solution is made acid or alkaline could occur simultaneously at many points along their length, and the corresponding decrease in solution viscosity would be rapid. On the other hand, recoupling of the chain fragments after neutralization of the solution would be dependent upon a suitable orientation (end to end) of the reacting units, and therefore probably would be a slow process compared to the previous degradation of the chain molecules. The rise in solution viscosity would be correspondingly slow.

The behavior of the neutralized solutions in the ultracentrifuge can be explained by the presence of the very long molecules formed through repolymerization. Although not originally present in very large numbers, these long molecules would be concentrated by sedimentation. They would then tend to bind one another into a network with some of the properties of a gel, which would produce the artificial sharpening of sedimentation diagrams and progressively decreasing sedimentation rates which were observed.

The sensitivity of the sodium thymonucleate molecules to *p*H changes from neutrality, even at room temperature, emphasizes the necessity for extreme care in the extraction of nucleic acids from their natural sources. Methods of isolation which involve the use of acids or bases, particularly at elevated temperatures, cannot be expected to yield products whose physical properties are useful guides to the nature of nucleic acids as they exist in the living cell. This point has been made before by others, but it cannot be too strongly emphasized, since some confusion exists in the literature because it has not always been considered.

Acknowledgment.—We wish to express our gratitude to the Wisconsin Alumni Research Foundation and to the University Research Committee for the financial assistance which has made these studies possible. We also wish to thank Dr. J. W. Williams for his counsel and help throughout this work.

Summary

Measurements have been made of the effect of *p*H changes on the viscosities of solutions of a high molecular weight sodium thymonucleate. The data suggest that this salt acts in neutral solution as a linear high polymer which is rapidly depolymerized to a considerable extent when the *p*H is changed to 2.6 or to 11.6. The effect is reversed when the acid and alkaline solutions are neutralized. The material then repolymerizes slowly. Sedimentation velocity and diffusion experiments show that both the degraded and the repolymerized nucleic acids have a wider distribution of molecular weights than the original substance and that some of the molecules in the repolymerized portion are much larger than those which were present in the original solution.

MADISON, WISCONSIN RECEIVED JUNE 11, 1943

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Catalytic Dehydrogenation. I. Catalytic Conversion of Alcohols into Aldehydes, Paraffins and Olefins

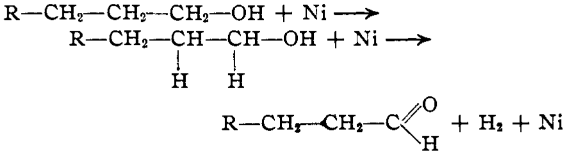
BY ELMER J. BADIN

The liquid-phase nickel-catalyzed conversion of representative members of the homologous series of primary aliphatic alcohols into the corresponding aldehyde, an unsaturated hydrocarbon of one less carbon atom and the saturated hydrocarbon of one less carbon atom has been studied. Although catalytic dehydrogenation to the aldehyde has been carried out by various investigators using different catalysts, especially in the vapor phase, further "deformylation" has not been completely studied. By deformylation is understood the splitting out of carbon monoxide and hydrogen from the aldehyde.

In view of the fact that hydrocarbons with an odd number of carbon atoms and higher paraffins containing more than eight carbon atoms are difficult to obtain or prepare by the usual chemical methods, catalytic dehydrogenation followed by deformylation and hydrogenation, occurring in one step without the use of pressure or an external source of hydrogen, affords an easy method of preparing these hydrocarbons. The reaction may be regarded as a preparative one for aldehydes and hydrocarbons.

The catalyst used in this series of experiments was Raney nickel and the reaction was carried out by heating the alcohol and catalyst in a reaction flask at atmospheric pressure and determining both the gaseous and liquid products. The effect of different reaction conditions was studied. Definite indications as to the course of the reaction have been obtained and will be discussed later. Since the reaction appears to consist essentially of dehydrogenation, deformylation and hydrogenation taking place in the order mentioned it may be formulated in consecutive steps.

