155. *Electrolytic Reduction of Organic Compounds. Part IV. Bimolecular Products from Sorbic Acid at a Solid and a Liquid Gallium Cathode: Analogy with Overvoltage.*

By Kenneth B. Wilson and Christopher L. Wilson.

The reduction of sorbic acid in alkaline solution at a gallium cathode to give a mixture of dihydro-acids and bimolecular product is described.

On raising the temperature a marked increase in the formation of bimolecular product occurs when the gallium melts (29°). Attention is drawn to the similarity between this behaviour and that of overvoltage.

Further experiments with solid cathodes, and the effect of current density at mercury cathodes, confirm the view that bimolecular (pinacol-like) products are favoured by high overvoltage conditions.

In Part I of this series (Isaacs and Wilson, J., 1936, 202) it was shown that, in the reduction of sorbic acid at various cathodes appreciable amounts of bimolecular product (I), which for the sake of convenience will henceforth be referred to as pinacol, were obtained only at mercury cathodes. The suggestion that this could be related to the high overvoltage

$$\text{Sorbic Acid, } C_5H_7{\cdot}CO_2H \begin{array}{ll} \nearrow \text{Pinacol } (C_5H_8{\cdot}CO_2H)_2 & \text{(I.)} \\ \searrow \text{Dihydro-acids, } C_5H_9{\cdot}CO_2H & \text{(II.)} \end{array}$$

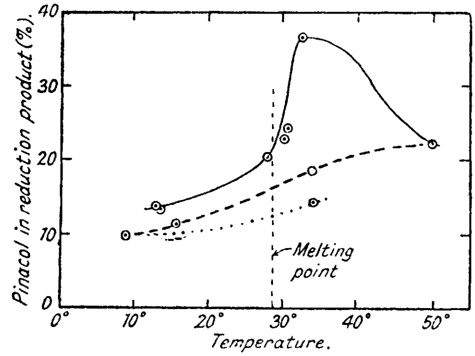
of mercury was improbable, since at cathodes of cadmium, which also possesses a high overvoltage, pinacol was not formed. It seemed possible, therefore, that the unique behaviour of mercury might be connected with its liquid nature. The following simple picture illustrates how this could arise. Pinacol formation probably involves the dimerisation of radicals (cf. Ingold and Burton, J., 1929, 2022; Semerano and Polacsek, *Gazzetta*, 1938, **68**, 292; Semerano and Betternelli, *ibid.*, 1936, **66**, 744), although, as yet, no proof of this has been forthcoming. Nevertheless, the special feature of a mercury cathode could be explained by supposing that adsorbed radicals, produced by a half-stage reduction, possess enhanced two-dimensional freedom and, therefore, a greater chance of uniting with one another. The alternative to dimerisation would be further reduction to dihydro-compound (II).

Experiments to test the validity of the foregoing hypothesis have been carried out by comparing the behaviour of the solid and the liquid form of the same cathode. For this purpose only three metals, gallium (m. p. 29°), Wood's metal (m. p. 69°), and mercury (m. p. — 39°), are available, and experiments have been carried out using each in turn as cathode. It was expected that melting the cathode would result in the appearance of pinacol in the reduction product.

Although the first set of results for gallium, shown by the continuous curve of Fig. 1, confirms expectation, it is not so obvious why pinacol should still be formed when the cathode is solid, unless it is supposed that the surface, even of the solid metal, behaves to some extent like that of the liquid. It was at this stage in the work that a somewhat different point of view was introduced by the observation that the shape of Fig. 1 was strikingly similar to that, given in Fig. 2, relating overvoltage, at low current density, and temperature (Bowden and O'Connor, *Proc. Roy. Soc.*, 1930, *A*, **128**, 326; Stelling, *Z. Elektrochem.*, 1935, **41**, 787). This was the first clear intimation that a relation of some sort existed between overvoltage and pinacol formation. Further experiments with gallium, whilst apparently confusing in themselves, in reality confirmed this finding. For example, when attempts were made to retrace the original curve by starting at the higher temperature, the new points fell on the broken line. Finally, when the temperature was again raised, the pinacol figures followed the lowest dotted line. Although somewhat disconcerting, this type of erratic behaviour must be expected if pinacol formation is closely related to hydrogen overvoltage, since the latter is known to be extremely sensitive to surface condition; this can hardly be controlled in experiments of this sort. Indeed, it was noticed that during the reductions, which were carried out without treating or cleaning the cathode in any way between the individual experiments, a black powdery deposit of gallium gradually accumulated on the surface of the cathode even when this was liquid. Finally, when the series was completed, the cathode was cleaned by electrolysis of warm dilute hydrochloric acid; subsequent reduction of sorbic acid then gave a pinacol figure lying fairly near the uppermost curve.

