Recombination of Hydrogen Atoms on Various Transition Metal Surfaces

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Apart from the well-known research of Bonhoeffer⁽1⁾, in which the order of recombination activity of metals was found to be in good accordance with the series of hydrogen over-voltage, comparison of the relative activities of various kinds of metals for the recombination of hydrogen atoms was made by Katz et al.⁽2⁾ However, our present knowledge about the recombination activity of transition metals is not sufficient for the detailed discussion.

From the works just cited, it is immediately noticed that the transition metals have the highest activity among all sorts of metals, noble metals follow them, and polyvalent metals have much lower activity as compared with the former two. However, it is not yet well understood why such a distinct change in activity appears when metal species are altered, even though it might be inferred that different electronic band structures are responsible for the difference in activity.

In order to examine the dependence of recombination activity principally on the *d*-band hole, the comparison of activities was made for several transition metals available for us.

We further attempted to obtain the information about the correlation between the work function and the recombination coefficient, which had attracted our attention ever since Suhrmann⁽3⁾ had made clear many years ago the linearity between them, for it seems to be open to question whether the exact linearity would hold over all kinds of metals at all.

Trapnell et al.⁽4⁾ intended to interpret the origin of different activities in terms of the so-called Pauling's *d*-character. It is another aim of the present work to make clear in what manner the *d*-character can be related to the catalytic activity.

Experimental

In order that the place where the recombination proceeds was confined to the metal surface concerned, a method adequate to be called "an effusion method" was adopted here instead of the usual flow method.

The relative activities of Ta, W, Mo, Ti, Co and Cr were determined with respect to Ni. In the series of Fe, Cr, Mn and Cu, Cu was chosen as a standard of comparison. In another series of Ti, Zr and Th, Ti was adopted as a standard metal. U was compared only with Mo.

Samples.—Most metal samples used were in the form of a circular disk (15 or 20 mm. in diameter and 0.1~0.3 mm. thick), but Ti and Zr were ribbon-like foil. Fe and Mn were electrically plated on one side of copper plate, while Cr was evaporated on copper plate in a vacuum.

Two kinds of metals, one of which was chosen as the standard metal, were stuck together back to back by soldering or spot welding or, in unavoidable cases, by means of synthetic resin adhesives. Their surfaces were polished with 06 emery papers, but no other treatment like chemical etching or electropolishing was done at all.

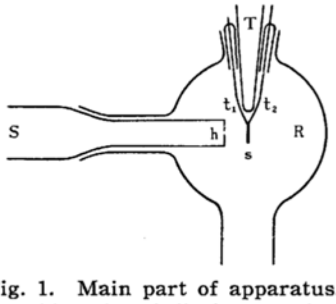

Fig. 1. Main part of apparatus.
S: The side tube of discharge tube
R: The reaction chamber
h: A small circular hole
t_1, t_2: Pt/Pt−Rh thermocouple
s: The sample
T: The top tube inside of which the city water was allowed to flow.

Apparatus and Procedure.—Only the main part of apparatus, made of hard glass, was shown in Fig. 1. Hydrogen atoms were produced in a Wood's discharge tube. The electric discharge was carried out by an alternating current from 5 kW. transformer giving up to 4000 V. The voltage across the electrodes was of the order of 1000~1500 V.

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1) K. F. Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924).
2) S. Katz, G. B. Kistiakowsky and R. F. Steiner, *J. Am. Chem. Soc.*, **71**, 2258 (1949).
3) R. Suhrmann and H. Csesch, *Z. physik. Chem.*, **B28**, 215 (1935).
4) K. G. Pickup and B. M. W. Trapnell, *J. Chem. Phys.*, **25**, 182 (1956).

The hydrogen gas including hydrogen atoms was allowed to effuse into the reaction chamber (B) through a small circular hole (h) provided at the end of the side tube (S). In this chamber the sample metal disk was hung by molybdenum wire (0.3 mm. in diameter) at the front of the hole. This chamber was strongly pumped off by an oil diffusion pump backed by a rotary oil pump, but could not be evacuated to less than 5×10^{-4} mmHg on account of leakage gas from the hole.

Even such a non-high vacuum seems to be sufficiently good to ensure that the reaction gas reaches the catalyzing metal surface not by diffusion but rather by effusion, considering the much shorter distance between the sample surface and the hole than the mean free path at the vacuum of 10^{-3} mmHg.

