187. *Electrolytic Reduction of Organic Compounds. Part III. β-Vinylacrylic Acid.*

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Electrolytic reduction processes have been divided into two categories depending on the nature of the cathode; these are (1) spongy nickel and platinised platinum cathodes, at which the reduction is essentially of a catalytic nature, and (2) most other metallic cathodes which simulate the reducing properties commonly attributed to dissolving metals and metallic couples (this vol., pp. 202, 574).

Although these conclusions were based partly on the mode of reduction of sorbic acid under various conditions, they were considered to be generally applicable to unsaturated systems. We were therefore surprised by the results recorded by Muskat and Knapp * (*J. Amer. Chem. Soc.*, 1934, **56**, 943), who reduced β-vinylacrylic acid at a spongy nickel cathode and stated that, after the absorption of approximately 1 mol. of hydrogen, the product (in a maximum yield of 30%) was almost entirely Δ^{β}-*n*-pentenoic acid.

It has been established that the partial catalytic reduction of β-vinylacrylic acid in alcoholic solution under the influence of platinum-black produces mainly Δ^{α}-*n*-pentenoic acid and *n*-valeric acid (*idem, Ber.*, 1931, **64**, 779; Farmer and Galley, J., 1932, 130). Furthermore, sorbic acid, both by catalytic reduction and by electrolytic reduction at prepared nickel and platinum surfaces, gives a mixture containing much Δ^{α}-*n*-pentenoic acid and *n*-hexoic acid. We have therefore reinvestigated the electrolytic reduction of β-vinylacrylic acid, using as analytical procedure a combination of the halogen absorption method (which we have shown to be adaptable to the estimation of the pentenoic acids) and ozonolysis (this vol., p. 205).

Reduction Products of β-Vinylacrylic Acid.

Reducing agent.	Medium.	Yield of reduction product (%).	*n*-Pentenoic acids (%).		*n*-Valeric acid (%).	" Pinacol-like " polymeride (%).
Spongy nickel cathode	EtOH + NaCl	63	25·1 (Δ^{α})	55·4 ($\Delta^{\beta} + \Delta^{\gamma}$)	19·5	0
	N/2-NaOH	80	15·6 (,,)	34·9 (,,)	49·5	0
Copper cathode ...	*N*/2-NaOH	85	0	99·2 (Δ^{β})	0	0
Mercury cathode...	$NaHCO_3$	97	0	75·0 (,,)	0	25·0
Sodium amalgam *	$NaHCO_3$	—	0	80 (,,)	0	?

* Burton and Ingold, J., 1929, 2022.

In the experiment indicated by the first row of the table we have used the same solvent and cathode as employed by Muskat and Knapp (*loc. cit.*). Our product, however, contained Δ^{α}-*n*-pentenoic and *n*-valeric acids. Similar results were also obtained at a spongy nickel cathode in alkaline solution.

The three pentenoic acids have also been reduced at a prepared nickel cathode, and it has been shown that the relative ease of reduction of these acids and the parent butadiene acid follows a series, vinylacrylic $\gg \Delta^{\alpha}- > \Delta^{\beta}- > \Delta^{\gamma}$-*n*-pentenoic acid, in both acid and alkaline solution.

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* These authors claim priority for the electrolytic reduction of a butadienoid system, but this was actually accomplished long ago (Mettler, *Ber.*, 1906, **39**, 2942).

Experiments with copper and mercury cathodes are also shown in the table, and the results clearly display the division of cathodes into the catalytic and non-catalytic classes. For comparison with data for the latter groups of cathodes, a result of Burton and Ingold's for amalgam reduction is included in the table. In these experiments loss of vinylacrylic acid can be accounted for by polymerisation, which most probably occurs during the isolation of the reduction product and not during the reduction itself (cf., however, *idem, ibid.*). When mercury is the active metal, a considerable proportion of the material is converted into pinacol-like dimeride.

On the whole, the results in the table given above are in excellent agreement with those obtained for sorbic acid (this vol., pp. 202, 574).

