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Partial Molal Enthalpies of Adsorption of Hydrogen and Oxygen on Platinum and on Carbon-Supported Platinum

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Previous attempts to obtain molal enthalpies of adsorption of hydrogen and oxygen on platinum are considered critically and reasons for the difficulty in obtaining reliable results have been pointed out. Values of the partial molal enthalpy of hydrogen and oxygen on platinum have been obtained as a function of coverage and temperature using an adiabatic calorimeter with a precision of 1% or better. It is deduced that both systems form mobile layers at room temperature, but at lower temperatures the adsorption becomes localized and the thermal effect of localization is discussed. The partial molal enthalpies of adsorption of hydrogen on carbon-supported platinum show similar effects and some evidence is presented that a single layer of platinum supported on carbon does not chemisorb oxygen, but promotes oxidation of the carbon. Calorimetric evidence is presented to show that double and triple layers of platinum on carbon can be spread by successive action of hydrogen and oxygen.

Introduction

Previous measurements on the heat of adsorption of hydrogen and oxygen have been reviewed by Kwan.¹ In spite of the careful studies of heats of physical adsorption, using modern calorimetric methods,² there have been no calorimetric measurements of heats of chemisorption of hydrogen and oxygen on platinum reported to date which are reliable. The principal reason for the lack of reliability is that under ordinary conditions the equilibrium pressure of the adsorbate for coverages of less than a monolayer is usually less than 10^{-5} mm. and under these conditions the calorimeter comes to equilibrium very slowly. Thus, an apparatus is required with which the progress of the calorimeter toward equilibrium can be followed for hours duration without any appreciable uncertainty in estimating the heat loss. Only recently² have suitable methods been developed.

As part of the present investigation it has been found that a calorimeter can be made to come rapidly to equilibrium by introducing a few hundredths of a millimeter of helium into the calorimeter before any increments of the gas to be adsorbed are made. In none of the calorimetric measurements up to this time has this precaution been taken. In all previous measurements the calorimeter tended to come to equilibrium more rapidly during the early part of the adsorption of an increment of gas, but progress to thermal equilibrium became impossibly slow when the gas pressure approached zero as the final portions of the increment were being adsorbed. In a number of cases workers

based the calculated heat on the amount of gas adsorbed rapidly and corrected for the residual pressure of gas being slowly adsorbed. In making the extrapolation necessary to correct for heat leak the change in the temperature due to the progress to thermal equilibrium or any slow adsorption was, therefore, combined with the energy loss to the surroundings with no means of separating the two. The error thus caused is undoubtedly the major one, as will appear in the Experimental section of this paper.

It is concluded from Kwan's review¹ that the partial molal enthalpy of chemisorption of hydrogen on platinum black at room temperature is about 18 kcal. It is probable that the values obtained by Kwan himself from the isotherms are the most reliable values for the partial molal enthalpy of adsorption near the monolayer prior to the values presented here. It is not possible to obtain partial molal enthalpies of adsorption from the isotherms at low coverages, so little is known about the dependence of the enthalpies on coverage.

What has been said about the values of the partial molal enthalpies of adsorption of hydrogen on platinum applies equally well to the partial molal enthalpies of adsorption of oxygen on platinum. In this case it is impossible to obtain partial molal enthalpies of adsorption at room temperature and below from the isotherms because the adsorption pressure is too low near room temperature. Direct determination of the partial molal enthalpy of adsorption of oxygen on platinum has been made by Kistiakowsky, Taylor, and Perry³ and also by Maxted and Hassid.⁴ The values they found

(1) T. Kwan, *J. Res. Inst. Catalysis*, **1**, 80 (1949).

(2) For an excellent review, see D. M. Young and A. D. Crowell, "Physical Adsorption of Gases" Butterworth and Co., Ltd., London, 1961, pp. 306-311.

(3) G. B. Kistiakowsky, G. B. Taylor, and J. H. Perry, *J. Phys. Chem.*, **34**, 799 (1930).

(4) E. B. Maxted and N. Hassid, *J. Faraday Soc.*, **29**, 698 (1933).

