string which is imagined stretched along the box and attached at its ends (see Figs. 11 and 12). If the system of conjugated double bonds extends over several branches in a molecule (e.g. as in the case of guanidinium ion or of fulvene) the states of the π-electrons stand in analogy to the stationary states of the transversal oscillations of a correspondingly branched stretched string fixed at its end (see Figs. 13 and 14).

It is further shown that this new approach to the problem of chemical bonding leads to a simple interpretation of the phenomenon of mesomerism, and enables an easy calculation to be made of the total π-electron charge distribution along the chain, the knowledge of which is of importance in determining the reactive behaviour of the compound. It is also possible in this manner to calculate the energy levels of the π-electron states and thus to reach conclusions about the stability of the compound and to determine the position of its absorption bands in the ultra-violet and visible spectral regions.

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The Autoxidation of Ferrous Ions in Aqueous Solution

Some time ago[1] the following mechanism was proposed for the autoxidation of ferrous ions in aqueous solutions:

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^- \qquad (1)$$

$$Fe^{3+} + O_2^- \rightarrow Fe^{2+} + O_2, \qquad (2)$$
$$(O_2^- + H^+ \rightleftarrows HO_2),$$

$$Fe^{2+} + HO_2 \rightarrow Fe^{3+} + HO_2^-, \qquad (3)$$
$$(HO_2^- + H^+ \rightleftarrows H_2O_2),$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH, \qquad (4)$$

$$Fe^{+} + OH \rightarrow Fe^{3+} + OH^-. \qquad (5)$$

In the light of a recent theoretical discussion[2] of the mechanism of electron transfer processes in solutions, it appears that the primary process, equation (1), has to be given a somewhat different interpretation and should be represented by:

$$Fe^{2+} + O_2 \rightleftarrows (Fe^{3+} \cdot O_2^-) \qquad (6)$$

leading to the formation of an ion pair complex, with a corresponding gain of Coulombic energy. A consideration of equation (6) shows that there would still be a great tendency for the reverse process, with restitution of the initial state. It seems, however, that the reverse process can be inhibited to a considerable extent if there are suitable anions (e.g. F^-, $P_2O_7^{4-}$, OH^-) present in the solution which, by reacting with the complex, can lead to its stabilisation according to:

$$(Fe^{3+} \cdot O_2^-) + F^- \rightarrow (F^- \cdot Fe^{3+} \cdot O_2^-). \qquad (7)$$

The new complex may eventually break up according to:

$$(F^- \cdot Fe^{3+} \cdot O_2^-) \rightarrow (Fe^{3+} \cdot F^-) + O_2^- \qquad (8)$$

or

$$(F^- \cdot Fe^{3+} \cdot O_2^-) + H^+ \rightarrow (Fe^{3+} \cdot F^-) + HO_2 \qquad (9)$$

followed again by the sequence of reactions given previously. Thus, one of the functions of these anions is evidently to stabilise the primary complex, apart from complexing the ferric ions and suppressing reaction (2), as suggested previously. In agreement with these views, we have found[1] that under these conditions the rate of autoxidation is given by:

$$\text{rate} \propto [Fe^{2+}]\,[O_2]\,[F^-]. \qquad (10)$$

In the absence of these stabilising anions the primary complex should exhibit a great tendency to revert to the initial state and this is in full agreement with the fact that autoxidation of ferrous ions in dilute (acid) solutions is a very slow process. The slow conversion to ferric ions which takes place under these conditions has been reinvestigated and this has confirmed[1] the earlier findings of MACBAIN[2] and LAMB and ELDER[3]—that under these conditions the rate equation conforms to:

$$\text{rate} \propto [Fe^{2+}]^2\,[O_2]. \qquad (11)$$

This suggests that stabilisation of the primary complex can not only be brought about by reaction with suitable anions but that there is also a certain amount of stabilisation by the interaction with ferrous ions present in the solution, according to:

$$(Fe^{3+} \cdot O_2^-) + Fe^{2+} \rightleftarrows (Fe^{3+} \cdot O_2^- \cdot Fe^{2+}) \rightleftarrows \qquad (12)$$
$$(Fe^{3+} \cdot O_2^{2-} \cdot Fe^{3+})$$

leading to another complex which is also stabilised by Coulombic forces and which may subsequently break up,

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[1] J. WEISS, Naturwissenschaften *23*, 64 (1935).
[2] J. WEISS (in preparation).

[1] W. TAYLOR and J. WEISS (in preparation).
[2] J. W. McBAIN, J. Phys. Chem. *5*, 631 (1901).
[3] A. B. LAMB and L. W. ELDER, J. Amer. Chem. Soc. *53*, 144 (1931).

e.g. according to:

$$(\mathrm{Fe^{3+}\cdot O_2^{2-}\cdot Fe^{3+}}) + \mathrm{H^+} \rightarrow 2\,\mathrm{Fe^{3+}} + \mathrm{HO_2^-} \qquad (13)$$

followed again by the reaction sequence given above.

This somewhat more detailed interpretation of the primary process given above arises from the assumption that, in the case of an endothermic process, an unstable intermediate ionic complex may be stabilised by Coulombic interactions, a principle which appears to have wider applications in the mechanism of electron transfer processes in solution.

A full account will be published elsewhere. J. WEISS

University of Durham, King's College, Newcastle upon Tyne, 1, England, December 1, 1952.