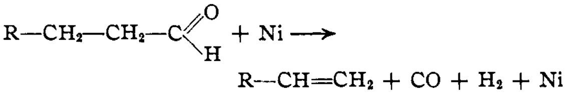
(1) Dehydrogenation of the alcohol to the aldehyde.



$$\mathrm{R{-}CH_2{-}CH_2{-}CH_2{-}OH + Ni \longrightarrow R{-}CH_2{-}\underset{H}{\underset{|}{CH}}{-}\underset{H}{\underset{|}{CH}}{-}OH + Ni \longrightarrow R{-}CH_2{-}CH_2{-}C\!\left\langle\begin{matrix}O\\H\end{matrix}\right. + H_2 + Ni}$$

The hypothetical intermediate has been written with one α-hydrogen as being involved in the dehydrogenation. This mechanism* has been indicated for hydrogenation by Anderson and MacNaughton.[1]

(2) Deformylation of the aldehyde to the olefin.



$$\mathrm{R{-}CH_2{-}CH_2{-}C\!\left\langle\begin{matrix}O\\H\end{matrix}\right. + Ni \longrightarrow R{-}CH{=}CH_2 + CO + H_2 + Ni}$$

Although the double bond evidently rearranges to the β-position after its formation,[2,3] the product first formed is probably the α-unsaturated olefin. A study of this rearrangement has not been made in the present work.

(3) Hydrogenation of the olefin to the saturated hydrocarbon.

$$\mathrm{R{-}CH{=}CH_2 + H_2 + Ni \longrightarrow R{-}CH_2{-}CH_3 + Ni}$$

The hydrogen in this step is that formed in steps (1) and (2). Since carbon monoxide and hydrogen are formed as products of the reactions, they might be expected to react to produce methane. This actually occurred although to a very small extent and was assumed to proceed according to the equation

$$\mathrm{CO + 3H_2 + Ni \longrightarrow CH_4 + H_2O + Ni}$$

The main portion of the carbon monoxide and hydrogen, however, were evolved as such.

It is interesting to note that the over-all mechanism of the reaction as outlined above, especially with respect to the conversion to the saturated hydrocarbon, does not agree with that of Suen and Fan,[4] who state that heptaldehyde in the vapor phase in the presence of hydrogen and a nickel catalyst decomposes into hexane by first being reduced to the alcohol which then eliminates carbon monoxide and hydrogen and yields *n*-hexane. Böeseken and van Senden[5] have stated a mechanism for the vapor phase conversion of heptaldehyde to *n*-hexane with a nickel catalyst differing from that of Suen and Fan and agreeing with the present work. A possibility suggested by Böeseken and van Senden that the aldehyde is converted into the olefin by splitting out formaldehyde does not seem feasible; traces of formaldehyde, formed probably by reaction with H_2 and CO, were also found in the present work. Wojcik and Adkins,[6] using Raney nickel, have noted the pressure hydrogenolysis of alcohols to hydrocarbons with the formation of methane and water and without formation of any products other than hydrocarbons while Gault, Palfray and Tsu[7] have heated dodecanol with Raney nickel under pressure to yield undecane through the intermediate of the aldehyde. Paul[8] has dehydrogenated a series of alcohols with Raney nickel, finding that both condensation and decomposition of the aldehyde occurs. Halasz,[9] however, has dehydrogenated a series of alcohols including aliphatic alcohols in the liquid phase using Raney nickel without mentioning the formation of paraffins and olefins.

Hydrocarbons which were isolated in pure form, namely, *n*-heptane, *n*-octane, *n*-nonane, *n*-undecane and *n*-pentadecane were mixed with the corresponding unsaturated compound before purification. The aldehyde, similarly, was not separable from the unconverted alcohol by physical means. Since reversible hemiacetal formation is exothermic and occurs readily, undoubtedly a part of the aldehyde was present in this form. Ready separation of the aldehyde by either the 2,4-dinitrophenylhydrazine derivative or the bisulfite addition compound both reacting in acid media, the latter on hydrolysis giving the free aldehyde, would indicate that little condensation or polymerization of the aldehyde had taken place.