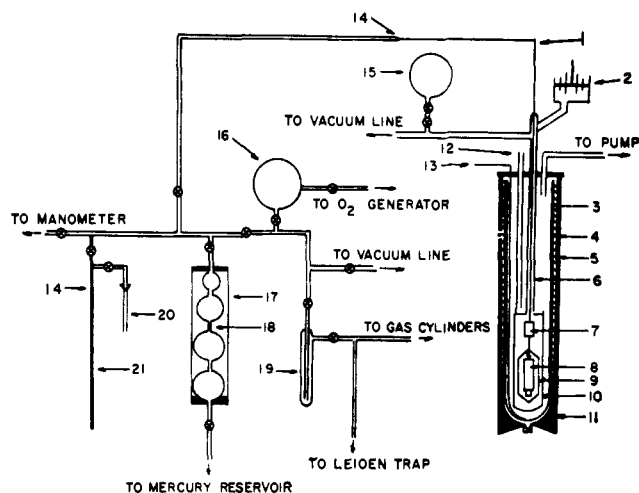


Fig. 1.—Schematic diagram of adiabatic calorimeter: 1, filling tube; 2, lead wire takeout cup; 3, dewar; 4, padding; 5, dewar case; 6, central pumping tube; 7, heat exchanger; 8, calorimeter container; 9, shield system; 10, cryostat can; 11, dewar cushion; 12, entrance for vacuum jacketed transfer tube; 13, insulated transfer tube; 14, Kovar-to-Pyrex glass seals; 15, helium exchange gas; 16, oxygen storage bulb; 17, water thermostated jacket for gas pipet; 18, calibrated gas pipet; 19, trap packed with activated charcoal; 20, water collection vial; 21, liquid helium trap.

group themselves around 45 kcal. and the inaccuracies in the measurements are so great that little can be concluded about the dependence of the heat of adsorption on coverage.

This is the situation which has caused confusion concerning the numerical dependence of partial molal enthalpies of chemisorption of hydrogen and oxygen on coverage. There has never been any serious effort made to study the temperature dependence of the enthalpies of adsorption of either hydrogen or oxygen on platinum, although a study has been made of the temperature dependence of partial molal enthalpies of adsorption of hydrogen on nickel by Eucken and Hunsmann.⁵ The results for hydrogen on nickel reveal the fact that the adsorption of hydrogen is reasonably rapid at temperatures considerably below those of the room, but near the boiling point of oxygen the rate of adsorption becomes inappreciable.

Partial molal enthalpies of physical adsorption on a uniform surface show evidence of lateral interaction.⁶ The result of the interaction is an increase in the partial molal enthalpy of adsorption with coverage, producing a maximum in the partial enthalpy of adsorption close to the monolayer. On a heterogeneous surface, this effect is counterbalanced by the fact that as the coverage of the surface proceeds, sites of lower energy are being occupied by the entering molecules. This effect tends to counterbalance the rise in partial molal enthalpies of adsorption due to lateral interaction. The result of this is that the curve tends to be flattened by the cancellation. In mobile chemisorption, lateral interaction can result from quantum mechanical exchange. It will manifest itself either by a flattening of the curve when a spectrum of energy sites exists or even may exhibit itself as a maximum in the curve.

The work of Eucken and Hunsmann⁵ is the only example, up to the present, of the application of accurate

calorimetric methods to the determination of partial molal enthalpies of chemisorption and the improvement in the meaningfulness of the data obtained with a good calorimeter is quite evident from their results. It thus seemed desirable to make studies in a precise calorimeter of the partial molal enthalpies of adsorption of hydrogen and of oxygen on platinum. Therefore, preliminary experimentation was done on the removal of oxygen from a platinum surface in order to obtain a surface of platinum at least uncontaminated by other adsorbed gases. This work,⁷ which was done with a precise adiabatic calorimeter, showed that it was possible to remove the oxygen on the surface by thermal titration. It was found that the oxygen on a platinum surface at the monolayer corresponded to one oxygen per platinum atom and, after the monolayer was reached, chemisorption of oxygen ceased entirely. Similar studies likewise showed that when less than a single layer of platinum was supported on carbon black, the platinum did not adsorb oxygen at all. The reason for this will appear presently.

