

126. *Electrolytic Reduction of Organic Compounds. Part II. Catalytic Hydrogenation of Sorbic Acid at Prepared Cathodes of Nickel and Platinum.*

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POLISHED cathodes of nickel and platinum will not reduce sorbic acid (Isaacs and Wilson, this vol., p. 204), but it is now recorded that the electrodeposition of spongy nickel or platinum-black on these cathodes converts them into efficient reducing agents. By employing the technique already described (*idem, ibid.*) the products of reduction have been analysed. In the following table, the results of typical experiments in aqueous media, each involving the partial reduction of 20 g. of sorbic acid, are summarised.

Reduction of sorbic acid at prepared nickel and platinum cathodes.

Cathode.	Medium.	Components of reduction product (%).			Unchanged sorbic acid (g.).
		<i>n</i> -Hexenoic acids.		<i>n</i> -Hexoic acid.	
		Δ^{α} -	Δ^{β} - + Δ^{γ} -		
Ni	70% HOAc	18.9	18.3	62.8	4.1
	N-NaOH	26.6	17.2	56.2	5.0
Pt	70% HOAc	45.9	5.2	48.9	11.6
	N-NaOH	Very little reduction.			

Prolongation of the reduction leads to an increase in the amount of hexoic acid, and it is apparent that the course of reduction at these cathodes contrasts sharply with that pursued at other metals. The latter produce mixtures of only Δ^{β} - and Δ^{γ} -*n*-hexenoic acids (*idem, ibid.*), and since the conditions of all our electrolytic experiments have been the same, the absence of Δ^{α} -*n*-hexenoic acid (and its anticipated reduction product, hexoic acid) indicates that in the experiments now described this acid cannot arise by prototropic isomerisation of the Δ^{β} -acid.

Farmer and Hughes (J., 1934, 1932) observed the production of Δ^{α} -*n*-hexenoic and *n*-hexoic acid during the partial hydrogenation of sorbic acid under the influence of nickel (Raney's catalyst). It appears, therefore, that a spongy nickel cathode reduces by a process which is essentially catalytic. A platinised platinum cathode behaves similarly, but comparison with the behaviour of hydrogen in the presence of platinum-black is not immediately possible; considerable uncertainty has attached to the exact course of this reaction (*idem, J., 1934, 304; Ingold and Shah, J., 1933, 885*). Consequently, we have made special experiments, and, using the analytical technique already referred to, have ascertained the products of the 50% hydrogenation of sorbic acid in alcoholic solution. Four different samples of Adams's catalyst were employed, the relative activities of which may be estimated from the times taken for the absorption at a constant rate of shaking; these are given in col. 2 of the following table of results.

Partial catalytic reduction of sorbic acid in presence of Adams's catalyst.

Catalyst sample.	Duration of shaking (mins.).	Composition of reduction product (%).		
		<i>n</i> -Hexenoic acids.		<i>n</i> -Hexoic acid.
		Δ^{α} -	Δ^{β} - + Δ^{γ} -	
1	90	31.3	5.5	63.2
2	90	38.0	6.8	55.2
3	33	40.7	6.5	52.8
4	28	43.6	7.1	49.3

If we may assume that the nature of the solvent does not seriously influence the results (cf. Farmer and Hughes, J., 1934, 1930), these figures, which agree qualitatively with those given by these authors (J., 1934, 304), complete the analogy between catalytic hydrogenation and the behaviour of the prepared cathodes. In conformity with this conclusion, aliphatic unsaturated acids possessing a double bond in various positions (not only $\alpha\beta$ -) relative to the carboxyl group have been reduced at a spongy nickel cathode (Pomilio, *Z. Elektrochem.*, 1915, 21, 444), phenol has given cyclohexanol at a platinised platinum cathode

(Bancroft and George, *Trans. Amer. Electrochem. Soc.*, 1930, **57**, 399), and phenanthrene has been partly hydrogenated at a cathode of palladised platinum (Breteau, *Bull. Soc. chim.*, 1911, **9**, 769). In contrast, it is to be expected that the carbonyl group, which is notoriously resistant to catalytic methods, can be reduced at smooth but not at platinised platinum as Müller has shown (*Z. Elektrochem.*, 1910, **16**, 236).

By acting as a reversible hydrogen electrode in aqueous and alcoholic solution, a particle of active catalyst in such a medium in the presence of hydrogen will have a potential approximating to that of a prepared cathode evolving hydrogen at a very small current density. It may therefore reasonably be assumed that the essential mechanism of both processes is the same. In non-ionising media and in the vapour phase, catalytic reduction doubtless proceeds through electrically neutral intermediates. On the other hand, it is now generally accepted that with non-transition metals and ionising media the reaction is ionic. Our future experiments will endeavour to define the limits of these two mechanisms.

