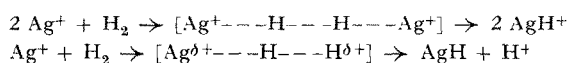Since chromium undergoes a unit valence change in the above reactions it is apparent that the transferred group is effectively a radical. Now presumably these radical reactions proceed with homolytic bond rupture whereas the oxidations in which an oxygen atom or a hydride ion are transferred proceed with heterolytic bond rupture. Yet both kinds of reaction proceed in aqueous solution and do not show marked differences in character. There is not, in fact, the sharp dichotomy to which we have become accustomed in organic chemistry between radical reactions (homolytic bond cleavage) and the so-called ionic reactions (heterolytic bond cleavage)[62]. The former reactions, because of the production of neutral reactive radicals, often proceed by chain mechanisms and the rates are often largely independent of solvent whereas the inorganic species, like Cr (III) which are produced by radical transfer are stable ions. In this connection it is interesting that HALPERN has shown that the homogeneous reaction of hydrogen with Ag^+ proceeds by two paths probably involving homolytic and heterolytic bond splitting respectively[55].

$$2\,Ag^+ + H_2 \rightarrow [Ag^+\text{---}H\text{---}H\text{---}Ag^+] \rightarrow 2\,AgH^+$$
$$Ag^+ + H_2 \rightarrow [Ag^{\delta+}\text{---}H\text{---}H^{\delta+}] \rightarrow AgH + H^+$$

Hydrogen Atom Transfer to Oxidant.—The reaction of silver ion with hydrogen just referred to is an example of this process. In addition there are many well substantiated examples of oxidations proceeding by way of hydrogen atom transfer from organic compounds to free radicals[63].

HUDIS and DODSON have suggested that hydrogen atom transfer may be involved in the exchange between Fe^{+2} and Fe^{+3} in aqueous solution[64]. One might have expected some similarity to the $Fe(CN)_6^{-3}$–$Fe(CN)_6^{-4}$ exchange which proceeds by way of an electron jump through the firmly bound but polarizible coordination spheres of the central ions. However the exchange between Fe^{+2} and Fe^{+3} proceeds at only one half the rate in D_2O as in H_2O. The viscosity difference would account for only 20–30% of this effect and there seems to be little doubt that the solvent molecules play an important part in the reaction. Hydrogen atom transfer from hydrated ferrous ion, $Fe(II)\,(H_2O)_6$, to hydrolyzed ferric ion, $Fe(III)$, $(H_2O)_5OH$ would account for these results, these two ions being involved, in the light of the kinetics, in the major reaction path[64].

$$(H_2O)_5Fe(II)\text{-O}\underset{\substack{H}}{\overset{\substack{H}}{\text{---H---O-Fe(III)}}}\,(H_2O)_5$$
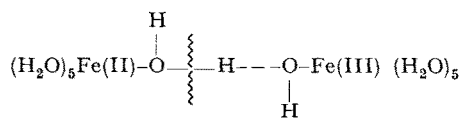
The required zero free energy change is accomodated by this mechanism since reactants and products are identical. However the isotope effect may be due, not to hydrogen-oxygen bond breaking in the activated complex, but rather to a large solvent effect. It has been shown[65] that an isotope effect of some magnitude exists even for the reaction of $Cr(NH_3)_5Cl^{+2}$ with Cr (II), a reaction which was shown to take place by chlorine atom transfer[59]. It

appears that more information on the solvating characteristics of H_2O and D_2O is required before the solvent isotope effect can be safely applied to the reactions of ions in solution.

Conclusions

The purpose of this article has not been to discredit in any way the commonly used definitions of oxidation in terms of electron transfer. Nor is it by any means intended to imply that oxidations do not occur in some cases by what could be called an electron transfer process. However sufficient evidence exists, some of which has been cited herein, to show that the mechanisms of a great many other oxidation reactions would be grossly oversimplified if they were considered as electron transfer processes. Most of these reactions are, in fact, represented quite satisfactorily by the familiar mechanisms of modern organic chemistry.

Résumé

L'emploi des isotopes a prouvé que beaucoup d'oxydations procèdent d'échanges d'atomes ou de groupes d'atomes de l'oxydant au réducteur ou vice versa. Ici, le mécanisme des oxydations comportant l'échange de telles matières en tant qu'atomes d'oxygène, ions hydrides, atomes d'hydrogène et atomes de chlor sont étudiées et discutées.

CONGRESSUS

DENMARK

The Finson Memorial Congress

Copenhagen, July 31 to August 5, 1960

The 3rd International Congress on Photobiology will be held in Copenhagen July 31–August 5, 1960. President of the Finson Memorial Congress is BØRGE CHR. CHRISTENSEN, M.D., Dr. Sc., The Finson Memorial Hospital, Strand boulevard, Copenhagen. The Secretary General of the Congress is Dr. techn. B. BUCHMANN, Biofysisk Laboratorium, Juliane Mariesvej 30, Copenhagen. The program of the Congress will consist of contributed papers and of a series of symposia on the following topics:

Biological action spectra;
Initial mechanisms involved in radiation effects;
Phototherapy;
Photoreceptors in aquatic organisms;
The results of the 3rd International Geophysical Year in regard to radiation;
Plant Cell response to visible light excluding photosynthesis;
Biological clocks;
The effects of long visible and near infrared radiation;
Photoreactivation–invited papers for a session.

Inquiries may be sent to the President or to the Secretary General of the Congress.

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