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* Other possibilities for the mechanism of dehydrogenation exist and are being investigated in this Laboratory.

[1] Anderson and MacNaughton, THIS JOURNAL, **64**, 1456–1459 (1942).

[2] Brooks and Humphrey, *ibid.*, **40**, 832 (1918).

[3] Suen and Fan, *ibid.*, **65**, 1244 (1943).

[4] Suen and Fan, *ibid.*, **64**, 1460–1462 (1942).

[5] Böeseken and van Senden, *Rec. trav. chim.*, **32**, 23 (1913).

[6] Wojcik and Adkins, THIS JOURNAL, **55**, 1293 (1933).

[7] Gault, Palfray and Tsu, *Compt. rend.*, **209**, 999–1000 (1939).

[8] Paul, *ibid.*, **208**, 1319–1321 (1939); *Bull. soc. chim.*, **8**, 507–519 (1941).

[9] Halasz, *Compt. rend.*, **209**, 1000–1002 (1939); *Ann. chim.*, **14**, 318–376 (1940).

Experimental

Apparatus.—The reactions were carried out in a glass-jointed apparatus consisting of a 500-ml. reaction flask and a small distillation column (30-cm. tall packed with porcelain saddles) connected to a water cooled condenser and a 500-ml. receiver. A short length of rubber tubing connected the receiver to a 200-ml. trap in a Dewar flask containing an eutectic mixture of dry-ice and acetone. The rate of gas evolution was measured by water displacement from a 500-ml. graduated tube over periods of from thirty to sixty seconds timed by a stop watch. The reaction flask was maintained at the proper temperature (±3°) by a Wood's metal bath in which the flask was immersed to above the level of the liquid in the flask. A calibrated thermometer was used to measure the reaction temperature.

Catalyst.—Raney nickel was prepared according to the directions of Covert and Adkins[10] and was stored under 99% isopropyl alcohol. It was weighed out and used in a moist condition; the moist catalyst as used contained 30% by weight of isopropyl alcohol.

Gas Analysis.—Preliminary tests on the gas evolved had shown that it was combustible, capable of reducing palladous chloride solution, not condensable in a dry-ice trap, and not absorbable in concentrated sulfuric acid. The gases were analyzed for carbon monoxide and hydrogen by passing them over cupric oxide at 300° and for methane by passing the carbon monoxide and hydrogen-free gas over cupric oxide at 550°. The percentages of free hydrogen and carbon monoxide were within ±1% while methane determinations were within ±3%. To obtain final figures for the amounts of each gas evolved, corrections were made for the amounts of nitrogen and oxygen originally present in the apparatus.

Aldehyde Determination.—The amount of aldehyde formed in each experiment was based on the yield of the corresponding 2,4-dinitrophenylhydrazone. A weighed sample (2 to 3 g.) was reacted with an excess of 2,4-dinitrophenylhydrazine in 3 *M* hydrochloric acid solution. The higher molecular weight compounds were dissolved in 50 to 100 ml. of 95% ethanol before reaction. Aldehyde determination by means of the bisulfite addition compound gave lower values.

Olefin Determination.—Olefins were determined by titration with bromine using the bromide–bromate method. A weighed sample (0.7 g.) was dissolved in 15 ml. of carbon tetrachloride and titrated in the usual manner at 15°.

Decanol-1.—The reaction flask containing 150.0 g. (0.947 mole) of decanol-1 (Paragon Testing Laboratories, redistilled, m. p. 3–5°) was placed in the bath and the temperature raised to 200°. The Raney nickel (7.5 g.) was added and the temperature quickly raised to 230° where it was maintained for a period of three hours. The volatile products distilled out as formed; very little aldehyde or decanol-1, however, was removed from the reaction flask by this distillation.

