422. *Studies on the Nature of Chemisorptive Bonds. Part I. Some Observed Regularities.*

By E. B. Maxted.

Some observed regularities in connection with chemisorptive bonds on metallic hydrogenation catalysts have been summarised as a basis for the experimental work described in succeeding papers of the series. The capacity of an adsorbate to form a strong chemisorptive bond to a catalyst such as platinum appears to be determined by certain types of electronic structure, which are defined in the paper for three types of strongly held adsorbed species represented respectively by compounds containing catalytically toxic elements of the sulphur or the phosphorus group, by toxic metallic ions, and by strongly adsorbed molecules containing multiple bonds, such as carbon monoxide and ethylene. The conditions which are necessary for strong bonding form evidence for the importance of *d*-band structure in adsorption and in hydrogenation catalysis by transition metals. Thus, as has already been indicated by magnetic measurements (Dilke, Eley, and Maxted, *Nature*, 1948, **161**, 804) for methyl sulphide adsorbed on palladium, the adsorption of poisons of this type, with the consequent destruction of the catalytic activity, appears to involve electron transfer from the adsorbate into the *d*-band of the transition-metal catalyst, probably with the suppression of the fractional electron deficiencies in this band which, from a consideration of magnetic susceptibilities, seem to play a part in determining the catalytic activity. In the case of the poisoning of platinum catalysts with metallic ions, it is found that catalytic toxicity (which is an indication of strong adsorption) occurs only with metallic ions in which all five orbitals of a *d* shell, immediately preceding next-order *s* or *p* valency shells, are electronically occupied.

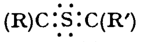
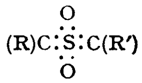
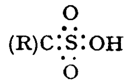
Regularities apparently also exist which correlate the catalytic activities of metals of the palladium and platinum groups with their paramagnetic susceptibilities.

Although the occurrence of some form of chemical bonding in chemisorptive linkages is inherent in the term chemisorption, little is known of the nature of such bonds. The subject is of special interest in connection with the mechanism of contact catalysis in which, in many cases, the components of the system catalysed—or some of these—become associated with a solid catalyst by the formation of chemisorptive bonds. The following two papers deal with adsorption on metallic hydrogenation catalysts; and, as an introduction to the experimental work described in these, it has been considered advisable to summarise some observed regularities which underlie and form the reason for these experimental studies.

In the first place it would seem that any investigation as to what structures are conducive to the production of the chemisorptive links formed in catalysis must include considerations of the structure both of the substances which are adsorbed and of the catalyst itself. This applies not only to hydrogenation but also to other types of contact catalysis in which, on grounds of specificity or strength of bonds and for other reasons, it appears that chemical bonding rather than general adsorption by van der Waals forces is involved. It appeared that a convenient first approach to the subject might be made by considerations derived from a study of catalyst poisoning, since the exhibition of toxic properties by a poison constitutes an easily recognisable indication of a strong bond.

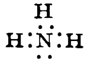
It is known that strong bonds with metallic hydrogenation catalysts of the three transition groups represented by nickel, palladium, and platinum, with their neighbours, are formed by several general types of substance including, first, molecules containing sulphur, selenium, tellurium, phosphorus, arsenic, or antimony, secondly, a large number of metallic ions and, thirdly, substances, containing certain unsaturated bonds, such as carbon monoxide, cyanogen compounds, or ethylene, which is far more strongly adsorbed than, for instance, hydrogen.

Toxicity of Non-metals of Groups Vb and VIb.—In the case of catalyst poisons of the sulphur or the phosphorus class, it has been found (Maxted and Morrish, *J.*, 1940, 252) that toxicity is dependent on the presence, in the valency shell of the toxic element, of free electron pairs which are evidently necessary for the formation of the link with the catalyst, since the toxicity—*i.e.*, the power of forming a relatively strong chemisorptive bond—disappears if the structure of the molecule is such that the normally toxic element is associated with a completely shared electron octet. Thus, as has been shown in earlier papers, organic sulphides or thiols are toxic towards a platinum catalyst whereas sulphones or sulphonic acids are non-toxic :

Toxic	 $(\mathrm{R})\mathrm{C}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}:\mathrm{C}(\mathrm{R}')$ Sulphide.	 $(\mathrm{R})\mathrm{C}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}:\mathrm{H}$ Thiol.
Non-toxic (shielded type)	 $(\mathrm{R})\mathrm{C}:\overset{\mathrm{O}}{\overset{\cdot\cdot}{\underset{\underset{\mathrm{O}}{\cdot\cdot}}{\mathrm{S}}}}:\mathrm{C}(\mathrm{R}')$ Sulphone.	 $(\mathrm{R})\mathrm{C}:\overset{\mathrm{O}}{\overset{\cdot\cdot}{\underset{\underset{\mathrm{O}}{\cdot\cdot}}{\mathrm{S}}}}:\mathrm{OH}$ Sulphonic acid.

