

From the latter locality, in addition to the cubic crystals, pyritohedrons are also common. The largest crystal in the collection (see photograph) has octahedral faces on it. The longer edge of the largest pyritohedral face measures 31 mm. and the edge of the octahedral face measures 6 mm. The crystals are grown one into another giving an aspect of inter-penetration twinning. The intergrowth of crystals seen in the photograph weighs 1,005 gm. A chemical analysis of the crystals gave:— Sulphur 53.46 per cent., Iron 45.36 per cent.

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September 29, 1943.

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INFLUENCE OF POTENTIAL AND NATURE OF RADIATION ON THE NEW LIGHT-EFFECT IN CHLORINE UNDER ELECTRICAL DISCHARGE

EARLIER results^{1,2,3} on the production of a new light-effect, viz., Δi the diminution on irradiation of i the discharge current, were observed under conditions selected chiefly to reveal the main phenomenon, within the range and sensitivity of the then available indicator. This precluded a wide-range investigation of the nature of Δi changes, when all except one of the determining factors were unaltered. Thus, e.g., whilst Δi , the light-effect, was quite marked over a wide range of V the applied potential using a violet light-filter, it was just detectible with red, employing any of the familiar, intense light sources and maximum V . This limitation was absent using the Cambridge A.C. microammeter, which has both improved and simplified appreciably the whole technique of the study of this new phenomenon.

Fig. 1 records results for Δi observed with the above instrument as V was varied over an

The light source was a 200 watt bulb run at 180 volts. In agreement with earlier results^{2b} for Δi due to a fixed V , it is seen that the light-effect with the violet filter (curve 2) is substantially similar to that for unfiltered white light (curve 1), and that comparatively, Δi due to red is markedly low. The use of a pile of two violet filters (curve 3) as against one (curve 2) illustrates the effect of a reduction of intensity in diminishing Δi .

In relative units, the total incident energy corresponding to the white, violet, violet (double filtered) and red was 34.1, 16.5, 8.7 and 22.2 respectively. These results suggest that frequency is more important than the intensity in the production of this phenomenon.^{2,3} That violet is more absorbed than red by chlorine is an additional factor.^{2b,3} It may also be mentioned that within the limitations of the means at our disposal this light-effect was found to be negligibly small in the infra-red.³ It is interesting that the general influence of an increase of V in increasing the light-effect in chlorine is but small and is comparatively sensible under the white or the violet light, when Δi is large.

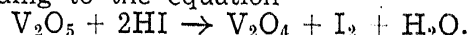
Benares Hindu University,
September 2, 1943.

S. S. JOSHI.
P. G. DEO.

1. *Curr. Sci.*, 1940, **9**, 536. 2. (a) *Nature*, 1941, **147**, 806; (b) 1943, **151**, 561. 3. *Proc. Ind. Sci. Cong.*, Pres. Address to Chem. Sec. (1943), pp. 70-75.

THE INDUCED OXIDATION OF HYDRIODIC ACID WITH VANADATE AS INDUCTOR

THE reaction between vanadate and hydriodic acid has been studied by numerous workers but the course of the reaction is not yet definitely established. Perkins¹ and Gooch and Curtis² among others found that the amount of iodine liberated was in excess of that corresponding to the equation



We have conducted experiments to determine the total amount of iodine liberated in the presence of air under varying concentrations of vanadate and hydrogen ion. It was found by us that when the hydrogen-ion concentration was kept constant the discrepancy between the experimental and theoretical amounts (according to the above equation) of iodine increased with the decrease in the concentration of vanadate; when the vanadate concentration was kept constant the discrepancy increased with decreasing concentration of the hydrogen ion.

Ramsay³ stated that the theoretical amount of iodine corresponding to reduction of pentavalent vanadium to the tetravalent stage is indeed obtained when the reaction is allowed to take place in an atmosphere of carbon dioxide excluding the presence of air. Experiments conducted by us in an atmosphere of carbon dioxide and in vacuum under widely varying concentrations of vanadate and hydrogen ion showed that the amount of iodine liberated in the absence of oxygen corresponds quantitatively to reduction to the tetravalent

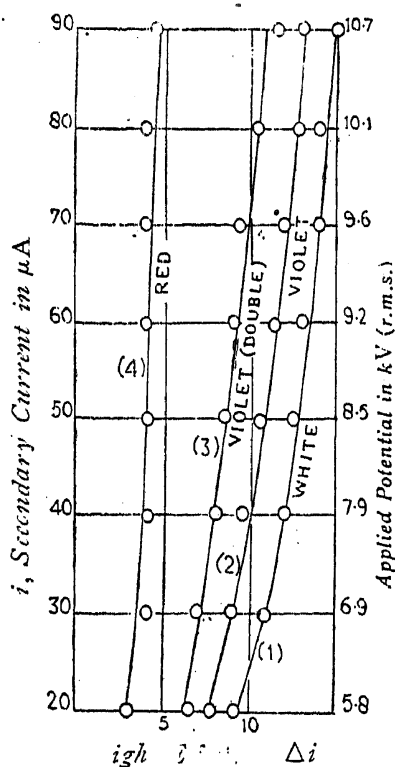


FIG. 1

appreciable range; the corresponding values of the secondary current are also indicated.