Curves for the rate of gas evolution and gas composition were obtained and, by graphical integration of the area under the experimental curves, a total volume of gas of 33.1 liters (S. T. P.) containing 0.75 mole of hydrogen, 0.48 mole of carbon monoxide, 0.13 mole of methane, and 0.12 mole of oxygen plus nitrogen was calculated. This corresponded to 1.14 moles of hydrogen and 0.61 mole of carbon monoxide as the primary gaseous reaction products.

After separating a 4.8-g. aqueous layer (consisting partly of water from the formation of methane and partly of the catalyst solvent), the material in the receiver was dried with anhydrous sodium sulfate and then distilled through a laboratory saddle-packed column. Similar experiments in which this material was distilled through a 12-plate column gave comparable results. After removal of the nickel by filtration, the material in the reaction flask was found to boil above 200°. The yields of organic products were thus, (I) 78.0 g., 98% of which had b. p. 144–149°; (II) 48.9 g. of boiling point above 200°. The 78.0-g. cut (I) consisted of a mixture of *n*-nonane and nonene and had the following properties: $n^{20}_{\rm D}$ 1.4122, d^{22}_{4} 0.721, negative test with Schiff reagent after one minute, deep orange red coloration produced when shaken with sulfuric acid in which it was partly soluble. Titration of this cut with bromine gave a value of 6.92 meq. of bromine per g. corresponding to 44% nonene and 56% *n*-nonane. A 50.0-g. sample of this, purified by washing three times with an equal volume of concentrated sulfuric acid, then with water, aqueous sodium carbonate and water, and then dried over sodium sulfate–potassium carbonate mixture and distilled, gave a 50% physical yield of *n*-nonane having the following properties: b. p. 150–151°, $n^{23}_{\rm D}$ 1.4045, d^{25}_{4} 0.7122 (*n*-nonane, b. p. 150.7°, $n^{20}_{\rm D}$ 1.4056, d^{20}_{4} 0.7179).

The 48.9-g. portion (II) consisting of a mixture of decanol-1, *n*-decyl aldehyde, and the hemiacetal had $n^{20}_{\rm D}$ 1.4356, was soluble in concentrated sulfuric acid, and gave a positive test (deep purple color) with Schiff reagent after one minute. A 2.579-g. sample of this fraction yielded 2.841 g. of the 2,4-dinitrophenylhydrazone corresponding to an aldehyde content of 51%.

The 2,4-dinitrophenylhydrazone derivative on recrystallization from 95% ethanol with charcoal gave yellow needles of m. p. 104°. *Anal.* Calcd. for $C_{16}H_{24}N_4O_4$: N, 16.67. Found: N, 16.71. The results of this experiment are tabulated in Table I as experiment 4.

Hexadecanol-1.—150.0 g. (0.619 mole) of hexadecanol-1 (m. p. 49–50°, E. I. du Pont de Nemours and Company, redistilled) and 7.5 g. of Raney nickel were treated as in the previous example. The reaction flask was maintained at a temperature of 255° for three hours. After separating off a 4.0-g. aqueous layer (consisting of water and catalyst solvent) and filtering off the catalyst, the combined organic material was distilled *in vacuo* using a saddle-packed modified Claisen head. The following cuts were obtained: (I) 75.0 g., 178–184° (65 mm.); (Ia) 16.0 g., 180–186° (48 mm.); (II) 43.5 g. above 200° at 48 mm.

Fractions (I) and (Ia) were mixtures of *n*-pentadecane and pentadecene. The 16.0-g. portion (Ia) was concluded to be the same as (I) but elevated in boiling point due to a very small amount of aldehyde or alcohol. (I) had $n^{24}_{\rm D}$ 1.4341, d^{24}_{4} 0.760 and (Ia) had $n^{23}_{\rm D}$ 1.4357 and d^{24}_{4} 0.760. Bromine titrations of (I) and (Ia) gave figures of 2.71 and 2.28 meq. of bromine per g., corresponding to pentadecene contents of 29 and 24%, respectively. A small portion of (I) purified by washing three times with concentrated sulfuric acid, then with water, aqueous sodium carbonate, and then water, and dried over sodium sulfate–potassium