Muskat and Knapp (*loc. cit.*) have presented a classification of reducing agents, grouping them as follows : (1) reducing ions (*e.g.*, chromous chloride), (2) dissolving metals, and (3) catalytic agents. It was stated that in contrast with the course of catalytic hydrogenation, reagents of group (2) usually add hydrogen terminally to conjugated systems. As a consequence of their findings (already referred to on p. 810) in the reduction of vinylacrylic acid at a spongy nickel cathode, electrolytic methods of reduction were placed in group (2). This is partly true, since we have shown that metallic cathodes, other than prepared nickel and platinum, exhibit reducing properties analogous to dissolving metals, but the experimental basis upon which Muskat and Knapp's allocation was made was too superficial.

EXPERIMENTAL.

Materials.—β-Vinylacrylic acid was prepared by Kohler and Butler's modification (*J. Amer. Chem. Soc.*, 1926, **48**, 1041) of Döbner's method (*Ber.*, 1902, **35**, 1137). Crystallisation of the product from ether–petroleum (1 : 3) gave small colourless prisms, m. p. 77—78°, unchanged by recrystallisation. Δ^{α}-, Δ^{β}-, and Δ^{γ}-*n*-Pentenoic acids were prepared by standard methods (Linstead and collaborators, J., 1933, 574, 559, 582) and had b. p. respectively 102—103°/17 mm., 90—92°/14 mm., and 93°/20 mm.

Method.—The preparation of the cathodes, conditions of reduction, and isolation of the products were as previously described for sorbic acid (Isaacs and Wilson, *loc. cit.*). Under the conditions defined previously (*idem, ibid.*) all three pentenoic acids reacted quantitatively with bromine in 6 hrs., and addition of iodine to the Δ^{β}- and the Δ^{γ}-acid was complete in 12 hrs., after which period Δ^{α}-*n*-pentenoic acid had reacted to the extent of only 2%. For the isolated reduction product the bromine and iodine absorptions are represented by *B* (Δ^{α}- + Δ^{β}- + Δ^{γ}-*n*-pentenoic acids) and *J* (Δ^{β}- + Δ^{γ}-*n*-pentenoic acids) respectively.

Details of Reductions.—*Expt.* 1 (Muskat and Knapp's conditions). Vinylacrylic acid (10 g.) in ethyl alcohol (400 c.c., 95%) with saturated sodium chloride solution (20 c.c.) was reduced at spongy nickel by 0·5 amp. for 28 hrs. (theo. for 4H, 24 hrs.). The product consisted of (*a*) 6·3 g. of a colourless liquid, b. p. 97—98°/18 mm. (Found : *B*, 80·5; *J*, 55·4. Valeric acid, 19·5; Δ^{α}, 25·1; $\Delta^{\beta} + \Delta^{\gamma}$, 55·4%), and (*b*) 2·7 g. of residual polymeride which could not be distilled.

Expt. 2. *Nickel in alkaline solution.* Vinylacrylic acid (8 g.) in *N*/2-sodium hydroxide (500 c.c.), reduced by 18 amp.-hrs. of current (theo. for 4H, 10 amp.-hrs.), gave (*a*) 6·4 g. (80%) of a colourless liquid, b. p. 89—90°/13 mm. (Found : *B*, 50·5; *J*, 34·9. Valeric acid, 49·5; Δ^{α}, 15·6; $\Delta^{\beta} + \Delta^{\gamma}$, 34·9%), and (*b*) 0·6 g. undistillable residue. 5·1 G. of (*a*) after standing for 24 hrs. with excess bromine, were distilled, and gave a liquid, b. p. 90—91°/17 mm. (2·2 g.), identified as *n*-valeric acid by formation of the amide, m. p. 104·5° (Robertson, J., 1919, 1220, gives 106°) (Found : C, 59·1; H, 10·9; N, 13·4. Calc. : C, 59·3; H, 11·0; N, 13·8%).

