducing anthracene with sodium and amyl alcohol.

Anal. Calcd. for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 92.96; H, 6.97.

Further hydrogenation produced **octahydroanthracene,** m. p. 70.5–71° (cryst. from methanol).

Tetrahydroquinoline.—Benzenesulfonyl derivative, m. p. 64–65°; nitro-nitroso derivative, m. p. 145–146.5°.

Piperidine.—Benzenesulfonyl derivative, m. p. 90.5–91.5°; hydrochloride, m. p. 239–240°.

Discussion

Hydrogenation of organic compounds with sodium as a catalyst generally occurred at temperatures between 170 and 250°; pyridine alone of the substances studied was reduced at a lower temperature. Lithium was a relatively poor catalyst for the hydrogenation of naphthalene and it seems possible that the tetralin obtained may have been formed by hydrolysis of an intermediate addition product of naphthalene and the metal. It will be noted that all of the substances hydrogenated have been shown by Schlenk and Bergmann to be capable of adding the alkali metals.[5] Compounds to which alkali metals do not add—hexene, dipentene and benzene—cannot be catalytically hydrogenated in this manner.

Finely divided calcium in most cases parallels the action of sodium as a catalyst, though in general less tar and resin are formed than with the latter. Hydrogen does not reduce benzene in the presence of calcium, which therefore shows the

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(4) Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y.

(5) Schlenk and Bergmann, *Ann.*, **463**, 1 (1928).

same selective activity toward double bonds activated by phenyl groups as does sodium. Any mechanism to account for the activity of the alkali metals will possibly have to be extended to calcium.

Some of the hydrogenation observed when sodium is used as a catalyst is due to hydrogenolysis of the product of addition of sodium to a double bond, since sodium hydride was obtained in some of these reactions, and not in appreciable quantities by heating metallic sodium alone with high pressure hydrogen under the same conditions.[6]

Some of the hydrogenation must be due to specific catalytic activity of the sodium hydride, as observed in experiments of Hugel and co-workers.[1,2] The assumption could be made that sodium hydride adds to the double bond, and is then regenerated by hydrogenolysis, leaving a reduced organic compound. Certainly this cannot always be true, since metallic calcium is comparable with sodium as a catalyst and yet both calcium hydride and metallic calcium should add to a double bond much less readily than sodium hydride or sodium.

Summary

1. A number of organic compounds have been hydrogenated with high pressure hydrogen at 130–260°, in the presence of lithium, sodium, potassium or calcium metals as catalysts.

2. The only substances so far found that can be hydrogenated are those to which the alkali metals add. This suggests a connection with the work of Hugel and co-workers[1,2] who found that sodium hydride similarly catalyzes the hydrogenation of unsaturated compounds which form sodium addition products.

3. The mechanism of the hydrogenations is discussed.

STANFORD UNIVERSITY, CALIFORNIA

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(6) McCurdy, unpublished observations, Stanford University, 1941. Hugel and Friess claim to have prepared sodium hydride by heating sodium with high pressure hydrogen at 235–425°, but McCurdy was unable to duplicate their results at temperatures of 200–300° and pressures up to 2000 lb./sq. in. (no absorption of hydrogen), with the use of the apparatus of the present article. Some unknown catalyst must have influenced the work of Hugel and Friess.

[CONTRIBUTION FROM THE INSTITUTE OF MATERIA MEDICA, SHANGHAI, CHINA]

The Preparation and Properties of Peimine and Peiminine

BY T. Q. CHOU AND T. T. CHU

In 1932, one of us(1) reported the isolation from the Chinese drug, Pei-Mu, identified as *Fritillaria Roylei*, two alkaloids, peimine and peiminine, to which the formulas $C_{19}H_{30}O_2N$ and $C_{18}H_{28}O_2N$, respectively, wereas signed. Peimine melted at 223°, being optically inactive, while peiminine had a melting point of 135° and a specific rotation of $[\alpha]^{24}_{D}$ $-62.5°$. Their pharmacological action was subsequently studied.(2) Chi, Kao and Chang(3) later assigned the formula $C_{26}H_{43}O_3N$ to both peimine and peiminine and the melting point of the latter was stated by them to be indefinite, sintering at 140°, melting at 147–148°, resolidifying at 157° and finally melting at 212–213°, whereas a specimen of peiminine dried at 110° in a vacuum melted directly at 212–213°. More recently Li(4) confirmed, however, the formula $C_{19}H_{30}O_2N$ for peimine and gave the melting point of peiminine as 130–133°. This discrepancy led us to reinvestigate these two alkaloids with the object of establishing more conclusively their composition and properties and at the same time working out a practical process for their isolation.

The present analytical data indicate that the composition of peimine agrees well with the formula $C_{26}H_{43}O_3N$ assigned to it by Chi, instead of $C_{19}H_{30}O_2N$ which resulted from an error in its nitrogen determination; but that of peiminine is better represented by $C_{26}H_{41}O_3N$, differing from peimine by two atoms of hydrogen. This is substantiated by the fact that peimine and peiminine are convertible into each other by oxidation in one case and reduction in the other, details of which will be described later in a separate paper. The indefinite nature of the melting point of peiminine as observed by Chi can be attributed to its water of crystallization. When freshly prepared and air-dried, peiminine melts at 135–137° to a clear liquid, no change taking place on further heating to about 200°; on drying at 110°

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(1) Chou, *Chin. J. Physiol.*, **6**, 265 (1932).

(2) Chen, Chen and Chou, *J. Am. Pharm. Assoc.*, **22**, 638 (1933).

(3) Chi, Kao and Chang, THIS JOURNAL, **58**, 1306 (1936); **62**, 2896 (1940).

(4) Li *J. Chin. Pharm. Assoc.*, **2**, 235 (1940).