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[10] Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

TABLE I

SUMMARY OF EXPERIMENTAL RESULTS

No.	Alcohol (primary) used	Alcohol, moles	Wt. % Ni used	Reaction conditions Hours	Temp., °C.	Mole % conversion to: Paraffin	Olefin	Aldehyde
1	Pentanol	1.70	5	3	140	Trace	Trace	3
2	Octanol	1.15	5	3	195	6	5	24
3	Nonanol	0.624	5	3	215	17	14	24
4	Decanol	.947	5	3	230	36	29	17
5	Decanol	.633	5	0.5	230	18	8	23
6	Dodecanol	.805	5	1	225			
				2	250	36	21	24
7	Hexadecanol	.619	5	3	255	50	20	10
8	Hexadecanol	.412	10	3	250	53	16	..
9	Hexadecanol	.412	5	3	225	49	16	..
10	Hexadecanol	.412	5	3	250	51	21	..
11	Hexadecanol	.412	5	3	275	45	23	..

carbonate mixture and distilled had the following properties: b. p. 174–175° (55 mm.), $n^{22}\text{D}$ 1.4318, d^{25}_{4} 0.7644 (*n*-pentadecane: b. p. 173° (50 mm.), $n^{25}\text{D}$ 1.431, d^{20}_{4} 0.7688).

The 43.5-g. cut (II) was a white solid consisting of a mixture of hexadecanol-1 and *n*-hexadecyl aldehyde. A 2.50-g. sample gave 1.55 g. of the 2,4-dinitrophenylhydrazone which had been washed with cold (10°) petroleum ether (b. p. 60–70°) to remove the unchanged hexadecanol-1. This figure corresponded to an aldehyde content of 35%. Since the aldehyde was separated by the bisulfite addition compound in very low yield, the reaction should be used only for the preparation of paraffins from hexadecanol-1 and alcohols of molecular weight higher than hexadecanol-1.

The results of this experiment are collected in Table I as experiment 7.

Results and Discussion

A summary of the experimental results is presented in Table I. In all cases the rate of gas evolution reached a maximum from one to four minutes after the start of the reaction and then, depending on the reaction temperature, decreased following a smooth curve. In cases where the reaction temperature was sufficiently high to cause a rapid reaction, the reaction was over before the usual three hours allowed for the experiment.

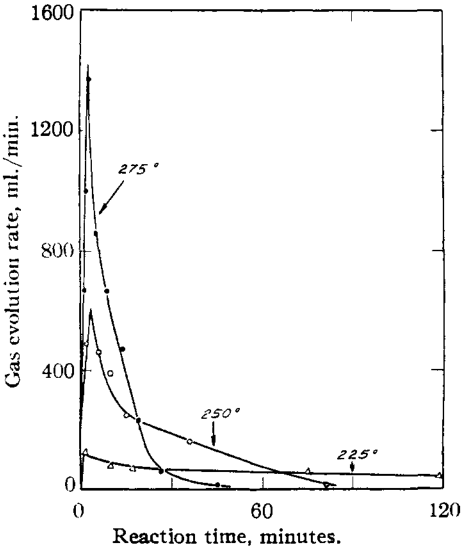

Fig. 1.

By far the most important factor in determining the extent of the reaction was the temperature. In experiments 9, 10 and 11 the reaction was carried out with hexadecanol-1 at temperatures of 225, 250 and 275° using 5% of catalyst. The curves for the gas evolution rates measured at 20° are shown in Fig. 1. At 225° gas evolution continued at the end of three hours, at 250° the reaction was over at the end of one hour, while at 275° the gas evolution had practically ceased after forty-five minutes. Using the gas evolution as a measure of over-all reaction rate, it is obvious that a much faster reaction occurs at the higher temperatures and that the catalyst became inactive sooner although practically the same percentage conversions were obtained.