stage. These experiments rule out the suggestion of earlier workers⁴ that the excess liberation of iodine observed in the presence of air may be due to the reduction of the penta-valent vanadium being carried beyond the tetravalent stage. We have carried out experiments to see if this excess liberation of iodine in the presence of air is due to (a) the simple autoxidation of hydriodic acid by atmospheric oxygen catalysed by tetravalent vanadium or (b) the oxidation of hydriodic acid by atmospheric oxygen induced by the primary reaction between vanadic acid and hydriodic acid. We found that at the hydrogen-ion concentration employed in the experiments the liberation of iodine due to cause (a) is negligible and cannot account for the enormous liberation of iodine actually observed. The excess liberation of iodine observed in the presence of air is, therefore, due to the induced oxidation of hydriodic acid. We also found that the induction factor (F)

$$F = \frac{\text{Number of molecules of hydriodic acid oxidised by oxygen}}{\text{Number of molecules of hydriodic acid oxidised by vanadic acid}}$$

varies with concentration of vanadate and hydrogen ion. Recently we⁵ reported that oxalate ion catalyses the reaction between vanadic acid and hydriodic acid. The presence of the catalyst also influences the magnitude of the induction factor.

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September 25, 1943.

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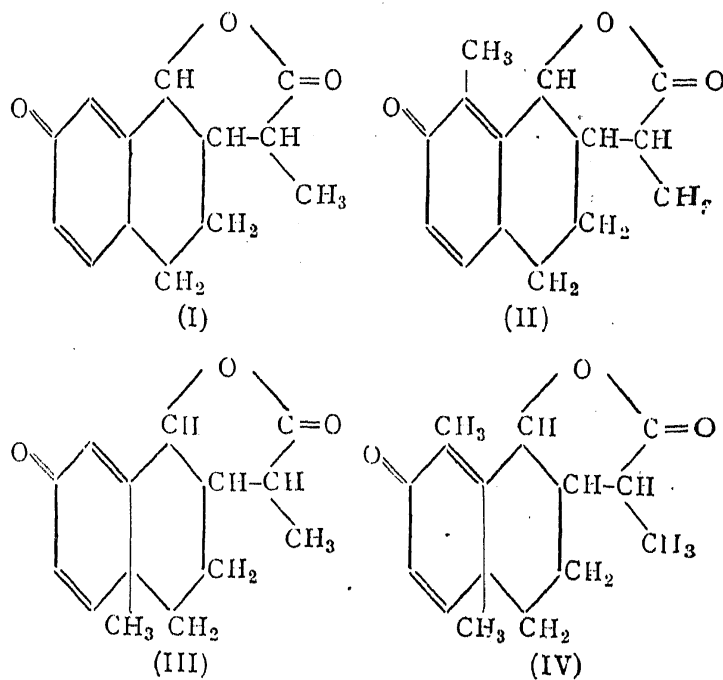
1. Perkins, *Amer. J. Sci.*, 1910, **29**, 4, 540. 2. Gooch, and Curtis, *Ibid.*, 1904, **17**, 4, 41. 3. Ramsay, *J. Amer. Chem. Soc.*, 1916, **38**, 2369. 4. Ditz and Bardach, *Z. anorg. chem.*, 1915, **93**, 97. 5. Viswanadham and Gopala Rao, *Curr. Sci.*, August 1914, No. 8, 229.

AN ABSOLUTE ASYMMETRIC SYNTHESIS

AN absolute asymmetric synthesis consists in the preparation of an optically active molecule without using at any stage of the synthesis an optically active reagent and without using any of the methods of resolution. Some cases of asymmetric synthesis using polarised light, etc., have been reported but an unequivocal synthesis without the use of such agencies has not been reported. Such an asymmetric synthesis has now been observed for the first time in our work on the synthesis of santonin and related compounds.

The synthesis of santonin (IV) has already been reported.¹ Using similar methods we have prepared compounds (I), (II) and (III).

As all these compounds were expected to be racemic an attempt was made to resolve them by the usual methods. Compounds (I) and (II) were really racemic and could be readily resolved through their strychnine salts into the dextro and lævo forms. The dextro form of (I) had $[\alpha]_D^{28} = +112$ and its lævo form



had $[\alpha]_D^{28} = -112$. Similarly the dextro form of (II) had $[\alpha]_D^{28} = +158.5$ and the lævo form had $[\alpha]_D^{28} = -158.5$.

The synthetic samples of (III) and (IV) were on the other hand optically active with $[\alpha]_D^{28} = -104$ and $[\alpha]_D^{28} = -154$ respectively. (IV) was converted into the sodium salt and fractionally precipitated as the strychnine salt by strychnine hydrochloride or strychnine. From the strychnine salt precipitated, on decomposition, it was possible to regenerate (IV) having $[\alpha]_D^{28} = -172$ (m.p. 171) identical with natural santonin. The filtrates from above gave a lævo rotatory compound having $[\alpha]_D^{28} = -108$ (m.p. 171) but no dextro rotatory isomer could be isolated. Thus an absolute asymmetric synthesis had occurred at some stage of the synthesis of these compounds. Our previous statement that synthetic santonin was racemic, therefore, requires correction. A careful study of the various stages for optical activity revealed that asymmetric synthesis must have occurred either during methylation of the formyl derivative or during its subsequent condensation with the ketone. All the rotations were determined in chloroform solution.

Further work on the mechanism of this asymmetric synthesis is in progress.

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