EXPERIMENTAL.

Hydrogenation of Sorbic Acid with Adams's Catalyst.—Sorbic acid (28 g.) in alcohol (150 c.c., 95%) and platinum catalyst (0.1 g.) were shaken with hydrogen until approximately 1 mol. had been absorbed. After evaporation of the solvent, the residue was boiled with petroleum (200 c.c., b. p. 60–80°), cooled to 0°, the solution filtered from separated sorbic acid and evaporated, and the residue distilled from a fractionating Claisen flask at a fraction of a mm. pressure and a rate not exceeding 2 drops per minute. A clean separation from sorbic acid was thus obtained. Towards the end of this distillation, Δ^{α} -*n*-hexenoic acid usually solidified in the condenser and was identified by m. p. and mixed m. p. with an authentic specimen (cf. Farmer and Hughes, J., 1934, 305).

Redistillation of the reduction product, which confirmed the absence of sorbic acid, was carried out before analysis by the halogen absorption method already described in detail (Isaacs and Wilson, *loc. cit.*). In this way Δ^{α} - and ($\Delta^{\beta} + \Delta^{\gamma}$)-hexenoic and hexoic acids were estimated. In addition, hexoic acid was isolated by adding excess of bromine to the reduction product and distilling it. The first fraction was converted into the amide and identified by m. p. and mixed m. p. with an authentic specimen.

*Stability of Δ^{α} -*n*-Hexenoic Acid towards Platinum-black.*—*cyclo*Hexene in the presence of palladium at 35° has been shown to give a mixture of benzene and *cyclo*hexane (Zelinski and Paulov, *Ber.*, 1933, **66**, 1420); it was considered feasible that a similar change might occur with Δ^{α} -*n*-hexenoic acid in the presence of highly active platinum-black. In this way the disagreement which has existed in the literature might have been explained.

Δ^{α} -*n*-Hexenoic acid (11.4 g.), platinum oxide (0.1 g.), and alcohol (100 c.c.) were shaken in a securely stoppered bottle (300 c.c.) filled initially with hydrogen. The platinum oxide was rapidly reduced. After 17 hours' shaking, the product was distilled, but gave no trace of sorbic acid.

Behaviour of Hexoic Acid in the Presence of Platinum-black and an Unsaturated Substance.—Farmer and Galley (J., 1933, 691) have stated that, although Δ^{α} -*n*-hexenoic acid is hydrogenated more rapidly than allyl alcohol, the reverse holds true in a mixture of these substances. This result may have been due to the instability of hexoic acid in the presence of a highly active catalyst and allyl alcohol. Allyl alcohol (7.8 g.), hexoic acid (12.6 g.), and platinum oxide (0.1 g.) in alcohol (20 c.c.) were shaken in a bottle with hydrogen (50 c.c.) and subsequently for 12 hours. No trace of sorbic or Δ^{α} -*n*-hexenoic acid could be detected in the product.

Details of Catalytic Reductions.—In each case, the acids in the class denoted by (a) were isolated, and those in (b) were titrated. *Expt. 1.* Absorption was complete in 90 minutes. Recovered material on distillation gave: (a) sorbic acid (7.25 g.) and Δ^{α} -hexenoic acid (3.76 g.); (b) hexoic acid (11.13 g.), Δ^{α} - (1.74 g.) and $\Delta^{\beta} + \Delta^{\gamma}$ -hexenoic acids (0.97 g.).

Expt. 2. Absorption complete in 90 minutes. Recovered material consisted of: (a) sorbic acid (10.75 g.) and Δ^{α} -hexenoic acid (1.25 g.); (b) hexoic acid (7.84 g.), Δ^{α} - (4.15 g.) and $\Delta^{\beta} + \Delta^{\gamma}$ -hexenoic acids (0.96 g.).

Expt. 3. Absorption took 33 minutes, the catalyst being the sample, 16 months old at the time of this experiment, used by Ingold and Shah (*loc. cit.*). Recovered material: (a) sorbic acid (9.6 g.) and Δ^{α} -hexenoic acid (4.43 g.); (b) hexoic acid (8.88 g.), Δ^{α} - (2.40 g.) and $\Delta^{\beta} + \Delta^{\gamma}$ -hexenoic acids (1.09 g.).

Expt. 4. The catalyst was extremely active, 1 mol. of hydrogen being absorbed in 28 minutes.

