

574. *The Anodic Behaviour of Lead in Halide Solutions.*

By G. W. D. BRIGGS and W. F. K. WYNNE-JONES.

The anodic polarisation of a freshly cut lead surface has been carried out in HCl, KCl, KBr, KI, and KF solutions. The simultaneous growth of crystalline deposits on the electrode was studied by optical microscopy, and the relation between the structure of the anodic layers and the form of the polarisation curves was investigated. Electrochemical reactions other than the formation of lead halides were rarely observed except in iodide solutions. The results are discussed with particular reference to the passivation of lead in sulphuric acid.

THE anodic dissolution of metals under conditions in which an insoluble salt layer is formed on the surface has been much investigated, Müller in particular contributing a long series of papers¹ between 1927 and 1937. However, very little work other than that of Kurtz² has been published on the anodic behaviour of lead in halide solutions, although its passivation in sulphuric acid solutions has been studied in detail.³ The present paper describes the anodic polarisation of freshly cut lead surfaces at constant current density in a variety of halide solutions and includes a study of the crystalline salt layers by optical microscopy. Particular attention has been paid to the relation between the growth and structure of these layers and the form of the polarisation curves.

EXPERIMENTAL

The electrodes used were made from lead rod cast in the laboratory. The metal, "chemical lead" Type A, B.S.S. No. 334/1934, was heated in a 30-c.c. Pyrex beaker to 10–20° above its m. p., and drawn up by suction into a glass tube of the required diameter, usually 6 mm. This was allowed to cool in air, the glass removed by crushing in a vice, and the rod cut into lengths of 1–1.5 cm. A stout copper wire was soldered to one end of the rod, and the whole covered with insulating material, the most satisfactory procedure being to apply first a coat of Bakelite resin and bake this hard, then a coat of the commercial stopping-off compound "Lacomit." The polarising surface was prepared by cutting a cross section of the rod beneath the surface of the electrolyte. For this purpose the electrode was supported in a closely fitting Perspex jig and a single cut made with a sharp steel chisel. Similar methods of surface preparation have been used by Müller,^{1, 3a} Kabanov,^{3b} and Kurtz,² but the exact procedure is not made clear by them. We adopted the method described above so as to employ as far as possible conditions similar to those used by Kurtz in his work on the Pb–PbCl₂ electrode. Before use the lead surface was covered with fine parallel scratches produced by cutting, some of which may be seen in the photomicrograph (Fig. 3d).

The electrolytic cell employed has been illustrated by Briggs and Thirsk.⁴ The essential

¹ E.g., Müller, *Trans. Faraday Soc.*, 1931, **27**, 737; see Hedges, *Ann. Reports*, 1934, **31**, 129, for list of papers to 1934.

² Kurtz, *Compt. rend.*, U.R.S.S., 1935, **8**, 305.

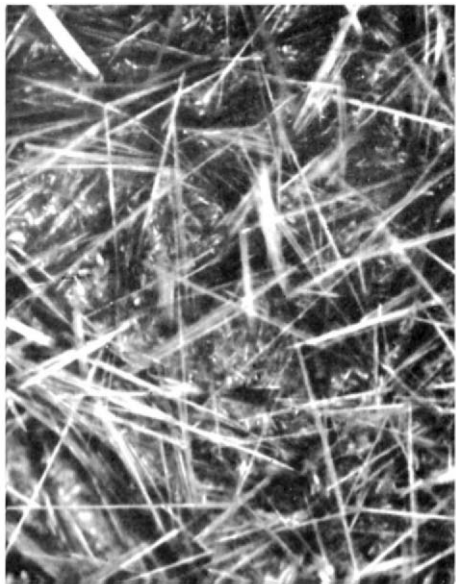
³ (a) Müller and Machu, *Sitzungsber. Akad. Wiss. Wien*, 1933, II, B, **142**, 557; (b) Kabanov, Proc. 2nd Conference on Corrosion, Akad. Sci., U.S.S.R., Moscow, 1943; (c) Jones, Lind, and Wynne-Jones, *Trans. Faraday Soc.*, 1954, **50**, 972.

⁴ Briggs and Thirsk, *ibid.*, 1952, **48**, 1171.

FIG. 3.
a-d.



(a) 0.5N-KBr, before abrupt change in potential,
4.5 mA/cm.² (× 93).