Experimental

Apparatus.—The differential enthalpies of adsorption were measured in adiabatic calorimeters I and M, the details of which are given elsewhere.^{8,9} The important feature of these calorimeters in addition to the conventional adiabatic design¹⁰ is the addition of a heat exchanger which is kept at the same temperature as the sample container and brings the gas to the container temperature before adsorption. This heat exchanger is between the cryostat top and the adiabatic shield. The platinum black was packed into the sample container between equally spaced platinum disks. A conventional high vacuum pumping and gas filling system were used in connection with the calorimeter. The system had incorporated into it a German silver trap which could be immersed in liquid helium to desorb gases from the sample. Figure 1 is a schematic diagram of the system with explanatory legend.

The temperature rise from the adsorption reaction was measured with strain-free platinum resistance thermometers A-3 and L and N No. 1512847. These thermometers had been compared with laboratory standards and the temperatures given are in terms of the National Bureau of Standards scale.¹¹ This scale was chosen because tables for this laboratory's scale below 90°K. have not yet been prepared.¹² For the purpose of reference 0°K. = 273.16°K. and 1 cal. = 4.1840 joules.

The pressure in the system was measured on a wide bore mercury manometer by means of a Gaertner cathetometer with two telescopes equipped with micrometer eye pieces. A calibrated gas pipet was attached to the manometer system to measure gas volumes.

The temperature rise for each gas addition was about six-tenths of one degree for hydrogen and about one to two degrees for oxygen. The measurement of the heat capacity of the platinum sample was made with a precision of one-tenth of one per cent and temperature measurements made to a precision of half a millidegree. The heats measured therefore should have a precision of a few tenths of a per cent.

Materials.—The platinum samples were obtained from the Englehard Co., Newark, N. J. The platinum black was taken from lot No. 5898 which was analyzed and found to have a minimum purity of 99.87% platinum. The major impurity was palladium, amounting to less than one-tenth of one per cent. The sample has a maximum chloride ion concentration of one-half of one per cent. The platinum black sample weighed 93.17 g. and had an initial nitrogen monolayer capacity of 3.3 cc./g., which

(7) H. Chon, R. A. Fisher, and J. G. Aston, *J. Am. Chem. Soc.*, **82**, 1055 (1960).

(8) J. Greyson and J. G. Aston, *J. Phys. Chem.*, **61**, 610 (1957).

(9) D. Nace and J. G. Aston, *J. Am. Chem. Soc.*, **79**, 3627 (1957).

(10) J. G. Aston, J. L. Wood, and T. D. Zolki, *ibid.*, **75**, 6202 (1953).

(11) H. J. Hoge and F. G. Brickwedde, *J. Res. Natl. Bur. Standards*, **22**, 362 (1939), R. P. 1188.

(12) G. W. Moessen and J. G. Aston, 4th Symposium on Temperature, Columbus, Ohio, 1961.

(5) A. Eucken and W. Hunsmann, *Z. physik. Chem.*, **44**, 163 (1961).

(6) J. G. Aston, H. Chon, and E. S. J. Tomesko, *Advances in Chemistry Series*, No. 33, American Chemical Society, Washington, D. C., 1961, p. 325.

was reduced through sintering to 2.0 cc./g. at the end of all measurements. Examination of the sample under an electron microscope with magnification up to 30,000 revealed that the individual particles were agglomerated to such an extent as to be indistinguishable except for sawtooth edges on large patches.

A value of the heat of adsorption of hydrogen on a completely different sample (Baker) gave results for the heat of adsorption of hydrogen in agreement with the present ones.

A small amount of the platinum black used in these experiments was put into a glass container with a vacuum jacket around the sample and a thermocouple attached to the sample. Hydrogen was admitted to the oxygen-covered platinum black under high vacuum at 280°K. Light flashes could be seen within the capsule obviously indicating a high crystallite temperature due to the heat evolved. The surface area of this sample decreased by 55% during the titration. It is apparent then that the major part of the sintering comes from the inability of the platinum black to dissipate the heat generated by the sintering. The use of small pressures of helium to facilitate heat conduction essentially eliminates this sintering. A simple calculation indicates that to reach such high surface temperatures requires diffusion of oxygen to the outer layer of black.

