Electron Bombardment as a Means of Material Transfer

HITHERTO, the two recognized methods for transferring material from one electrode to others in vacuum have been (1) heat treatment, (2) sputtering by positive ion bombardment. In the course of some work at the G.E.C. Laboratories, it appeared that it was also possible to achieve similar effects by the use of electron bombardment.

Targets of barium, strontium, cæsium and sodium were bombarded with electrons of varying energy, and the effects of the bombardment —the transferring of these materials to other electrodes in the vacuum —were demonstrated by the changes in thermionic emitting properties of a test cathode of strontium oxide.

In the normal case of a coherent target, the processes involved in the transfer do not include a rise in the body temperature of the target ; but, where the target particles are loosely held and the current density is high, it has been possible to see the characteristic colour of the metallic vapour, indicating a kind of instantaneous vacuum distillation. The bombardment appears to produce positive ions of the metal, rather than neutral atoms, since it was possible to focus them back to the cathode by the focusing action of the electric field between the target and test cathode.

Electron microscope studies of the cathode surface showed the brightening arising from the building up of one or more layers of electro-positive material ; indeed, the enhanced space current is very likely due to 'thin film' emission.

The threshold bombarding voltage varies from element to element. It is usually high, of the order of some hundreds of volts, and both voltage and total energy appear to be necessary factors in the build-up.

It is hoped to publish these results in full at a later date.

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Selective Hydrogenation of Polyethenoid Fatty Compounds : a Possible Mechanism

IT has long been known[1,2] that, when a mixture of linoleic and oleic glycerides is catalytically hydrogenated, the linoleic groups are reduced to the mono-ethenoid condition before any appreciable quantity of saturated (stearic) glycerides is produced. Whereas this selectivity is extremely marked in glycerides or other mixtures of unsaturated esters, it is much less prominent when corresponding mixtures of unsaturated acids are hydrogenated[2]. Further, Richardson et al.[3] observed that selectivity is not so fully developed during hydrogenation of whale or other marine animal oils, wherein polyethenoid acids of the C_{18}, C_{20} and C_{22} series are prominent ; and Harper, Hilditch and Terleski[4] showed that up to a very late stage in the hydrogenation of whale oil or cod liver oil, definite proportions of unsaturated glycerides containing more than one ethenoid group persist.

In 1944 Lemon[5] showed that, in the first phase of hydrogenation of linolenic ($\triangle 9,12,15$-octadecatrienoic) glycerides, considerable amounts of a $\triangle 9,15$-octadecadienoic derivative are formed, the central ($\triangle 12$) ethenoid group having been selectively hydrogenated. Lemon's observations were recently confirmed and extended by Bailey and Fisher[6], who have given evidence (i) that $\triangle 9,12$- or $\triangle 12,15$-octadecadienoic compounds are produced concurrently with the $\triangle 9,15$-isomer (and probably in about the same total proportion) ; (ii) that, contrary to the almost completely selective conversion of linoleic ($\triangle 9,12$-octadecadienoic) compounds to mono-ethenoid compounds, linolenic groups appear to pass partly into mono-ethenoid forms concurrently with the hydrogenation of other linolenic groups to the diethenoid compounds (i) ; and (iii) that the relative rates of hydrogenation ('reactivities') of oleate, $\triangle 9,15$-octadecadienoate, linoleate ($\triangle 9,12$) and linolenate ($\triangle 9,12,15$) groups are approximately in the ratios 1 : 3 : 20 : 40.

It seems to me that all the above evidence (some of which at first sight appears almost contradictory) is in harmony with the concept that what has hitherto been termed "selective hydrogenation of polyethenoid aliphatic compounds" is in fact restricted to, and a function of, compounds in which a single —CH_2— group separates two ethenoid groups ; and that the mechanism of the selective addition of hydrogen to the unsaturated system is almost certainly connected with the ready detachment of a hydrogen atom from the central —CH_2— group in this position :

—CH:CH.CH₂.CH:CH—　　　(diethenoid, linoleic).
—CH:CH.CH₂.CH:CH.CH₂.CH:CH—　(triethenoid, linolenic).
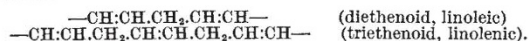
In the analogous case of the action of molecular oxygen (autoxidation) on compounds which contain these unsaturated systems, Farmer et al.[7] have shown that the products consist of hydroperoxides of the form —CH(OOH).CH:CH— ; moreover, in the di- and tri-ethenoid systems under discussion, they have suggested that under the influence of oxygen a system —CH:CH.CH.CH:CH— is transiently produced, since partial isomerization to conjugated forms —CH:CH.CH.CH₂— (or the corresponding hydroperoxides) takes place. Gunstone and Hilditch[8], confirming and extending these observations, have shown further that the relative rates of autoxidation of methyl oleate, linoleate and linolenate under comparable conditions are approximately in the ratios 1 : 12 : 25, and have commented upon the great increase in activity of the 'reactive' methylene group when it is in juxtaposition to an ethenoid group on either side.