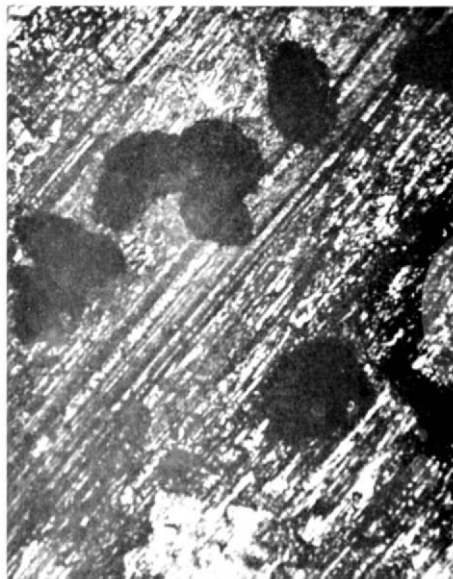


(b) 0.5N-KBr, after abrupt change in potential,
4.5 mA/cm.² (× 93).



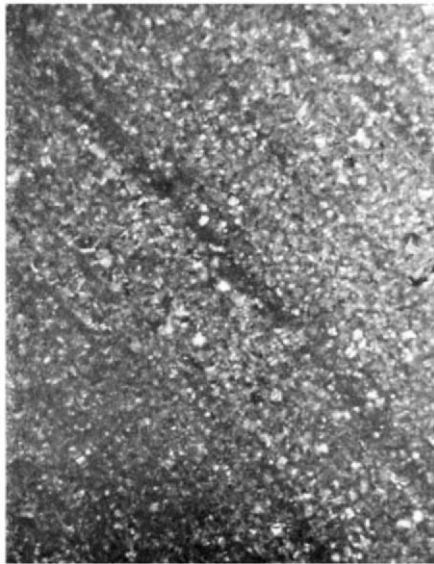
(c) 0.5N-KCl, 1.6 mA/cm.² (× 93).

a, b, c, oblique illumination; d, vertical illumination.



(d) 0.5N-KCl + 1% of dextrin, 1.6 mA/cm.² (× 93).

Fig. 3.
e-h.



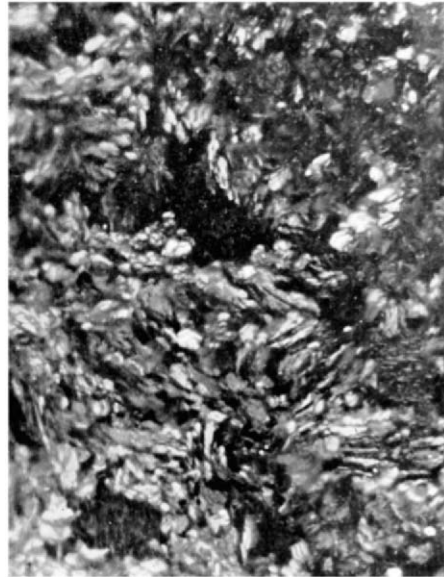
(e) 0.5N-H₂SO₄, 1.6 mA/cm² (× 200).



(f) 0.5N-KI, 1.6 mA/cm² (× 167).



(g) 0.1N-KI, 1.6 mA/cm² (× 93).



(h) 0.02N-KI, 1.6 mA/cm² (× 133).

e, f, g, h, oblique illumination.

features of its arrangement are that the electrode surface is placed vertically in the solution opposite to the end of a glass tube of similar diameter, the latter providing a connection between the anode and the cathode compartment of the cell. A silver chloride or silver bromide reference electrode was used, either placed in the same solution as the lead electrode or, in the case of fluoride and iodide solutions, connected through a salt bridge. A Luggin capillary was employed with its tip placed about 1 mm. from the anode surface.

The polarising circuit was of a simple type in which a constant current was maintained by means of a suitably high resistance in series with the cell, the current flowing being measured by the potential drop across a standard resistance in the same circuit.

Solutions were made from "AnalaR" potassium halides and saturated with the appropriate lead halide by shaking at 40° with the solid compound and allowing to cool to room temperature. The lead halides were prepared by addition of potassium halide solution to lead nitrate solution and were recrystallised from hot water except in the case of the very insoluble lead fluoride.