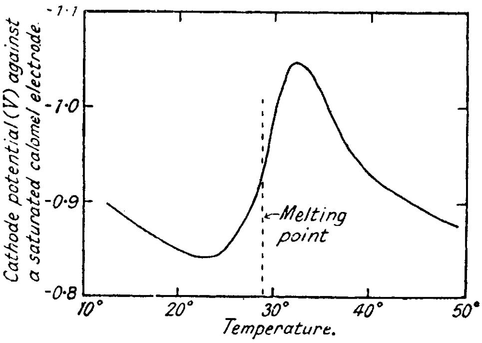
It may be considered that any similarity between Figs. 1 and 2 can only be fortuitous since the current densities and media used by us (0·15 amp./sq. cm., neutral solution) and by Bowden and O'Connor (2×10^{-4} amp./sq. cm., acidic solution) differ so markedly. However, not only is there definite evidence (Hickling and Salt, *Trans. Faraday Soc.*, 1940, **36**, 1226; Kabanov, *Acta Physicochim. U.R.S.S.*, 1936, **5**, 193; *J. Physical Chem., U.S.S.R.*, 1936, **8**, 486) that the familiar linear relationship between overvoltage and the logarithm of the current density holds up to current densities even higher than those employed in the present work, but the presence of certain organic molecules either as solvent (*e.g.*, ethyl alcohol, Hickling and Salt, *Trans. Faraday Soc.*, 1941, **37**, 224) or as depolariser (*e.g.*, benzaldehyde, Leslie and Butler, *ibid.*, 1936, **32**, 989) has been shown not seriously to affect the normal overvoltage curve. Change of p_H, too, in the region considered, has little, if any, effect on overvoltage (see below).

FIG. 1.



Pinacol formation from sorbic acid at gallium.
(*Sorbic acid*, 20 *g.; catholyte*, 500 *c.c. of* ½N-NaHCO$_3$.
Current density 0·15 *amp./sq. cm.*)

FIG. 2.



Overvoltage at gallium.

Results at Wood's metal surfaces (50% Bi, 25% Pb, 12·5% Sn, 12·5% Cd) were even more erratic than those at gallium. In 2N-potassium hydroxide solution, the amounts of pinacol varied between 2 and 10% over the range 10—96°. Liquefaction of the cathode had no obvious effect. During reduction the cathode became covered with a grey powdery deposit of pure lead. If this were mechanically removed during a reduction, there was an indication that pinacol tended to be high.

With mercury at —30° (liquid) and —48° (solid) only an aqueous-alcoholic–sulphuric acid electrolyte could be used. Under these conditions the reduction product consisted entirely of pinacol (as ester).

Other Solid Cathodes.—If the analogy with overvoltage is to hold, it would be expected that all cathodes, solid and liquid, would follow an overvoltage sequence for pinacol formation, it being assumed that surface roughening and contamination, which usually occur during a reduction, do not obscure the result. Some results with various cathodes are given in Table I. The effect of starting with a roughened cathode is illustrated by tin and cadmium, which, perhaps, explains our earlier (J., 1936, 202) failure to isolate pinacol at cadmium cathodes, since we used a spongy cathode. It would seem, in spite of the difficulty of obtaining reliable figures, that pinacol tends to form at high overvoltage cathodes, and, if we anticipate a later result for mercury, the sequence (pinacol % in parentheses), Hg (33), Sn (21), Zn (21), Pb (17), Cd (16), Cu (0), is not very different from that representing overvoltage, *viz.*, Hg, Cd, Pb, Sn, Cu (Hickling and Salt, *Trans. Faraday Soc.*, 1940, **36**, 1226).

TABLE I.

Pinacol Formation from the Sorbate Ion at Various Cathodes.

(Sorbic acid, 20 g. Catholyte, 500 c.c.)

Cathode.	Medium (aqueous).	C.D.* (amp./sq. cm.).	Temp.	Initial cathode surface.	Pinacol in reduction product (%).
Cadmium	½N-$NaHCO_3$	0·0089	21°	Spongy †	Trace
	2N-KOH	0·143	14	Smooth	16
Lead	2N-KOH	0·143	11	Spongy †	20
	2N-KOH	0·143	13	Smooth	17
Tin	½N-$NaHCO_3$	0·0095	18	Smooth	26
	½N-$NaHCO_3$	0·0095	18	Blackened §	14
	2N-KOH	0·143	14	Smooth	20
	2N-KOH	0·143	14	Smooth	22
Zinc	½N-$NaHCO_3$	0·0095	19	Smooth	12
	2N-KOH	0·143	14	Smooth	21
Thallium	½N-$NaHCO_3$	0·143	18	Smooth ‡	0
Copper	½N-$NaHCO_3$	0·143	20	Spongy †	0
Silver	½N-$NaHCO_3$	0·143	17	Smooth	No reduction

* Based on apparent surface area.
† Produced by electrolytic deposition.
‡ Rapidly disintegrated in use.
§ By reduction of sorbic acid at high current density.