Expt. 3. *Copper in alkaline solution.* 10 G. of the acid in *N*/2-sodium hydroxide (500 c.c.), after passage of 18 amp.-hrs. of current (theo. for 2H, 6 amp.-hrs.), gave (*a*) a liquid, b. p. 93—94°/16 mm. (8·5 g., 85%) (Found : *B*, 99·3; *J*, 99·2; $\Delta^{\beta} + \Delta^{\gamma}$, 99·2%), and (*b*) 0·7 g. of undistillable polymeride.

Ozonolysis of (*a*) (2·780 g.) in chloroform solution at 0° and decomposition of the ozonide with water gave, by passage of the evolved vapours through 2 : 4-dinitrophenylhydrazine in 2*N*-hydrochloric acid, 5·81 g. acetaldehyde-2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 162° (Found : C, 43·2; H, 3·6. Calc. : C, 42·9; H, 3·6%). This corresponds to 93·4% of Δ^{β}-pentenoic acid in (*a*) (Muskat and Knapp, *loc. cit.*, claimed a maximum yield of 87% of acetaldehyde from their " pentenoic " acid). The aqueous solution from the ozonide fission was refluxed for 2 hrs., hydrogen peroxide (40 c.c., 20-vol.) added, and the mixture left overnight. To a portion of this solution calcium acetate solution was added, but no oxalic acid was thereby detected (Found : Δ^{α}, 0%). Evaporation of the remainder of the solution to dryness failed to indicate the presence of succinic acid (Found : Δ^{γ}, 0%) (cf. Burton and Ingold, *loc. cit.*).

Expt. 4. *Mercury in neutral solution.* Vinylacrylic acid (12 g.) was dissolved in sodium bicarbonate solution and electrolysed at 0·5 amp. for 18 amp.-hrs. (theo. for 2H, 7 amp.-hrs.) whilst a constant stream of carbon dioxide was passing through the catholyte. The product consisted of (*a*) 8·7 g. of a liquid, b. p. 93—94°/16 mm. (Found : *B*, 99·6; *J*, 99·8; $\Delta^{\beta} + \Delta^{\gamma}$, 99·6%), and (*b*) 2·6 g. of a light brown viscous liquid, b. p. 210—213°/16 mm. (slight decomp.), 170—172°/<1 mm. (analogous to the sorbic acid " pinacol ").

2·500 G. of (*a*) were ozonised as before, and gave 5·29 g. of acetaldehyde-2 : 4-dinitrophenylhydrazone, m. p. 161·5°, mixed m. p. 162° (Found : C, 42·9; H, 3·8%), corresponding to 94·5% of Δ^{β}-pentenoic acid. Addition of lead acetate solution to the aqueous solution from the ozonide fission gave a precipitate which was decomposed in aqueous suspension by hydrogen sulphide. Evaporation of the filtrate from the lead sulphide gave malonic acid, m. p. 132·5° (decomp.), mixed m. p. 133° (presence of Δ^{β}-pentenoic acid). The remainder of the solution from the ozonide fission after treatment with hydrogen peroxide gave no trace of succinic acid (Found : Δ^{γ}, 0%).

Relative Rates of Reduction.—By alternately placing equally concentrated solutions of unsaturated acids A and B in the reduction cell of the differential apparatus (Isaacs and Wilson, *loc. cit.*), it was possible to measure the amounts of hydrogen absorbed in the two cases. Successive values for the acid A differed slightly owing to progressive deterioration of the cathode, but the mean of two successive figures was compared with the intervening one for the acid B. In such a manner a quite definite and reproducible series was established (the subscripts 1 and 2 refer to 70% acetic acid and *N*/2-caustic soda solution respectively) :

$$\text{Vinylacrylic}_1 > \text{Vinylacrylic}_2 \gg \Delta^{\alpha}{}_1 > \Delta^{\alpha}{}_2 > \Delta^{\beta}{}_1 > \Delta^{\beta}{}_2 > \Delta^{\gamma}{}_1 > \Delta^{\gamma}{}_2.$$

The authors thank Professor C. K. Ingold for his interest and encouragement, and acknowledge grants from the Chemical Society and Imperial Chemical Industries Ltd.

UNIVERSITY COLLEGE, LONDON. [*Received, April* 21*st*, 1936.]