RESULTS

Polarisation Curves.—Polarisations were carried out in solutions of hydrochloric acid and potassium chloride, bromide, fluoride, and iodide. Concentrations of 0.02N to 2N were employed, and current densities of 0.2—10 mA/sq. cm., all solutions being saturated with lead halide and kept at 20°. A selection of polarisation curves for several halides is shown in Fig. 1, those for 0.5N-sulphuric acid being included for comparison.

Microscopic Examination.—Photomicrographs illustrating the growth of lead halide layers are shown in Fig. 3. The stages at which electrodes were removed for examination are marked by arrows on the polarisation curves in Fig. 1.

During polarisation, crystalline layers were formed on the electrode surfaces but there was little visual evidence for other reactions, apart from occasional intermittent gassing and the liberation of iodine in concentrated iodide solutions.

The polarisation curves showed a variety of forms which are illustrated by the examples in Fig. 1. Most of these curves may be regarded as belonging to one of two distinct types.

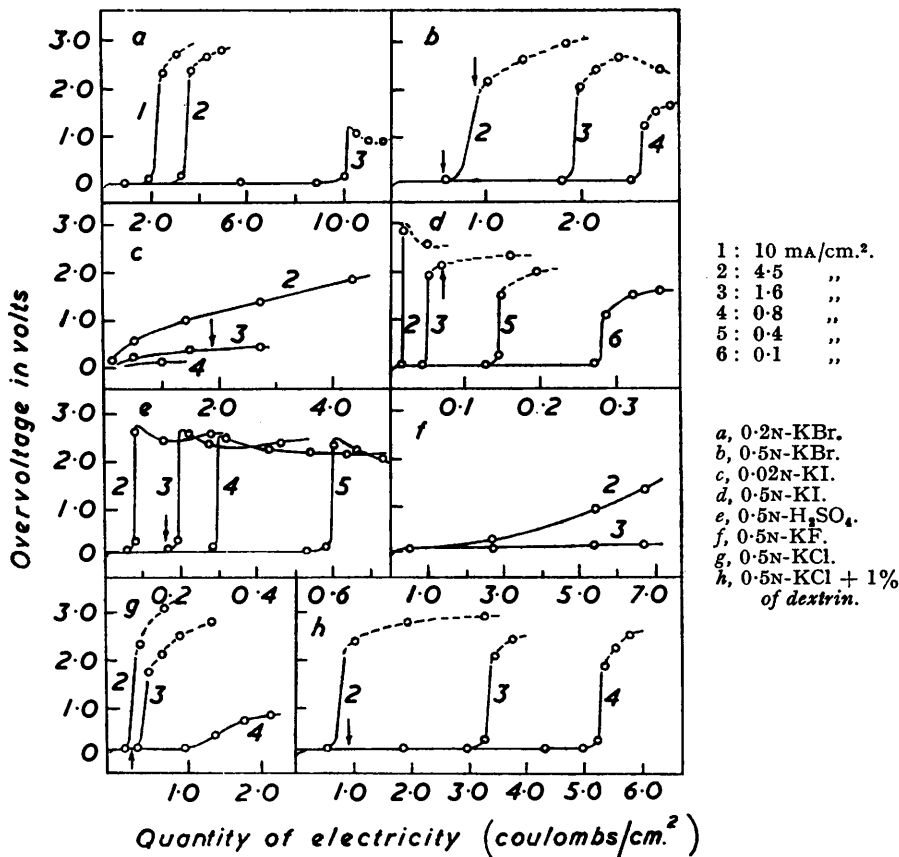
In the first type the trace of potential against quantity of electricity is smooth and of small slope, curving upwards from the commencement of polarisation but without any abrupt changes in direction. These curves were obtained in 0.02N-potassium iodide and 0.02N—2N-potassium fluoride solutions (see Figs. 1c, f), and they sometimes seemed to be associated with loose deposits, since crystals were often observed to fall from the electrode during polarisation.