Amalgam Formation with Mercury.—In some attempts to detect an increase in pinacol with rising current density in the manner that overvoltage is known to increase, sorbic acid was reduced in alkaline solution at a mercury cathode. An increase in the expected direction was indeed observed, as Table II shows, so long as amalgam formation was not evident. As soon, however, as amalgam was observed to form (at the high current density), or particularly if amalgam formation was deliberately encouraged, the pinacol figures fell. For the detection of amalgam we adopted the following device. The cathode was gently stirred and slowly circulated through an external vessel containing dilute sulphuric acid. The presence of amalgam was immediately evident by the evolution of hydrogen in this auxiliary wash vessel. In the first four experiments of Table II, amalgam was absent until over 90% of the sorbic acid had been reduced; in the other two, considerable amalgam was present, almost from the start.

TABLE II.

Effect of Current Density on Pinacol Formation in the Reduction of Potassium Sorbate at Mercury Cathodes.

(Sorbic acid, 20 g. Catholyte, 500 c.c. of 2N-KOH. Temp., 20°.)

C.D. (amp./sq. cm.)	0·015	0·05	0·07	0·14	0·72	0·14
Pinacol in reduction product (%)	16·5	24·5	28·0	32·5	18·5	17·5 *

* Amalgam formation encouraged by using a shallow, unstirred layer of mercury.

TABLE III.

Effect of Medium on Pinacol Formation from Sorbic Acid.

[Sorbic acid, 20 g. Catholyte, either (*a*) 30% aqueous sulphuric acid, 167 c.c., with organic solvent, 333 c.c., or (*b*) 2N-KOH, 500 c.c.]

Cathode.	C.D. (amp./sq. cm.).	Catholyte.	Temp.	Pinacol in reduction product (%).
Mercury	0·03	H_2SO_4 *	15°	70
	0·03	EtOH–H_2SO_4	13	89 (esters)
	0·10	Me·CO_2H–H_2SO_4	73	94
	0·14	Dioxan–H_2SO_4	37	100
	0·14	2N-KOH	14	32
Tin	0·14	Dioxan–H_2SO_4	23	98·5
	0·14	2N-KOH	14	21
Wood's metal (solid)	0·14	Dioxan–H_2SO_4	64	86
	0·19	2N-KOH	67	8·4

* No organic solvent: the sorbic acid was not very soluble.

Effect of Medium.—One of the more interesting features of sorbic acid reduction is the large increase in pinacol formation on passing from an alkaline to an acid electrolyte.

Data illustrating this are collected in Table III. Overvoltage is more or less independent of p_H provided that this be not too high (Glasstone, J., 1924, **125**, 2646; *Analyst*, 1925, **50**, 327; Wagner and Traud, *Z. Elektrochem.*, 1938, **44**, 391), in which event there is evidence (Bowden, *Trans. Faraday Soc.*, 1928, **24**, 473; *Proc. Roy. Soc.*, 1929, *A*, **126**, 107; Bowden and Kenyon, *Nature*, 1935, **135**, 105) that increasing alkali may raise the overvoltage at mercury. The pinacol figures, however, go in the opposite direction, and so it is more probable that the effect is due to the replacement of the sorbate ion as depolariser by the sorbic acid molecule.

If the behaviour of sorbic acid is typical of αβ-unsaturated acids, it is possible to chose beforehand the optimum conditions for obtaining either dihydro- or pinacol product. For the former, a low-overvoltage cathode, particularly spongy copper, in alkaline solution is satisfactory, and for the latter, mercury in acid, strict attention being paid to purity of reagents and freedom from contamination, is to be preferred. With sorbic acid it is possible to produce almost quantitative yields of either reduction product.

By employing sodium amalgam as cathode instead of mercury in the reduction of benzaldehyde in alkaline solution, the amount of pinacol produced has been shown to decrease from 50 to 0·5%. It is possible, therefore, that the overvoltage analogy operates here, but we have not yet accumulated sufficient accurate data to confirm this, owing, apparently, to the difficulty of separating benzyl alcohol from unchanged benzaldehyde.

EXPERIMENTAL.

The technique involved in the reduction of sorbic acid has been described in detail (Wilson, *Trans. Amer. Electrochem. Soc.*, 1939, **75**, 362). Gallium (31 g.) was contained in a small glass dish resting on the bottom of the cell; the superficial area was 7 sq. cm. Wood's metal was purchased from Messrs. B. D. H.

In the experiments involving mercury at low temperatures, the reduction cell was kept cool by immersing it in a mixture of " Drikold " and acetone kept in a large Dewar flask about 6" in diameter. The reduction cell was covered by a close-fitting lid to prevent access of moisture.

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