The temperature rise of the sample caused by recombination heat liberating on it was followed by measuring the electromotive force of Pt/Pt-Rh thermocouple attached to the sample by use of a K-type potentiometer. The sample metal disk could be allowed to turn over by virtue of the ground glass joint. Inside the tube (T), in the bottom of which molybdenum lead was sealed, the city water was allowed to flow in order to diminish the effect of the drift of room temperature on the measurements. This procedure was useful to eliminate the error resulting from temperature variation, because the drift of city water temperature was smaller than that of room temperature by a factor of about 5.

Hydrogen. — Commercial cylinder hydrogen was used. The gas was allowed to bubble through a saturated solution of sodium hydroxide. After being dried with sulfuric acid, it was passed over the platinized asbestos (ca. 400°C), and dried again over the phosphoric pentoxide. Hydrogen thus dried was sent to 3 l. flask equipped with a manostat capable of keeping the pressure constant within 0.1 mmHg.

Hydrogen was allowed to diffuse into the discharge tube through a capillary. At this stage the pressure was lowered enough to permit the electric discharge.

In order to keep the catalytic action of discharge tube wall as constant as possible, hydrogen at a pressure of about 150 mmHg was saturated with water vapour on the saturated solution of sodium hydroxide.

Result. — The electromotive forces of two thermocouples, one of which was attached to the sample and the other was immersed in a city-water stream, was read simultaneously for the intervals of 5 min. over the range of 1 to 2 hr. before and during the course of electric discharge. The values averaged over all the reads are taken as expressing the temperatures of the sample and the city-water. The difference of these temperatures varied before and after the discharge was switched on. This variation of temperature difference was adopted as the rise of temperature due to the recombination heat.

At first the temperature rise for the metal aimed at was determined, then the same procedure was applied to the standard metal of another side. The ratio of the former to the latter was adopted as a measure of the recombination coefficient. The values thus determined were summarized as follows:

a) for the case when nickel was adopted as a standard metal, Co(118), Ni(100), Ta(88), Mo(86), W(84), Ti(83) and Cr(71):

b) for the case when copper was a standard metal, Fe(167), Cr(120), Mn(111) and Cu(100).

The latter case could be converted into the former case as given below:

Fe(99), Cr(71), Mn(66), and Cu(59).

In the series of Ti, Zr and Th, the order of activity was determined as follows:

$$\mathrm{Zr} > \mathrm{Ti} > \mathrm{Th}$$

From the comparison of U with Mo, the relation

$$\mathrm{Mo} > \mathrm{U}$$

was obtained.

Discussion

In this section, present results have been discussed from several points of view through comparison of activity with physical properties. At first we confine ourselves to metals belonging to the first long period of the periodic table.

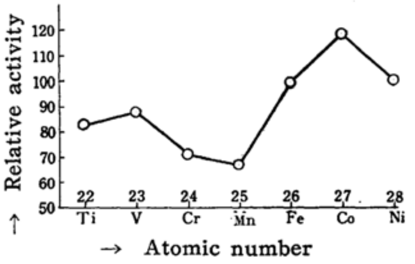

Fig. 2. The dependence of relative activity on atomic number, where Ta is taken in place of V.

In Fig. 2 is given the dependence of the recombination activity on atomic number, where tantalum is used in place of vanadium. It is perceived that this plot has two peaks at group V and group VIII. On the other hand, if the cohesive energy[5] is plotted against the atomic number, Fig. 3 curve a is obtained. It is noticed that this plot has also two peaks at the same positions. When other physical properties, e. g., the effective electron number per atom[6], density of states per eV. per atom[7], etc., are plotted against the atomic number, plots similar to the above are obtained as shown in Fig. 3 curve b. From the resemblance of these plots to the plot in

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[5] C. Kittel, "Introduction to Solid State Physics", John Wiley & Sons, New York (1956), p. 99.

[6] Ibid., p. 132.

[7] Ibid., p. 259.

Fig. 2, it is suggested that these physical properties are more or less related to the catalytic activity.

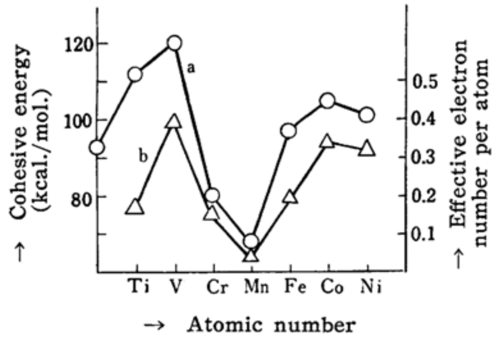

Fig. 3. Curve a, plot of cohesive energies versus the atomic number and curve b, plot of the effective electron number versus the same.