The second type of curve showed an initial period of low overpotential followed by a more or less abrupt rise sometimes exceeding 3v. Sometimes this rise was slow and sluggish as, e.g., at low current densities in 0.5N-potassium chloride and 0.5N-hydrochloric acid, but frequently it was very rapid as in 0.5N-potassium iodide and in potassium bromide at all concentrations (Figs. 1a, b, d). The latter curves were selected for more detailed study on account of their resemblance to the polarisation curves for lead in sulphuric acid, examples of which are shown in Fig. 1e. The most striking difference was that in the curves for halide solutions a steady potential corresponding to formation of PbO_2 was not established, but instead the potential oscillated rapidly and irregularly. These changes were too rapid and erratic to follow with a manually operated potentiometer and so are conventionally indicated in the figures by broken lines. On interruption of the current, the potential usually decayed rapidly to the equilibrium value for that solution, although irreproducible arrests were sometimes observed at about 0.5v positive to this value.

In those curves which exhibited a sudden jump in potential after a period of low overpotential dissolution, the quantity of electricity passed through the electrode during the initial stage was not constant but increased as the current density was lowered. This may be seen clearly in Fig. 1, in which potential is plotted against charge passed, the current being constant. The phenomenon has been previously studied for lead in sulphuric acid solutions by Müller and Machu^{3a} and Kabanov^{3b} and a relation of the form $i^n t = \text{constant}$, sometimes known as Peukert's equation, has been found to connect the current density i with the duration of the low overpotential stage of "passivation time" t . Our observations for lead in halide solutions could also be fitted to a relation of this type, the index n remaining constant for a given solution within the range of current densities employed. If the above expression is rewritten as $\log t = \text{const.} - n \log i$, it is evident that, for values of t and i which fit, the plot of $\log t$ against i should be linear with slope $-n$. Plots of these values are shown in Fig. 2, for 0.5N-potassium

iodide and 0.1N-potassium bromide, and although individual values of t show a larger scatter about a mean value, a good approximation to linearity is achieved. Values of n , which varied between 1.3 and 1.9, are recorded in Table 1 for several solutions.

FIG. 1.



Arrows show the points at which the corresponding photomicrographs in Fig. 3 were taken.

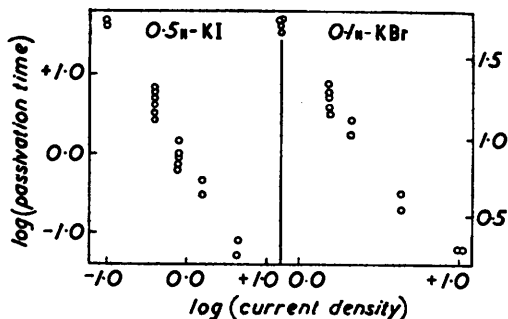


FIG. 2. Relation between \log (current density, i) and \log (passivation time, t) for lead anode in (a) 0.5N-KI and (b) 0.1N-KBr.

Apart from varying with the current density in the manner described above, the passivation time varied from one electrolyte to another over a wide range of values when the current density was fixed. This is illustrated by the figures collected in Table 2, which show that at a current density of 1.6 mA/cm.² the passivation times varied from 25 sec. in 0.5N-potassium iodide to nearly 2 hours in 0.02N-potassium bromide. No general correlation of the passivation times

with the solubility of the layer-forming salt is possible, however, since our solutions were saturated with the appropriate lead compound before use. Moreover, whilst lead sulphate and iodide are very much less soluble than the chloride or bromide, it is difficult to quote appropriate figures for the solubilities of the lead halides in concentrated halide solutions, as it is known from the work of Allmand and Burrage⁵ and Fromherz⁶ that complex formation occurs to a considerable extent.

TABLE 1.

Solution	C.D. range (mA/cm. ²)	<i>n</i>	Solution	C.D. range (mA/cm. ²)	<i>n</i>
2·0N-KBr	1·6—10	1·9	0·02N-KBr	1·6—10	1·7
0·5N-KBr	0·8—10	1·9	0·5N-KCl	0·8—4·5	1·6
0·1N-KBr	0·8—10	1·3	0·5N-KI	0·1—4·5	1·7

TABLE 2. Passivation time at 1·6 mA/cm.²

Solution	<i>t</i> (min.)	Solution	<i>t</i> (min.)	Solution	<i>t</i> (min.)
0·5N-HCl	3·0	2·0N-KBr	42	0·02N-KBr	110
0·5N-KCl	3·0	0·5N-KBr	19	0·5N-KI	0·4
0·5N-KCl + 1% dextrin	12·5	0·1N-KBr	18	0·5N-H ₂ SO ₄	1·5

Further insight into the relation between the growth of the crystalline layers and the passivation and polarisation phenomena at the electrode was gained by optical microscopy, which showed at least three types of layer formation.