Some preliminary measurements were made on the sample without the use of an exchange gas in the container, and the major portion of the sintering undoubtedly took place before exchange gas was used. All measurements reported here did have helium as exchange gas present in the sample container. The effect of the low pressure of helium (10^{-2} mm.) as exchange gas was to reduce the equilibrium times for the adsorption to less than 0.5 hr. and reduce sintering by increasing the heat conduction in the container. The platinum black which was used in the initial titration experiments established the presence of a complete monolayer of oxygen.⁷ In these experiments all oxygen was removed by the addition of hydrogen to catalytically form water. For earlier data¹³ taken in this laboratory, the equilibrium times were several hours and sintering of the sample was much larger than in the present measurement. In these earlier measurements the initial total nitrogen monolayer capacity of the black was reduced from 1090 cc. STP to about 400 cc. STP.

The carbon-supported platinum contained 20% platinum by weight. The sample weighed 32.04 g. and had a total nitrogen monolayer capacity of 244.4 cc./g. STP. The amount of platinum on the carbon black amounted to 6.408 g. Assuming that hydrogen absorbs in the ratio of one hydrogen atom per platinum atom, the hydrogen monolayer capacity is 368.0 cc. H₂ STP. It is apparent from the data that this was the case only after several runs, the first of which had a monolayer capacity of only about 280 cc. STP. In all cases, a small pressure of helium was added for heat conduction during the calorimetric measurements.

The oxygen was prepared by the thermal decomposition of potassium permanganate, neglecting the first portions of the gas, and then by passage of the gas through potassium hydroxide and silica gel. The middle fraction was further purified by condensing the gas in a trap immersed in liquid nitrogen and subsequent evaporation. The middle portion of the liquid was collected and stored in a previously evacuated glass bulb.

The hydrogen used was taken from the laboratory supply which is generated electrolytically and stored in cylinders. It has less than 0.01 mole % impurity.

Preparation of the Surface.—A clean surface was obtained by removing the monolayer of oxygen by thermal titration with hydrogen.⁷ This technique involves, simply, the observation of the differential heat of reaction of hydrogen with oxygen on platinum. When the stoichiometric ratio is reached, the differential heat of reaction decreases sharply. The adsorbed water was conveniently removed by heating the calorimeter to 85° and desorbing water into a trap cooled to liquid helium temperature after pumping away the helium in the calorimeter cooled to below 200°K. In the case of the pure platinum black, the amount of oxygen removed quantitatively corresponded to the amount of oxygen removed as estimated from the differential heats.

Measurements of the Differential Enthalpies of Adsorption.—The platinum surface was cleaned as described, and an amount of helium (10^{-2} mm.) was added to the sample container. With the exchange gas, equilibrium times were on the order of 20 to 30

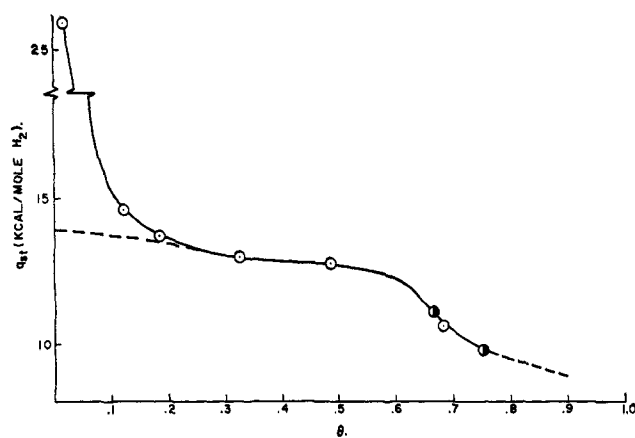


Fig. 2.—Partial molal enthalpies of adsorption of hydrogen on platinum black at 280°K.