Product : (a) sorbic acid (9.43 g.) and Δ^{α} -hexenoic acid (3.53 g.) ; (b) hexoic acid (8.38 g.), Δ^{α} - (3.88 g.) and Δ^{β} - + Δ^{γ} -hexenoic acids (1.21 g.).

The isolated samples of the Δ^{α} -acid had m. p. 32° and were shown by titration to contain, in addition, not more than 2% of the Δ^{β} - + Δ^{γ} -acids; the above figures are appropriately corrected.

Electrolytic Reductions.—*Preparation of cathodes.* Nickel. Pure nickel gauze (30 mesh) was coated with a substantial deposit of spongy nickel by electrolysis for 1—2 hours of an ammoniacal solution of nickel ammonium sulphate, the current being 8—9 amps./sq. dm. of gauze. After being thoroughly washed, the cathodes were preserved under distilled water.

Platinum. A revolving cylindrical gauze cathode (as used in electrochemical analysis) was coated with platinum-black by electrolysis of platinum chloride solution (3 g. in 100 c.c., with 0.02 g. of lead acetate).

Details of Reductions.—70% Aqueous acetic acid containing sodium acetate (0.5M) and *N*-sodium hydroxide were used as solvents for sorbic acid and the sodium salt respectively. The method has been previously described, and the symbols *B* and *J* have the same significance as before (Isaacs and Wilson, *loc. cit.*).

Expt. 1. Nickel in acetic acid. Sorbic acid (16 g.) was reduced with 35 amp.-hrs. of current (theoretical for dihydro-acid, 8 amp.-hrs.) and gave (a) sorbic acid (2.0 g.) and (b) a liquid, b. p. 101 — $102^{\circ}/12$ mm. (12.4 g.) (Found : *B*, 8.3; *J*, 8.4. Hexoic acid, 91.7; Δ^{α} , 0; Δ^{β} + Δ^{γ} , 8.3%). 11.5 G. of (b) were treated with excess of bromine for 24 hours and distilled, giving a liquid, b. p. 110 — $111^{\circ}/19$ mm. (9.8 g.), identified as hexoic acid by m. p., -2° (Gartenmeister, *Annalen*, 1886, 233, 277, gives m. p. -2°), and formation of the amide, m. p. 98.5° (Robertson, *J.*, 1919, 115, 1220, gives 101°) (Found : C, 62.2; H, 11.3; N, 12.0. Calc. : C, 62.5; H, 11.4; N, 12.1%).

Expt. 2 (as 1). Sorbic acid (20 g.) was reduced at 1 amp. for 18 hours (theoretical for tetrahydro-acid, 20 hrs.) and gave (a) sorbic acid (13.9 g.) and (b) 13.9 g. of a liquid, b. p. 108 — $109^{\circ}/17$ mm. (Found : *B*, 37.2; *J*, 18.3. Hexoic acid, 62.8; Δ^{α} , 18.9; Δ^{β} + Δ^{γ} , 18.3%). Redistillation of (b) at a rate not exceeding 2 drops/min. and a pressure of less than 1 mm. gave, as last fraction, Δ^{α} -hexenoic acid, m. p. 32.2° ; mixed m. p. with authentic specimen (m. p. 32.3°) 32.2° .

Expt. 3. Nickel in alkaline solution. Sorbic acid (20 g.) and 25 amp.-hrs. gave (a) sorbic acid (5.0 g.), (b) 13.6 g., b. p. 102 — $103^{\circ}/11$ mm. (Found : *B*, 43.8; *J*, 17.2. Hexoic acid, 56.2; Δ^{α} , 26.6; Δ^{β} + Δ^{γ} , 17.2%). Redistillation of (b) as above gave Δ^{α} -hexenoic acid, m. p. 32.0° , mixed m. p. 32.1° .

Expt. 4. Platinum in acetic acid. Reduction of sorbic acid (20 g.) for 24 amp.-hrs. gave (a) sorbic acid (11.6 g.) and (b) a liquid, b. p. 108 — $109^{\circ}/17$ mm. (6.5 g.) (Found : *B*, 51.1; *J*, 5.2. Hexoic acid, 48.9; Δ^{α} , 45.9; Δ^{β} + Δ^{γ} , 5.2). Redistillation gave 0.8 g. of Δ^{α} -hexenoic acid, m. p. 31.9° , mixed m. p. 32.0° .

Expt. 5. Platinum in alkaline solution. Preliminary experiments in the differential apparatus (Isaacs and Wilson, *loc. cit.*) showed very low efficiency; the experiments were not pursued.

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