In 0·5N-sulphuric acid and 0·5N-potassium iodide solutions the electrodes were coated with crystals of uniform size and shape having diameters of several μ (Figs. 3*e*, *f*). These layers appeared to spread sideways, maintaining a uniform thickness, until the whole electrode surface was covered, at which point the abrupt increase in potential occurred. The passivation times in 0·5N-potassium iodide were appreciably shorter than in 0·5N-sulphuric acid at the same current density (Table 2) but this can be explained by the fact that the iodide layer was composed of plate-like crystals (Fig. 3*f*), of which some were inclined obliquely to the surface but the majority lay "flat" on the electrode. A similar effect has been noted by Huber⁷ at cadmium anodes in potassium hydroxide solution. The thickness of layer required for covering was therefore smaller than for the lead sulphate layer, made up of much more rounded crystals. In both these instances chemical passivation with change in electrode process occurs, lead dioxide being formed in sulphuric acid solution, and iodine and oxygen being liberated in 0·5N-iodide solution provided that current density was in excess of about 1 mA/cm.².

The layers formed in potassium chloride and bromide solutions were more coarsely crystalline, thicker, and of non-uniform structure (Figs. 3*a*—*d*). In most instances there was a fairly abrupt change in potential after a passivation period, provided the current density was sufficiently high, but this change in potential was not always related to a definite stage in the growth of the crystalline layer. Figs. 3*a* and 3*b* respectively show a lead bromide layer formed in 0·5N-potassium bromide immediately before and immediately after the potential jump had occurred. It is clear from the photographs that the potential jump coincides with the sudden formation of a layer of small crystals near the electrode surface, these crystals filling the spaces between the large needles which have grown during the passivation period. In 0·5N-potassium chloride, on the other hand, an apparently complete layer was formed on the electrodes before the jump in potential occurs. This is illustrated by Fig. 3*c*, which shows a lead chloride layer formed in 0·5N-potassium chloride at 1·6 mA/sq. cm. during the period of low overpotential dissolution.

The influence of layer structure on the behaviour of the electrode is illustrated by Fig. 3*d*. Here the addition of 1% of dextrin to the 0·5N-potassium chloride electrolyte has caused growth during the passivation period to be confined to a few individuals of large size, which show the characteristic suppression of crystal faces shown by Miles⁸ to occur when lead chloride crystallises from dextrin-containing solutions. The change in the corresponding polarisation curves, shown in Figs. 1*g* and *h*, respectively, are noteworthy. In potassium chloride containing dextrin the passivation period is increased by a factor of about 4 and the potential jump when it occurs is much more abrupt, especially at low current densities. Apparently, the restriction of growth to a few individuals favours the active dissolution of the anode and extends the

⁵ Allmand and Burrage, *J.*, 1926, 1703.

⁶ Fromherz, *Z. phys. Chem.*, 1931, 153, 382.

⁷ Huber, *J. Electrochem. Soc.*, 1953, 100, 376.

⁸ Miles, *Proc. Roy. Soc.*, 1931, A, 132, 266; *Phil. Trans.*, 1935, A, 235, 125.

passivation period until a sudden crystallisation covers the remaining surface, as in the bromide solutions described above.

In potassium fluoride solutions, the polarisation curves showed no marked discontinuities, resembling those for the anodic formation of silver chloride on silver as observed by Lal, Thirsk, and Wynne-Jones.⁹ The layers, which were made up of small, loosely packed crystals, were probably formed by an analogous process of rapid covering, followed by fairly uniform thickening. Similar smooth curves associated with loose, coarsely crystalline layers, were obtained in 0.02N-potassium iodide (Figs. 1c, 3h), but in iodide solutions there was a complete transition in the phenomenon according to the concentration of the electrolyte. Thus the loose crystals obtained in 0.02N-potassium iodide contrasted sharply with the uniform coating of small, closely attached crystals formed in 0.5N-potassium iodide, and the corresponding polarisation curves were strikingly different, those for the more dilute solution sloping gently, and those for stronger solutions showing a sharp jump in potential after a flat, low, overpotential stage (Figs. 1c, d). At the intermediate concentration of 0.1N, the phenomenon was extremely complex. The electrode (Fig. 3g) was partly unattacked, partly coated with minute crystals, and partly covered by drifts of yellow crystals which formed patches easily visible to the unaided eye. The polarisation curves showed no definite form, potentials usually being unstable.