Zusammenfassung

Der Primärprozess des bereits vor einiger Zeit gegebenen Mechanismus der Autoxydation von Ferroionen in verdünnten wässrigen Lösungen wurde erneut diskutiert, besonders im Hinblick auf die Rolle von elektrostatischen Wechselwirkungen bei der Bildung des primären Ionenkomplexes. Es zeigt sich, dass Coulombsche Wechselwirkungen, auch mit anderen in der Lösung vorhandenen Ionen, von Bedeutung für die Stabilisierung des primären Ionenkomplexes sein können, und es ist sehr wahrscheinlich, dass, ganz allgemein, solche Wechselwirkungen bei Elektronenübergangsprozessen in Lösungen in Betracht gezogen werden müssen.

Steroids XL
The Oxidation of Unsaturated Steroidal Alcohols with Manganese Dioxide[1]

Within the last few years the employment of manganese dioxide for the oxidation of polyene aliphatic primary and secondary alcohols to the corresponding aldehydes and ketones respectively has been finding increasing application[2]. Quite recently the scope of this type of reaction was considerably widened by the demonstration[3] that even simple singly unsaturated primary alcohols, such as allyl alcohol, could be oxidized smoothly to the α,β-unsaturated aldehydes. We have been studying for some time the action of manganese dioxide on a variety of unsaturated steroidal alcohols. This study has led to a number of interesting observations, and has resulted in a convenient new route to testosterone, and a simple synthesis of steroidal $\Delta^{4,6}$-dien-3-ones.

The first examples to be studied were Δ^{4}-cholesten-3β-ol and Δ^{4}-22a-spirosten-3β-ol, containing the Δ^{4}-3-ol system (I*a*). In view of the insolubility of many steroids in light petroleum the solvent usually employed for oxidations with manganese dioxide[2], a variety of other solvents were investigated. It was found that oxidation proceeded rapidly by shaking (I*a*) at room temperature with freshly precipitated manganese dioxide in inert solvents such as benzene, chloroform, ethylene chloride, acetone, etc., conversion to the Δ^{4}-3-ones (I*b*) being complete in *circa* 2 hours; the latter could be isolated in excellent yield. Similarly oxidation of Δ^{5}-22a-spirostene-3β:7α-diol 3-acetate (II*a*)[1] led to the Δ^{5}-7-one (II*b*), $\Delta^{9,11)}$-22a-5α-spirostene-3β:12-diol (III*a*)[2] gave the $\Delta^{9(11)}$-12-one (III*b*), and $\Delta^{5:17(20)}$-pregnadiene-3β:21-diol[3] furnished the corresponding 21-aldehyde. All these products were isolated in satisfactory yield.

Δ^{4}-Cholestene-3β:6β-diol (IV*a*)[4] in benzene solution with manganese dioxide at room temperature was only oxidized at C-3, and Δ^{4}-cholesten-3-one-6β-ol (IV*b*) was produced in 75% yield. This procedure represents a simple new synthesis of such 6-hydroxylated Δ^{4}-3-ketones, and has already been applied in other series [*inter al.*: 6β-hydroxy-progesterone (m.p. 181–183°, $[\alpha]^{20}_{D}$ + 105° (all rotations in $\mathrm{CHCl_3}$), $\lambda^{\mathrm{EtOH}}_{max}$ 236 mμ, log ε 4·22, found: C, 75·97; H, 9·32), 6β-hydroxy-Δ^{4}-androstene-3,17-dione[5] (m.p. 192–194°, $[\alpha]^{20}_{D}$ + 114°, $\lambda^{\mathrm{EtOH}}_{max}$ 236 mμ, log ε 4·25, found: C, 75·56; H, 8·81)]. When this reaction was carried out at reflux temperature, the corresponding diketones (IV*c*) were formed.

The observation that a saturated alcohol, such as the 17β-hydroxy grouping, is stable towards manganese dioxide at room temperature opened up the way for a new synthesis of testosterone. Δ^{4}-Androstene-3:17-dione was reduced with lithium aluminium hydride to what is presumably essentially a mixture of Δ^{4}-androstene-3β:17β-diol and the 3α:17β-diol[6], which in chloroform solution with manganese dioxide at room temperature was only oxidized at C-3 to yield pure testosterone in 90% overall yield[7]. Investigation into the reaction conditions of the oxidation stage revealed that the amounts of oxide and solvent could be reduced to such an extent without loss in yield, so as to make the large-scale commercial production of testosterone by this method the simplest and most economical yet devised.

The readily available Δ^{5}-3β-ols (type V) with manganese dioxide in refluxing benzene were found to yield the corresponding $\Delta^{4:6}$-dien-3-ones (VII) in conversions of *circa* 30%. In this way the following dienones (VII) were prepared (properties given only for new compounds): $\Delta^{4:6}$-22a-spirostadien-3-one[8], $\Delta^{4:6}$-cholestadien-3-one, $\Delta^{4:6}$-androstadiene-3:17-dione[8], $\Delta^{4:6}$-androstadien-17β-ol-3-one (6-dehydrotestosterone), $\Delta^{4:6}$-pregnadiene-3:20-dione (6-dehydroprogesterone)[8], $\Delta^{4:6}$-pregnadien-20β-ol-3-one (m.p. 197–199°, $[\alpha]^{20}_{D}$ + 15°, $\lambda^{\mathrm{EtOH}}_{max}$ 282 mμ, log ε 4·54, found: C, 80·41; H, 9·87), $\Delta^{4:6:16}$-pregnatriene-3:20-dione (prepared from $\Delta^{5:16}$-pregnadiene-3β:20β-diol)

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[6] Cf. W. G. DAUBEN, R. A. MICHELI, and J. F. EASTHAM, J. Amer. chem. Soc. *74*, 3852 (1952).

[7] This preferential oxidation has recently been carried out in these laboratories by means of Raney nickel in acetone, albeit in poorer yield (J. ROMO, G. ROSENKRANZ, and C. DJERASSI, to be published).

[8] Identified by comparison with an authentic specimen.