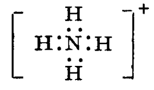
Indications have been obtained, by means of magnetic measurements (Dilke, Eley, and Maxted, *loc. cit.*), that electrons from, for instance, methyl sulphide probably enter the *d*-band of the adsorbing metal to give a co-ordinate link, the process being possibly accompanied by an elimination of any fractional electron deficiencies or holes in the *d*-band of the metal due to *d*–*s*-band overlap. It may be noticed that the sulphur atom should, after the electron transfer, be left with a formal positive charge the magnitude of which will depend on the extent of the transfer, an adsorption complex of the type $\overset{-}{M} \longleftarrow \overset{+}{S}(CH_3)_2$ being formed, in which the sign rather than the magnitude of the formal charges is indicated.

A further point of interest in connection with the above toxicity rule, namely, that strong bonds are not formed if free electron pairs in the valency shells of the sulphur atoms are absent, is to be found in the observation (Maxted and Walker, *J.*, 1948, 1093) that a nitrogen atom containing a free electron pair may be catalytically toxic. Thus, very carefully dried ammonia in, for instance, *cyclo*hexane solution was shown to be toxic towards a platinum catalyst, whereas the ammonium ion is non-toxic :



$$\begin{array}{c} H \\ H{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}{:}H \end{array}$$

Toxic.



$$\left[\begin{array}{c} H \\ H{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}{:}H \\ H \end{array}\right]^{+}$$

Non-toxic.

This capacity of a nitrogen atom of a suitable electronic configuration (cf. sulphur) to form a strong adsorptive bond with a metallic hydrogenation catalyst is of interest in that it completes the toxic series, N, P, As, Sb, (Bi), in Group Vb.

Toxicity of Metallic Ions.—The poisoning of platinum or similar catalysts by toxic metal ions falls into a somewhat different category, since the adsorption complex probably resembles an intermetallic compound. Regularities have been brought out by a further analysis of earlier work (Maxted and Marsden, *J.*, 1940, 469) which was undertaken to determine which metallic ions are toxic towards platinum. It will be seen from Table I that toxicity—namely, the power of forming a strong adsorptive bond—appears to be confined to those metals in which all five orbitals of a *d* shell, immediately preceding *s* or *p* valency orbitals, are occupied by electron pairs or at least singly; and, since no toxicity is observed if unoccupied *d* orbitals of this nature are present, or if no *d* orbitals are possible, it seems probable that *d* electrons are in some way concerned in the intermetallic bond between the toxic metal and the catalyst. The toxic metals thus differ from the non-metallic elements of Groups Vb and VIb for which strong bonds to a transition metal catalyst can apparently be formed by *s* and *p* valency electrons. The term external orbitals in the heading to the table includes the valency orbitals and the *d* orbitals immediately preceding these.

All the metallic ions listed as toxic in Table I can, by partition measurements, be shown experimentally to be strongly and preferentially adsorbed on platinum or similar catalysts even when they are present in only vanishingly small concentrations, this capacity for strong bonding to the catalyst being, as with other poisons, the essential feature for toxicity. The evidence that these strongly adsorbed ions themselves act as the effective poisons, without a change for instance into a metallic deposit, lies largely in the observed reversibility of the adsorption, namely, in the existence of well-defined adsorption–desorption equilibria. This reversibility has been tested in water and in aqueous acetic acid solution for a number of toxic metallic ions, including copper, silver, zinc, cadmium, mercury, indium, thallium, tin, lead, manganese, iron, nickel, and cobalt (Maxted, *J.*, 1925, **127**, 73; Maxted and Evans, *J.*, 1938, 2071; Maxted and Marsden, *loc. cit.*, and subsequent work), the adsorption isotherms connecting the amount adsorbed on the catalyst with the residual concentration in the supernatant liquid being in every respect similar to those given by other poisons, *e.g.*, by alkyl sulphides.

Although any subsequent change in chemical form would not in any case affect the question of the primary toxic nature of the adsorbed ion, which follows from its observed strong adsorption, it may be desirable to recapitulate some of the further evidence that the toxic effect is not in general complicated, at any rate at room temperature, by the formation of metal deposits, which is the principal possible further reaction, particularly under hydrogenating conditions. This possibility of a hydrogenation or reduction product is analogous, for instance, to the behaviour of thiophen which, although primarily adsorbed as such, passes in the adsorbed state under hydrogenating conditions almost entirely into thiophan. If, in the case of poisoning with a metallic salt solution, the observed inhibitive effect were due to any extent to mechanical covering by a metal, the greatest toxicity would be expected from the most easily reducible

TABLE I.