DISCUSSION

The behaviour of metal anodes at which an insoluble salt layer is formed has been discussed in detail by Müller.¹ The systems he investigated included lead, copper, and iron in sulphuric acid solution, the majority of his experiments being carried out with horizontal electrodes at which mechanical loss of reaction products was prevented by a shield. Müller suggested that crystals formed by supersaturation of the solution near the anode grew sideways over the surface during the low-overpotential passivation period. When this covering was completed there was an abrupt rise in the potential of the electrode due to the increased current density in the pores of the salt layer, leading, in favourable examples such as lead in sulphuric acid, to the production of higher-valency metal compounds and oxygen evolution. Kurtz² claimed to have observed this covering process at a lead electrode in chloride solution, and it appeared reasonable to assume that something similar was occurring in our solutions. The variations in passivation time could then be ascribed to differing thickness of the layers at the moment of completion, and also to variation in the amount of lead salts lost by convection during the formation of the thicker layers. More detailed examination by optical microscopy showed that in some instances there was a connection between the type of layer growth and the behaviour of the electrode, as shown by the effects of adding dextrin to the 0.5N-potassium chloride electrolyte, but the relationship was difficult to follow in detail. It seemed clear that whilst "passivation" of the electrode might coincide with the completion of a visible crystalline layer, as in 0.5N-potassium bromide, this was not necessarily true for other solutions such as 0.5N-potassium chloride, even though an approximately linear plot of $\log i$ against $\log t$ was obtained.

From our results, the main process occurring in halide solutions appeared to be the passage of lead into solution in the bivalent state, with the formation of sparingly soluble halide layers on the anode. This might continue indefinitely, although the accumulation of halide ultimately gave rise to considerable fluctuating overpotentials which appeared to be largely ohmic in character. The effect corresponded to "mechanical" or "covering" passivity as defined by Foerster¹⁰ and Müller¹ rather than to chemical passivity in which a change of electrode process occurs. Nevertheless, intermittent gassing was sometimes recorded at high current densities together with the occasional production of specks of a brown compound, and iodine was liberated in concentrated potassium iodide solution.

We imagine, therefore, that if the crystalline layer is formed in such a way that much of the lead surface is effectively covered and the free flow of liquid over the surface by convection is prevented, then at high current densities halogen ion might be so far depleted

⁹ Lal, Thirsk, and Wynne-Jones, *Trans. Faraday Soc.*, 1951, **47**, 70.

¹⁰ Foerster, "Elektrochemie Wässeriger Lösungen," Leipzig, 1923, p. 415.

at the base of some of the pores that further dissolution of lead would be restricted at these points. The current would then be concentrated on the remaining active parts of the surface until, if these were sufficiently reduced in area, the alternative process such as oxygen evolution would occur with the formation of a protective surface film and a further rapid change in the electrode potential. On the other hand, once dissolution of lead had ceased at any point, the halogen-ion concentration would be increased by mixing and diffusion. Since these ions are known from the work of Britton and Evans,¹¹ Hoar,¹² and others to induce film rupture, their accumulation would eventually cause breakdown of the protective film and a return to active dissolution. This process, which is essentially similar to that proposed by Hedges¹³ for periodic anodic phenomena, would therefore account for the unstable potentials and intermittent evolution of gas which were actually observed on electrodes. In view of the complex behaviour observed, such an explanation is necessarily tentative, and direct evidence is lacking except insofar as the presence of a protective film is suggested by the uneven attack in 0.1N-potassium iodide. We think that the lead iodide electrode would merit further study, especially from the point of view of determining the relative efficiencies of the anodic processes under conditions in which iodine is liberated and in which total or partial passivation of the lead may occur.

The authors have pleasure in acknowledging the advice and assistance given by Dr. H. R. Thirsk in connection with the optical microscopy described in this paper.

KING'S COLLEGE, NEWCASTLE UPON TYNE, 1.

[Received, January 31st, 1956.]

¹¹ Britton and Evans, *J.*, 1930, 1772.

¹² Hoar, *Trans. Faraday Soc.*, 1949, 45, 683.

¹³ Hedges, *J.*, 1928, 969; 1929, 1028.