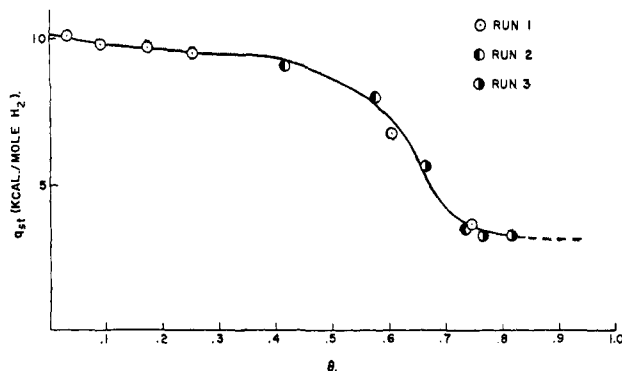


Fig. 3.—Partial molal enthalpies of adsorption of hydrogen on platinum black at 150°K.

min.; without the exchange gas, the equilibrium times were several hours. Equilibrium was considered established when there was no further galvanometer deflection for 10 min. Partial molal enthalpies of adsorption were calculated using the methods and equations described previously.¹⁴

Hydrogen.—The partial molal enthalpies of adsorption on platinum black were measured at 280 and 150°K. These results are shown in Fig. 2 and 3, in which the partial molal enthalpies of adsorption are plotted against the surface coverage θ . The monolayer capacity chosen was the final value, 2.0 cc./g. At the end of the measurements at 280°K. condensable gas was removed using a liquid helium trap after pumping away the helium with the calorimeter at low temperature. The condensable gas was water and 6.2 cc. STP (2.766×10^{-4} mole) of water vapor was collected. Evidently, oxygen had been left on the surface at the end of the titration and the high initial values are due to reaction of this oxygen with hydrogen. A dashed line has been drawn in Fig. 2 through empirically estimated values of the true enthalpy of adsorption at low coverages. This curve was estimated so as to obtain agreement with the amount of water removed from the sample upon completion of the measurements at 280°K.

The partial molal enthalpies of adsorption measured in the same way for hydrogen on the supported platinum at 280 and 150°K. are shown in Fig. 4 and 5. The monolayer value used to calculate θ was the final value of 368.0 cc. STP H₂, for the entire surface.

Oxygen.—The partial molal enthalpies of adsorption were determined on platinum black at 280, 200, and 77°K. These results are shown in Fig. 6, 7, and 8. The monolayer value used to calculate θ was 2.0 cc./g. STP. On addition of oxygen to the carbon-supported platinum oxygen was only taken up slowly and the heat evolved was eventually traced to oxidation of carbon promoted by platinum as was proved by isolating the carbon dioxide formed.

Conclusions

A previous publication¹⁵ has already summarized the general conclusions about the adsorption of hydro-

(14) G. L. Kington and J. G. Aston, *J. Am. Chem. Soc.*, **73**, 1929 (1951).

(15) J. G. Aston, *J. Phys. Chem.*, **67**, 2042 (1963).

(13) H. Chon, R. A. Fisher, E. S. J. Tomczko, and J. G. Aston, *Actes du Deuxieme Congres International de Catalyse*, 1961, Editions Technip, Paris, p. 217.

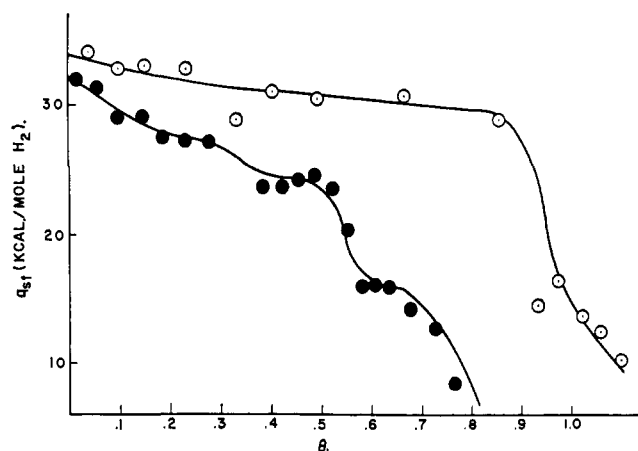


Fig. 4.—Partial molal enthalpy of adsorption of hydrogen on carbon-supported platinum at 280°K.: ●, before repeated treatment with hydrogen and oxygen; ○, after repeated treatment with hydrogen and oxygen.

