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London, S.W.7.
March 23.

¹ Waters, W. A., "The Chemistry of Free Radicals", 183 (Oxford University Press, 1946); compare Kharasch, M. S., Engelman, H., and Mayo, F. R., *J. Org. Chem.*, **2**, 288 (1937).

² Mayo, F. R., and Walling, C., *Chem. Rev.*, **27**, 351 (1940).

³ Price, C. G., "Mechanisms of Reactions at Carbon-Carbon Double Bonds", 63 (Interscience Publishers, Inc., 1940); see also Remick, A. E., "Electronic Interpretations of Organic Chemistry", 275 (J. Wiley and Sons, 1943).

⁴ Koelsch, C. F., and Boekelheide, V., *J. Amer. Chem. Soc.*, **66**, 412 (1944).

DR. BARTON's term 'high differential electron density' is quite useful for explaining more precisely my early, and vague, statement that "free radicals attack molecules preferentially at points of high electron density"¹. Obviously *electron-availability* is an essential requisite for free radical reactions. Free neutral radicals, such as Br·, CH₃·, or C₂H₅·, are electrophilic reagents in so far as they tend to complete their electron octets, and this end they can achieve (a) by combining with another unpaired electron, as in CH₃· + ·NO → CH₃-NO; (b) by combining additively at one of the easily available π-electrons of an olefinic bond; or (c) by abstracting an outer atom *plus* one electron from another molecule, as in Cl· + HCH₃ → Cl-H + ·CH₃. The ease of reaction is a > b > c, and this is the order of available electron densities at the atom which is attacked.

Dr. Barton concerns himself with process (b), and here it is the differential electron density at the two ends of the π-electron bond of the olefine which is important. It is to be judged, as he points out, by taking into account both inductive and mesomeric effects of substituents upon the static structure of the olefine, but not the inductomeric or electromeric processes which arise when an olefine molecule becomes polarized by an approaching heterolytic reagent¹. One should remember, however, that these radical reactions are all bimolecular, and hence the essential criterion of the reactive tendency is the energy difference between the initial and the transition states. Often, as in the cases of vinyl bromide, ethyl crotonate and ethyl cinnamate, this energy difference can be gauged most easily by writing down the structures of the alternative radical addition products; for example, Br-CH-CH₂-Ph and Br-CH(PH)-CH₂·, where mesomerism is obvious in the former, but not in the latter, case. This, of course, is the point of view of Mayo and Walling, and is much more accurate than my original electron density picture, which was not intended to cover all mesomeric systems.

In the case of aromatic systems, Dr. Barton's description of the experimental facts, though un-

fortunately current, is somewhat misleading, since the substitutions of aromatic compounds by free radicals have not, on account of inherent practical difficulties, been studied quantitatively. It would be truer to say that whereas the *para*-substituted product can always be isolated, both the *ortho*- and the *meta*-isomeride are often formed in comparable amount. Forthcoming papers in the *Journal of the Chemical Society* by Prof. D. H. Hey and myself will deal with this question.

W. A. WATERS

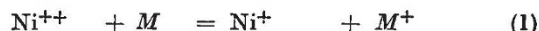
Balliol College,
Oxford.
June 3.

¹ Waters, *Trans. Farad. Soc.*, **37**, 770 (1941).

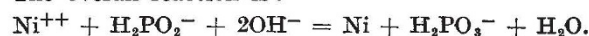
Nickel Plating by Chemical Reduction

Brenner and Riddell¹ have described a method for nickel and cobalt plating by chemical reduction of the metal salts with sodium hypophosphite under both acid and alkaline conditions. Aside from its utility, this reaction is one of considerable interest by virtue of its catalytic nature. Thus, in the concentrations they use, deposition occurs only if certain metals are immersed in the solution and, even in their presence, deposition is inhibited by the addition of such materials as potassium thiocyanate and lead in small amounts. It is suggested that some insight on both these effects and also on the unusual kinetics of the reaction is obtained by the mechanisms outlined below.

I. *Alkaline Solutions.* The initial reaction step is one of electron transfer involving nickel and hydroxyl ions at the catalytic metal surface, *M*.



The overall reaction is:



The interchange of electrons between the nickel ion and the surface will, following Michaelis², take place in one-electron steps. The Ni⁺ ion first formed can then acquire another electron or disproportionate³ to give the atom as in reaction (3).

This mechanism accounts for: (i) The necessity of a metal surface to act as an electron source and sink as in reactions (1) and (2). The generally unfavourable free energy change⁴ of reactions as OH⁻ + M_{aq.}⁺⁺ = OH + M_{aq.}⁺, where M_{aq.}⁺⁺ is the ion in solution, shows this oxidation-reduction reaction not to involve dissolved ions of the catalytic metal but electrons present at various levels in the bulk metal as such. (ii) The non-catalytic nature of glass and plastic in their inability to take part in the electron transfer reactions (1) and (2). (iii) The action of inhibitors and the incidence of passivity in their effect on the electron availability at the surface. (iv) The independence of reaction-rate on the nickel concentration in the rapid nature of the electron transfer steps. (v) The dependence of the rate in linear fashion on the hypophosphite concentration in reaction (4), which involves an atom transfer step. This reaction is favourable thermodynamically, Δ*G* being approximately -130 k.cal.⁴.