Let us consider a little further the correlation of activity with the cohesive energy. From the resemblance between the plot of cohesive energy versus the atomic number and that of activity versus the same, it is suggested that the bond strength of chemisorption which can be evaluated by an approximate method stated just below, may have an important connection with the catalytic activity. Recently, a method for evaluating the bond strength of chemisorption approximately by use of the experimental heat of sublimation and the electronegativity had been presented by Eley[8]. More recently, a somewhat different method was offered by Stevenson[9], in which the work function was used instead of the value of dipole moment in evaluating the ionic contribution.

If the semi-empirical values of bond strength of chemisorption evaluated by the above two kinds of methods are taken, plots quite similar to the relation between cohesive energy and atomic number must be obtained. From this fact, the conclusion may be drawn that metals having strong bond strength of chemisorption should have high activity. However, the statement given below has made such a view less convincing.

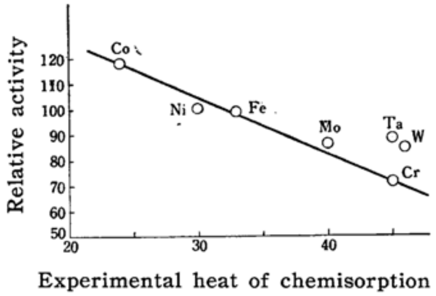

Fig. 4. The dependence of the relative activity on the experimental heat of chemisorption, where the data are taken from Stevenson's report.

Alternatively, if the recombination activities are plotted against the data on the experimental heat of chemisorption quoted by Stevenson, it is found that almost all points fall on a straight line aside from the slight upward deviation of tantalum and tungsten as shown in Fig. 4. From this fact, it is suggested that metals with strong bond strength of chemisorption are less active in contrast to the above statement deduced from the comparison of the dependence of cohesive energy on atomic number with that of activity on the same.

In order for the surface recombination to proceed, if the Rideal mechanism is assumed, hydrogen atoms need be chemisorbed first on bare metal surface and yet their bonds must have moderate strength to be ready to break on the attack of a chemisorbed layer by hydrogen atoms from the gas phase so as to reproduce hydrogen molecules, for it is supposed that the activation energy for the latter process can be approximated to be proportional to the chemisorption bond strength[10].

Obviously, the reason why polyvalent metals have low activity comes from the fact that the Brillouin zone is almost fully filled and, accordingly, only a few sites can be used for hydrogen atom chemisorption. On the contrary, in the case of transition metals with unfilled *d*-orbitals capable of supplying ample sites for the appreciable adsorption to occur, it seems likely that the bond strength of chemisorption may play a more important role in

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[8] D. D. Eley, *Discussions Faraday Soc.*, **8**, 34 (1950).

[9] D. R. Stevenson, *J. Chem. Phys.*, **23**, 203 (1955).

The surface M-H bond can be calculated from Pauling's equation

$$E(\mathrm{M-H})=1/2\{E(\mathrm{M-M})+E(\mathrm{H-H})\}+23.06(x_\mathrm{M}-x_\mathrm{H})^2$$

where $E(\mathrm{M-M})$ is one sixth of the experimental sublimation energy and $E(\mathrm{H-H})$ is the dissociation energy of hydrogen molecule. The difference of electronegativity, $x_\mathrm{M}-x_\mathrm{H}$, can be approximated as equal to the dipole moment of the bond in debyes, the values of which are known from the data on contact potential.

[10] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Process", McGraw-Hill Book Co., New York (1941), p. 152.

In the three-atom reaction $AB+C\rightarrow A+BC$, the activation energy can be approximated to be 0.055D′, where D′ is the dissociation energy plus zero point energy of AB molecule.

determining the catalytic activity than the number of sites. The correlation between the experimental heat of chemisorption and recombination activity may be understood, in a sense, in terms of different bond strength of chemisorption.

Even though it is not known at what degree of coverage recombination would proceed in the present experimental condition, the above slight deviation in the case of tantalum and tungsten might be attributed in part to such a character of adsorption as that when the heat of chemisorption of hydrogen on them decreases more markedly with increasing coverage than the case of nickel and iron[11].