Metal ions tested.					Electronic occupation of external orbitals.	Toxicity towards platinum.
Li^+	Be^{2+}				No *d* shell	Non-toxic
Na^+	Mg^{2+}	Al^{3+}			No internal *d* shell	,,
K^+	Ca^{2+}				3*d* ○ ○ ○ ○ ○ | 4*s* ○	,,
Rb^+	Sr^{2+}		Zr^{4+}		4*d* ○ ○ ○ ○ ○ | 5*s* ○	,,
Cs^+	Ba^{2+}	La^{3+}			5*d* ○ ○ ○ ○ ○ | 6*s* ○	,,
		Ce^{3+}				
			Th^{4+}		6*d* ○ ○ ○ ○ ○ | 7*s* ○	,,
Cu^+	Zn^{2+}				3*d* (:) (:) (:) (:) (:) | 4*s* ○	Toxic
Cu^{2+}					3*d* (:) (:) (:) (:) ⊙ | 4*s* ○	,,
Ag^+	Cd^{2+}	In^{3+}			4*d* (:) (:) (:) (:) (:) | 5*s* ○	,,
			Sn^{2+}		4*d* (:) (:) (:) (:) (:) | 5*s* (:)	,,
Au^+	Hg^{2+}				5*d* (:) (:) (:) (:) (:) | 6*s* ○	,,
	Hg^+				5*d* (:) (:) (:) (:) (:) | 6*s* ⊙	,,
		Tl^+	Pb^{2+}	Bi^{3+}	5*d* (:) (:) (:) (:) (:) | 6*s* (:)	,,
Cr^{2+}					3*d* ⊙ ⊙ ⊙ ⊙ ○ | 4*s* ○	Non-toxic
Cr^{3+}					3*d* ⊙ ⊙ ⊙ ○ ○ | 4*s* ○	,,
Mn^{2+}					3*d* ⊙ ⊙ ⊙ ⊙ ⊙ | 4*s* ○	Toxic
Fe^{2+}					3*d* (:) ⊙ ⊙ ⊙ ⊙ | 4*s* ○	,,
Co^{2+}					3*d* (:) (:) ⊙ ⊙ ⊙ | 4*s* ○	,,
Ni^{2+}					3*d* (:) (:) (:) ⊙ ⊙ | 4*s* ○	,,

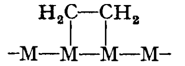
metals such as silver and gold, which is not the case. Further, any deposition of metal would not be expected in aqueous solution for many metallic ions which are toxic to platinum, including zinc, cadmium, indium, thallium, manganese, and possibly iron, cobalt, and nickel : moreover, as has been pointed out in previous papers, salts of catalytically poisonous metals have the same order of toxicity in acetic acid solution (in which still more of any possible metallic deposits would be soluble) as in water. It has also been found that the metallic salts which are poisonous for catalytic hydrogenation are also toxic in oxidation systems, for instance in the decomposition of hydrogen peroxide (Maxted, *J.*, 1922, **121**, 1760), their toxicity being again of the same order as for catalytic hydrogenation. Accordingly, the presence of hydrogenating conditions does not seem to be connected with the toxic character of these ions at room temperature.

It is of course well known from the work of Ipatiew and his co-workers (*Ber.*, 1927, **60**, 1982; 1928, **61**, 624, and other papers) that, at high temperatures and at high hydrogen pressures, aqueous solutions of many metallic salts can be reduced to the metal : thus, at a hydrogen pressure of 80 atm., the reduction of lead nitrate or acetate solution to lead is stated to begin at 275°; but, from the evidence given above, reduction to metal does not appear to occur at room temperature and pressure.

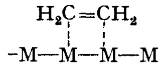
Strongly Adsorbed Substances containing Unsaturated Bonds.—A third condition for strong adsorption by a transition-group metal seems to be the possession of an unsaturated bond. This class of adsorbate is of considerable importance since it includes normal reactants—namely, the type of substance which is most usually subjected to catalytic hydrogenation—rather than extraneous catalyst poisons. By virtue, however, of rather wide differences in the strength of the adsorption bond for different individual members of the class, more strongly held unsaturated substances are also capable of acting as inhibitants towards the adsorption of less strongly held species. Thus carbon monoxide acts as a strong catalyst poison in the hydrogenation of ethylenic substances, benzene even in small concentrations retards the hydrogenation of *cyclo*hexene, and ethylene suppresses the chemisorption of hydrogen, with its attendant dissociation into atoms, at nickel or platinum surfaces : indeed, Twigg and Rideal (*Proc. Roy. Soc.*, 1939, *A*, **171**, 55) have shown that, in the hydrogenation of ethylene on nickel, no chemisorbed hydrogen atoms are present, and that the mechanism of the hydrogenation process involves the interaction of chemisorbed ethylene with hydrogen molecules which are less strongly adsorbed and may be held merely by van der Waals forces.

