[CONTRIBUTION FROM THE RESEARCH LABORATORIES, WYANDOTTE CHEMICALS CORPORATION]

The Hydrogenation of Sodium Bicarbonate to Sodium Formate

BY LESTER G. LUNDSTED

The hydrogenation of an aqueous solution of potassium bicarbonate to potassium formate in 70% yield over a palladium-black catalyst by Bredig and Carter[1] suggested the probability that a similar reaction could be carried out with the cheaper sodium bicarbonate over some of the more recently developed hydrogenation catalysts.

In order to select a suitable catalyst for this study, thirteen catalysts were tested in a preliminary way by attempting to hydrogenate a 5% aqueous solution of sodium bicarbonate. Under the conditions chosen, ten catalysts showed some activity for the reaction while three, copper chromium oxide and manganese and iron chromites, displayed no activity. In Table I will be found a list of the catalysts tested, the conditions used and the percentage of sodium formate found in the products based on the starting sodium bicarbonate. The percentages of sodium formate given are not necessarily the maximum obtainable over individual catalysts since optimum conditions were not determined. This was shown by two experiments with the Universal Oil Products Hydrogenation Catalyst in which the sodium formate in the products was increased from 24 to 75% by an increase in reaction time from two and one-half to eight and one-half hours.

TABLE I

PRELIMINARY TESTS OF CATALYSTS FOR THE HYDROGENATION OF SODIUM BICARBONATE[a]

Catalyst	Time, hr.	Sodium formate, %
U. O. P. hydrogenation catalyst	2.5	24.2
Nickel chromite	1.0	45.5
Copper and nickel	5.0	63.5
Zinc chromite	6.0	14.0
Nickel on kieselguhr	4.0	16.0
Copper chromium oxide	5.0	0.0
Raney nickel	6.0	49.0
Ruffert nickel pellets	5.0	64.6
Ruffert nickel	6.0	77.0
Nickel (from $Ni(OOCH)_2$)	1.0	16.0
Boron phosphate on charcoal	3.0	9.1
Iron chromite	6.0	0.0
Manganese chromite	1.3	0.0

[a] The tests were carried out under 1800 p. s. i. g. initial hydrogen pressure at a temperature of 200° using 4 g. of catalyst and 600 ml. of a 5% aqueous sodium bicarbonate solution.

The effect of variations in the reaction conditions on the percentage of sodium formate found in the products is shown in Table II for a series of studies with the Ruffert nickel catalyst in a wax support. Over the ranges studied an increase in either the quantity of catalyst or the hydrogen pressure increased the rate of hydrogenation as shown by the higher percentages of sodium formate in the products at the end of one hour. Longer reaction times increased the percentage of sodium formate found in the products when other conditions were such as to favor a low rate of reaction since under such conditions side reactions appeared to be at a minimum. Increasing the concentration of the sodium bicarbonate solution lowered the percentage of sodium formate in the products, although the actual quantity of sodium bicarbonate hydrogenated was greater. In such cases, an increased period of reaction served to raise the percentage of sodium formate in the products. An increase in the reaction temperature increased the rate of the reaction, but when the temperature became too high, side reactions increased to an extent which left little sodium formate in the product.

TABLE II

EFFECT OF VARIABLES ON THE HYDROGENATION OF SODIUM BICARBONATE OVER RUFFERT NICKEL CATALYST

Expt.	Variable	Catalyst, g.	Conc. of solution.,$_1$ %	Temp., °C.	Pressure	Time, hr.	Sodium formate, %
58	Catalyst	2	5	200	2000	1	52
42	concn.	4	5	200	2200	1	67
44		6	5	200	1700	1	72
58	Time	2	5	200	2000	1	52
55		2	5	200	2000	2	69
61		2	5	200	2000	3	70
63	Pres.	2	5	200	850	1	42
58		2	5	200	2000	1	52
56		2	5	200	3000	1	74
57		4	5	200	1000	1	47
42		4	5	200	2200	1	67
54		4	5	200	2800	1	78
59	Temp.	4	5	150	2000	1	14
42		4	5	200	2000	1	67
43		6	5	200	2000	1	71
		6	5	250	2000	1	10
67		8	5	150	2000	1	16
64		8	5	200	2000	1	58
42	Soln.	4	5	200	2000	1	67
62	concn.	4	$16^2/_3$	200	2000	1	54
66		4	$16^2/_3$	200	2000	2	62

Similar results can also be expected over other catalysts although the allowable variation in reaction conditions and the magnitude of the effect on the percentage of sodium formate in the product will differ from one catalyst to another.

Experimental

Materials Used.—The sodium bicarbonate used was a U. S. P. grade manufactured by Wyandotte Chemicals Corporation.

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[1] Bredig and Carter, *Ber.*, **47**, 541 (1914).

Catalysts Preparation.—The U. O. P. hydrogenation catalyst was obtained from Universal Oil Products Company, Riverside, Illinois. Raney nickel was purchased as an aqueous suspension from the Gilman Paint and Varnish Company, Chattanooga, Tennessee. The Ruffert nickel pellets and nickel catalyst supported in wax were obtained from The Ruffert Chemical Division of the Seymour Manufacturing Company.