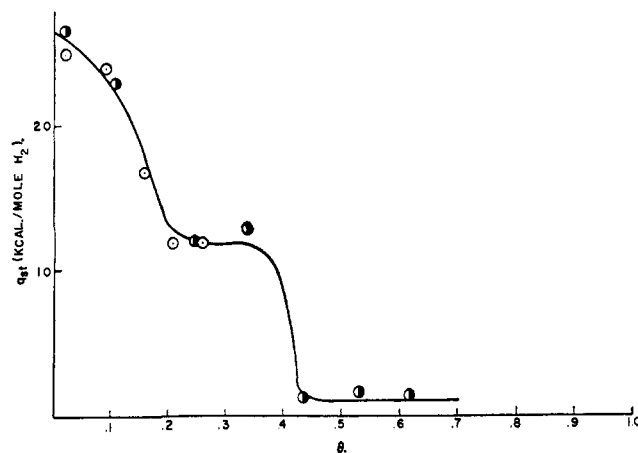


Fig. 5.—Partial molal enthalpies of adsorption of hydrogen on treated carbon-supported platinum at 150°K.

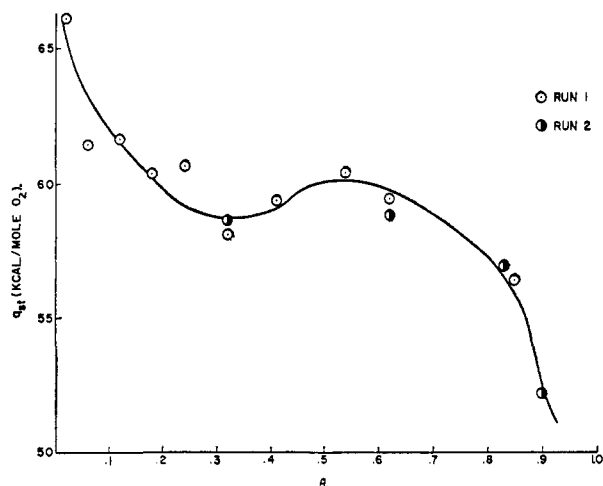


Fig. 6.—Partial molal enthalpies of adsorption for oxygen on platinum black at 280°K.

gen and oxygen on both bulk and supported platinum that can be drawn from the present experiments. Therefore, it is only necessary to explain more fully how the data lead to these conclusions.

The decrease in the partial molal enthalpy of adsorption of hydrogen between the temperatures 280 and 150°K. is about 5 kcal. at half a monolayer and a corresponding amount at other coverages. It has been

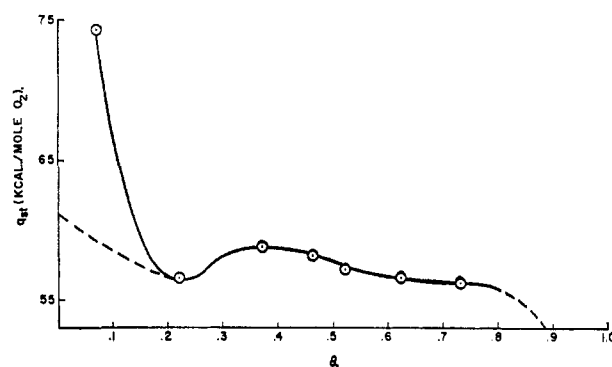


Fig. 7.—Partial molal enthalpies of adsorption for oxygen on platinum black at 200°K.

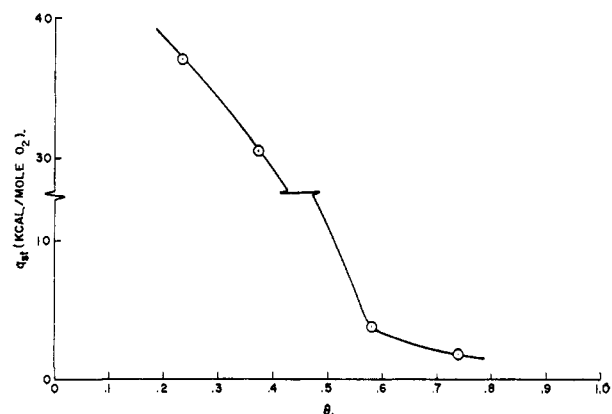
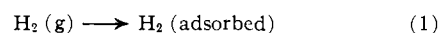


Fig. 8.—Partial molal enthalpies of adsorption for oxygen on platinum black at 77°K.