It will be noticed that the relative reactivities of hydrogenation for oleates, linoleates and linolenates observed by Bailey and Fisher[6] are markedly similar to the corresponding rates of autoxidation ; and that in both cases the effect of the grouping —CH:CH.CH₂.CH:CH— is to increase the rate to 12–20 times that for the monoethenoid system, whereas introduction of a second 'reactive' —CH_2— group merely again doubles the rate. While direct evidence that the 'reactive'

—CH_2— group is involved in the action between catalyst, hydrogen and unsaturated complex is, of course, non-existent, this hypothesis appears not unreasonable since it accounts fully for the following observed facts :

(i) The almost completely selective hydrogenation of the $\triangle 9,12$-octadecadienoic grouping, and the production of $\triangle 9,15$- (as well as $\triangle 9,12$- and $\triangle 12,15$-) octadecadienoic compounds from $\triangle 9,12,15$-octadecatrienoates.

(ii) Since the $\triangle 9,12,15$ compound (linolenate) contains two 'reactive' —CH_2— centres, simultaneous action at both centres in the same molecule is possible, leading to some direct conversion of linolenic to monoethenoid groups (as observed by Bailey and Fisher[6]).

(iii) Since some of the poly- (tetra-, penta-, hexa-) ethenoid glycerides of marine animal oils contain the group —CH:CH.[CH_2]₂.CH:CH— as well as —CH:CH.CH₂.CH:CH—, those unsaturated systems in which a 'reactive' —CH_2— group is not present will not exhibit 'selective hydrogenation' (cf. Richardson et al.[3] ; Harper et al.[4]).

Moreover, products of partial hydrogenation of poly-ethenoid compounds (for example, in the marine animal oils mentioned, and also the $\triangle 9,15$-octadecadienoate from linolenate) may no longer contain the grouping —CH:CH.CH₂.CH:CH— and will not exhibit the selective phenomenon. (Thus, Bailey and Fisher[6] give the relative 'reactivities' of $\triangle 9,15$- and $\triangle 9,12$-octadecadienoates as 3 : 20.)

(iv) The much lessened selective action in mixtures of unsaturated acids (as compared with corresponding esters) is likewise explicable, since an additional strongly polar group (—COOH) is then present to compete with the 'reactive' —CH_2— groups and thus upset the chemi-sorption equilibrium between the latter and the hydrogenation catalyst[2,9].

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A Simple Fluorescent Indicator

A SULPHONATION product of hydrochinol (1,4-dihydroxybenzene) described as 1,4-dihydroxybenzene disulphonic acid, or disulpho-hydrochinol, shows in an alkaline medium a strong blue fluorescence, especially in ultra-violet light. It is not a new substance. It was prepared last century by A. Seyda[1], who, however, did not record its fluorescence. Seyda's method of preparation was somewhat complicated. A simpler method was described by H. Kauffmann[2], the well-known worker on the relation between absorption of light and chemical constitution of organic compounds. He recorded the fluorescence.

A fluorescence limit for a solution in water of disulphohydrochinol is pH 6–7. At pH 8 the solution turns yellow. This compound is therefore a very useful fluorescent indicator. On account of its hygroscopic qualities, it is advisable to use the potassium salt. A few drops of a 0·1 per cent solution are enough for one titration. On the acid side the solution is not fluorescent in ultra-violet light ; on the basic side it shines bright blue.

Even the purest preparation shows in alkaline solution a strong blue fluorescence. In this way the objections raised by A. Hantzsch[3,4], who stated the fluorescence is due to an accompanying impurity, are disproved. On the other hand, H. Kauffmann's[5] deductions are corroborated.

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Behaviour of Activated Iron in Sodium Hydroxide Solutions

AFTER it had been shown that strong corrosion of iron may occur in alkaline solutions in the presence of special reagents[1], the question arose regarding the corrosion conditions in the absence of the organic reagent, that is, in solutions of pure alkali hydroxide. The literature on this point is rather meagre. It has now been found that in this case also there is a decided difference between activated and non-activated iron, which, however, is generally not visible during the first days after activation but appears very slowly. After about a week, the surface of the activated iron assumes a dull lead-like appearance, thereafter turning darker and darker. After a rather long time the surface finally turns brownish, rust-like. The time needed for the whole procedure seems to vary widely with the conditions of the experiment, but several months may pass before the final state is reached. Oxidizing substances, added to the alkaline solution at the