Copper chromium oxide,[2] nickel on kieselguhr,[3] nickel chromite[4] and zinc chromite[5] were prepared and used according to standard methods. Iron chromite and manganese chromite were prepared according to the method used for zinc chromite.

The boron phosphate on charcoal catalyst was prepared by mixing 58 g. of phosphoric acid (85%) and 30.9 g. of boric acid in 100 ml. of distilled water with vigorous stirring and heating at 85° for one hour. The mixture was evaporated to dryness with constant stirring on a hotplate, the residue taken up in 200 ml. of distilled water and heated to boiling until a homogeneous suspension was obtained.

Fifteen grams of Darco activated charcoal were added with vigorous stirring and the suspension evaporated to dryness. The resulting cake was dried at 120° for twelve hours and then ground up for use.

The nickel–copper catalyst was prepared by dissolving 145.3 g. of nickel nitrate hexahydrate and 120.8 g. of cupric nitrate trihydrate in 1500 ml. of distilled water at 85°. One hundred seventy ml. of ammonium hydroxide, diluted with two parts of water, were added with vigorous mechanical stirring over a period of ten minutes while the temperature was maintained at 80–85°. Stirring and heating were continued fifteen minutes after which the suspension was filtered on a Büchner funnel. The residue was washed three times by alternate suspension in hot water and filtration. After the last filtration the residue was sucked as dry as possible on the filter and then dried in an oven at 110° for three days. Before use the catalyst was reduced in a slow hydrogen stream at 450° for forty-five minutes.

Nickel formate was obtained from the Harshaw Chemical Company, Cleveland, Ohio. Before use, it was reduced at 350° in a slow hydrogen stream for one hour and then transferred directly to the reactor.

Method of Reaction.—The hydrogenations were carried out in a rocking bomb of 1200 ml. void according to the method of Adkins.[6] The reaction product was washed from the bomb with distilled water, made up to a known volume and aliquots analyzed for sodium formate by the method of Blackadder.[7] Additional aliquots were acidified and used for the determination of Duclaux constants to demonstrate the presence of formic acid in the acidified product.

Summary

Sodium bicarbonate, in aqueous solution, has been converted to sodium formate by hydrogenation over ten different catalyst. Nickel-containing catalysts appear to be the most effective type among those tested. Catalyst concentration, hydrogen pressure, reaction temperature, reaction time and solution concentration have been shown to effect the conversion of sodium carbonate to sodium formate over a nickel catalyst.

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[2] Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wisconsin, 1937, p. 13.

[3] *Ibid.*, p. 19.

[4] Adkins, Richards and Davis, This Journal, **63**, 1320 (1941).

[5] Sauer and Adkins, *ibid.*, **59**, 1 (1937).

[6] Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wisconsin, 1937, p. 40.

[7] Treadwell and Hall, "Analytical Chemistry," Vol. II, Ninth English Edition, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 561.

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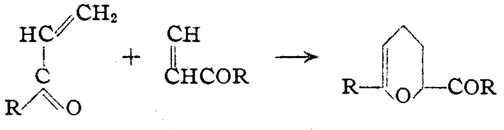
[Contribution No. 56 from the Department of Chemistry of the University of Tennessee]

The Thermal Dimerization of Acrylonitrile[1]

By Eugene C. Coyner[2a] and William S. Hillman[2b]

Various carbonylenic compounds, such as acrolein and methyl vinyl ketone, have been found by Alder and co-workers[3] to undergo thermal dimerization to give up to 55 per cent. yields of dihydropyran derivatives of the type represented by structure I.



R = H or CH_3

I

The present work was initiated with a view to carrying out this type of reaction with a nitrogen-containing analog, acrylonitrile, which it was thought, might correspondingly give a dihydropyridine derivative. However, under the optimum conditions found for the thermal dimerization of acrylonitrile, the only dimeric products isolated were not heterocyclic in nature, but were found to be *cis*- and *trans*-1,2-dicyanocyclobutane. Both products, upon hydrolysis, gave *trans*-1,2-cyclobutanedicarboxylic acid, whose structure was established by conversion to the known dihydrazide and by its resolution into the *d* and *l* forms.

Experimental

1,2-Dicyanocyclobutane.—All runs were carried out in an externally heated steel bomb of 250 cc. capacity under autogenous pressures (20–130 atmospheres). About 0.1 g. of hydroquinone was added to inhibit chain polymerization. Representative reaction conditions and the yields of acrylonitrile dimer obtained are given in Table I.

Table I

Dimerization of Acrylonitrile

Acrylonitrile	53[a] g.	53 g.	53 g.	100 cc.	100 cc.	100 cc.
Benzene, cc.	100	100	100			
Temp., °C.	245–250	275–280	295–304	195–200	200–210	245–265
Time, hours	7.5	2.0	0.5	24	3.5	0.8
Dimer, g.	1.5	2.6	2.4	5.5	1.2	2.8

[a] A glass liner was used.

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[1] Abstracted from a thesis by William S. Hillman submitted in partial fulfillment of the requirements for the M.S. degree.

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[3] Alder, Offermanns and Rueden, *Ber.*, **74B**, 905 (1941); Alder and Rueden, *ibid.*, 920.