In the adsorption of a molecule containing an unsaturated bond a new condition arises, in that, in place of the formation of some type of normal covalent bond by interaction with the electron system of the metal, the adsorption may take place by the participation of the metal in a resonance system of the bond-multiplicity type. This type of bond seems particularly probable for adsorbates which are already in a strongly resonating state, *e.g.*, for carbon monoxide; but it is also possible for ethylene, in which bond-multiplicity resonance is low or absent in an unadsorbed state, the resonance complex for ethylene adsorbed on a metal, M, corresponding with a bond hybridisation of components of the type (I) and (II), in which either

(I.)



$$\begin{array}{c} H_2C-CH_2 \\ |\quad\;\; | \\ -M-M-M-M- \end{array}$$



$$\begin{array}{c} H_2C=CH_2 \\ \vdots\quad\;\;\vdots \\ -M-M-M-M \end{array}$$

(II.)

of these structures may predominate. From an analogy to the dative bonds with sulphur and from the general importance which the structure of the *d* band of transition metals appears to possess in catalysis, it might be expected that this fractional bonding would be to the *d* band of the metal, in which fractional electronic deficiencies occur which seem to be the seat of the catalytic activity and, since adsorption is a necessary factor in the catalysis, also of the adsorptive bonding.

Correlation between Catalytic Activity and Magnetic Properties.—In the above sections the formation of a strong chemisorptive bond towards a metallic hydrogenation catalyst has been considered mainly from the standpoint of various types of strongly held adsorbates. Any approach to the probable nature of such bonds must however also include a consideration of what configurations in the adsorbing metals themselves appear to be conducive to bond formation.

If the three groups of transition elements employed for catalytic hydrogenation are set out in order of ascending atomic number, as in Table II, it will be seen that those metals which are ordinarily associated with the most effective catalytic properties for hydrogenation fall under one another and that the activities observed in practice appear to vary, in each horizontal series, in such a way that the activity rises horizontally to a maximum at the elements enclosed in the frame and subsequently falls steeply, in that copper, silver, and gold—all of which have a completely occupied *d* shell—possess a low or even zero activity for catalytic hydrogenation.

TABLE II.

Fe (26)	Co (27)	Ni (28)	Cu (29)
Ru (44)	Rh (45)	Pd (46)	Ag (47)
Os (76)	Ir (77)	Pt (78)	Au (79)

It is of interest to note that this activity sequence is followed by the value of the paramagnetic susceptibility—at least in the two platinum-metal series, in which measurements of this susceptibility are less complicated by ferromagnetism than in the iron group and can be carried out directly in the temperature range in which platinum-metal catalysts are usually employed—this susceptibility being determined by the structure of the *d*-band, including fractional *d*-electron deficiencies or positive holes due to *d*–*s*-band overlap (which vanish in the fully occupied vertical series, copper, silver, gold) and by terms due to correlation forces (see Mott and Jones, " Theory of the Properties of Metals and Alloys," Oxford, 1936, pp. 141, 196). Values for the magnetic susceptibilities, χ, in 10^{-6} c.g.s. electromagnetic units per g. and per g.-atom at 18°, are given for the two platinum-metal groups in Table III, from which a rise to a maximum at palladium and platinum, respectively, and a subsequent fall to less than zero for silver and gold will be seen, both of these metals being diamagnetic.

This apparent connection between activity and paramagnetic susceptibility, at any rate for the groups dealt with in Table III, seems to indicate that the catalytic activity is determined by the structure of the *d* band; and, above all, the disappearance of catalytic properties with the disappearance of fractional electron deficiencies in this band strongly suggests that these deficiencies play a critical part in hydrogenation catalysis and in adsorption connected with

TABLE III.

Metal	Ru	Rh	Pd	Ag
$\chi_{g.}$	+ 0·50	+ 1·11	+ 5·4	− 0·20
$\chi_{g.\text{-at.}}$	+50·8	+114·2	+476·2	−21·6
Metal	Os	Ir	Pt	Au
$\chi_{g.}$	+ 0·05	+ 0·14	+ 1·10	− 0·15
$\chi_{g.\text{-at.}}$	+ 9·5	+ 29·0	+214·7	−29·6

this. A similar inference can be obtained by considering the probable mechanism of inactivation by poisoning, in that it has been shown that the suppression of the catalytic activity of a typical transition element by the adsorption of methyl sulphide involves electron transfer into the *d* band of the metal; and it accordingly seems by no means improbable that the poisoning process may consist of, or include essentially, the elimination of the *d*-band deficiency.

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