However, there seems to be another explanation of the origin of low activities of some transition metals (e. g., Ti, Zr and Th). The transition metals can be grouped into two main classes[12], because of wide diversity of their behavior for hydrogen absorption. Namely, metals of group A absorb hydrogen endothermically and those of group B exothermically. As a whole, it is permissible to say that the former just corresponds to the more active group, and the latter to the less active group. Though it is not clear to what extent the parallelism between hydrogen absorption and adsorption would be preserved, some kinds of resemblance between them may be excepted to exist concerning the state of hydrogen atoms in and on metals. With this in mind, the different activities of group A and B metals can be explained in the following way: In the case of group B metals a hydride layer on which hydrogen atoms are adsorbed with difficulty, would be formed. Contrary to this, in the case of group A the usual monoatomic chemisorbed layer of hydrogen is formed serving as the intermediate compound of this recombination reaction.

Next, let us examine how the physical properties, e.g., work function, *d*-character and surface potential of chemisorbed hydrogen atom layer, may correlate to recombination activity.

In view of Suhrmann's old work it is permissible to say that the larger the work function, the higher the activity. As shown in Fig. 5 curve a, the values of work function[13] of the first long period metals show a tendency to increase with the atomic number, despite the existence of rather complex ups and downs. Such a tendency as that where both catalytic activity and work function increase with the atomic number seems to support Suhrmann's view in the limited sense. However, this view may be, if anhything, an approximation, considering the fact that with respect to recombination activity, for example, the relation $Ni < Co$, $Ti < Zr$, and $W < Mo$ was obtained by the present author, while the opposite relation holds for the work function.

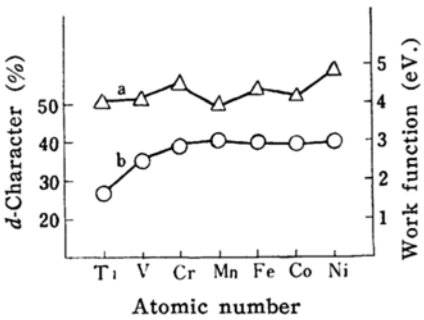

Fig. 5. Curve a, plot of the work function versus the atomic number and curve b, plot of the *d*-character versus the same.

Trapnell et al.[14] predicted that the *d*-character, which was defined by Pauling, might play an important role in the present reaction. From the present author's result it can be said that metals with large *d*-character have, on the whole, high activity. However, the monotonous increase of *d*-character with atomic number, as shown in Fig. 5 curve b is not adequate to explain the existence of two peaks in the activity-atomic number plot.

So long as the data[15] available up to date are concerned, metals can be roughly classified into two groups according to the magnitude of the absolute values of surface potential of chemisorbed hydrogen layer. The first group metals corresponding to the higher value, to which W (−0.48 or −0.65 V.) and Ta (−0.9, −1.2 or −0.43 V.) belong, have lower activity than the second corresponding to the lower value, to which Fe (−0.19 or −0.47 V.), Ni (−0.1 or −0.12 V.) and Co (0.06 V.) belong. This is naturally accepted from the statement given before, considering the fact that metals corresponding to large surface potential values have generally large experimental chemisorption heats. Accordingly, there seems to be no direct connection between

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[11] O. Beeck, *Discussions Faraday Soc.*, 8, 118 (1950).

[12] S. Dushman "Scientific Foundation of Vacuum Techniques", John Wiley & Sons, New York (1949), p. 553.

[13] H. B. Michaelson, *J. Appl. Phys.*, 21, 536 (1950).

[14] Loc. cit.

[15] J. J. Broeder, L. L. van Reijen, W. M. H. Sachtler and G. C. A. Schuit, *Z. Elektrochem.*, **60**, 838 (1956).

the degree of polarization of chemisorbed hydrogen atom and recombination activity.

Our attempt to explain the different recombination activities in terms of any one of physical properties proves less successful. This is probably because there is no strict theory capable of connecting the activity to the physical properties. At any rate, it is apparent that many more quantitative experiments remain to be done before a systematic account can be given concerning the origin of different activities of transition metals for this recombination reaction.

Summary

A study has been made of surface recombination of hydrogen atoms on various transition metals.

Hydrogen atoms were produced in the electric discharge tube by use of an alternating current. In order to prevent the reacting gas from reaching the undesired part of the sample, a method which may be called "an effusion method" was adopted here. The relative activity of two kinds of metal plates, stuck together by the solder or some such material, was determined, comparing the temperature rises of the sample by means of alternative exposure of each side surface to the reacting gas.

The following results were obtained:

a) Co> Fe> Ni> Ta> Mo> W> Ti> Cr
> Mn> Cu
b) Zr> Ti> Th
c) Mo> U

These orders of activity were examined from several points of view through the comparison of recombination activity with the work function, the *d*-character, the experimental heat of chemisorption, etc.

The present results are still fragmentary but may suffice to show a qualitative trend.

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