A typical gas composition curve is shown in Fig. 2 where the amounts of free carbon monoxide and free hydrogen produced are plotted against time. Since the slope of the carbon monoxide curve decreases positively with simultaneous negative decrease in the slope of the curve for the amount of hydrogen, extrapolations of the composition curves were made to zero time as shown. These curves, therefore, indicate that dehydrogenation takes place first and is immediately followed by deformylation after which the two reactions proceed simultaneously along with hydrogenation of a part of the olefin formed. The total number of moles of hydrogen evolved should equal the number of moles of alcohol dehydrogenated plus the number of moles of olefin formed. The number of moles of carbon monoxide formed should equal the number of moles of saturated plus unsaturated hydrocarbon.

The optimum temperature for aldehyde formation was lower than the temperature at which the greatest conversions to hydrocarbons were obtained. With a reaction time of three hours the largest amount of aldehyde was obtained in the region 200-215°, although when the time was reduced to one-half hour an equally large yield was obtained at 230°. Negligible deformylation of the aldehyde was found to occur below 140° and the greatest conversion to saturated hydrocarbon was obtained at a temperature of 250° using a reaction time of three hours. This increase of deformylation with temperature can be illustrated by data obtained for the three temperatures of 225, 250 and 275°. At these three temperatures the instantaneous percentages of carbon monoxide in the evolved gas obtained from curves of gas composition *versus* time were 16, 30 and 34%, respectively, at a time of nine minutes from the start of the reaction. In addition the per cent. of olefin increased slightly with increasing temperature, indicating that the hydrogenation step did not occur to such a great extent probably because of the rapid evolution of the gas from the reaction flask. Therefore, by regulating the conditions a greater or less yield of aldehyde, paraffin or olefin may be obtained by considering that, in the temperature range 200 to 275°, a lower temperature and decreased reaction time favors aldehyde formation whereas a higher temperature and increased reaction time favors paraffin and olefin formation.

Although the study of the effect of the amount of catalyst was not complete, the data indicate that the quantity used is not an over-all conversion determining step in the region from two to ten per cent. of catalyst and that, beyond a certain point, an excess of active surface has little effect on the reaction.

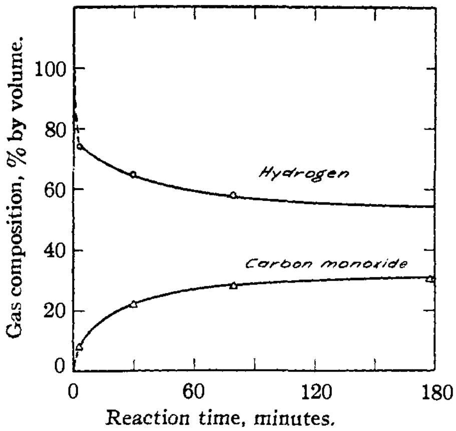

Fig. 2.—Hydrogen and carbon monoxide evolution, nonanol-1 at 215°.

Since dehydrogenation and dehydration often take place simultaneously, it might be expected that some dehydration of the alcohol would occur with the result that an olefin and, on hydrogenation, a paraffin of the same chain length as the original alcohol would be formed. However, the reaction apparently did not occur since neither the olefin nor the paraffin of chain length equal to the alcohol was obtained. This is in accord with the observation that metal surfaces favor dehydrogenation over dehydration.

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Summary

1. Primary aliphatic alcohols have been catalytically converted by Raney nickel in the liquid phase to aldehydes, unsaturated hydrocarbons, and saturated hydrocarbons by a reaction which appears to be general for primary alcohols.

2. Temperatures in the range 140 to 275° were studied and the amount of catalyst generally usea was 5%. Higher temperatures brought about an increase in the rate of reaction but a more rapid decrease in the activity of the catalyst.

3. Although the exact mechanism of the reaction has not been determined, evaluation of the data has shown that the reaction probably proceeds consecutively by dehydrogenation, deformylation, and hydrogenation, the extent to which each reaction occurs being influenced by the temperature and time.

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