shown previously in this laboratory that the adsorbed hydrogen atoms make negligible contribution to the heat capacity of the platinum system.¹³ Thus, ΔC_p for the process



is given by

$$\Delta C_p = -C_p(\text{g}) \approx -5R/2 \approx -5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

If the difference in the measured enthalpies at the two temperatures were strictly a heat capacity effect, the enthalpy decrease obtained at 150°K. should be 650 cal./mole of H_2 (5×130) lower than that at 280°K. The observed difference in the enthalpy of over five times this calculated amount can only be caused by a temperature effect on the rate of adsorption leading to a different quasi-equilibrium at the low temperature. There are quantum mechanical grounds for believing that chemisorption of hydrogen must involve at least partial disassociation of the molecule into two atoms. The hydrogen atoms at room temperature are in a one-to-one hydrogen atom to platinum surface atom ratio and form a mobile layer.¹⁶ Thus it seems probable the hydrogen atoms form a localized layer at 150°K. which is physically distinguishable from the mobile layer at 280°K. The difference in the measured enthalpies, about 5 kcal./mole of H_2 which is much greater than the calculated thermodynamic effect, can thus be attributed to a greatly decreased mobility of the layer in quasi-equilibrium with the gas at 150°K. Quantum mechanical exchange can increase the attractive energy between neighboring hydrogen atoms in the case of mobile

(16) T. Takaish and A. Kobayashi, *J. Chem. Phys.*, **26**, 1542 (1957).

adsorption leading to an increase in the absolute value of the partial molal enthalpy of adsorption at the higher temperature. The lack of mobility at 150°K. does not allow the atoms to move under the attractive forces.

Figure 4 shows two sets of data for hydrogen adsorption at 280°K. on carbon-supported platinum. In the first run (closed circles) the partial molal enthalpies fell to a value less than 10 kcal./mole of H₂ at considerably less than monolayer coverages assuming all of the platinum exposed. It thus seems that not all the platinum atoms are exposed, *i.e.*, that there were patches on the surface with more than one layer of platinum atoms. In the second run made after the sample was saturated with oxygen, the values fell to less than 10 kcal./mole of H₂ only after the monolayer was reached. A redistribution of the platinum obviously has taken place, the platinum atoms having spread to form a complete monolayer. Although, as has already been pointed out, the carbon-supported platinum does not chemisorb oxygen, the addition of oxygen is in some way responsible for the change.

As for the platinum black, a markedly lower value for the enthalpy at the lower temperature is noted. There is one difference on the carbon-supported platinum; at 150°K. the enthalpies drop to values of physical adsorption at about $\theta = 0.45$.

The curve for the adsorption of oxygen on platinum black at 280°K. (Fig. 6) shows a slight maximum

in the measured enthalpies with increasing oxygen coverage. Since the measurements were made with a precision of about 1% and the second set of measurements fall within this precision, the maximum is probably real; however, there is certainly a point of inflection. The measurements at 200°K. show the same effect at about the same coverage. This effect suggests a cooperative process involving the adsorbed oxygen atoms. It has already been observed that the molal heat capacities of oxygen on bulk platinum are those of a hindered translator.¹³ Hindered translation can only mean a mobile monolayer. At low coverages, the oxygen must adsorb in clusters which, as the coverage increases, coalesce into larger patches with heat evolution thus accounting for the flattening of the curve. Eventually a complete oxygen atom network covers the surface with one oxygen atom per platinum atom.

At 77°K., the cooperative effect is not manifest in the results even though it is apparent that oxygen does chemisorb. In keeping with this, there is a definite difference in the type of adsorption at 77°K. Evidently the adsorbed oxygen atoms have become localized.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

The Cation Radical of Tetrakis(dimethylamino)ethylene

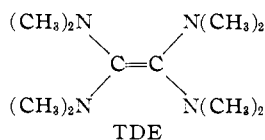
BY KEIJI KUWATA¹ AND DAVID H. GESKE

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Examination of the polarographic behavior of tetrakis(dimethylamino)ethylene (TDE) showed a two-step wave corresponding to oxidation to TDE⁺ and TDE⁺². The cation radical TDE⁺ was obtained by oxidation of TDE and reduction of TDE⁺² as well as by the homogeneous reaction of TDE and TDE⁺². The electron spin resonance spectrum of TDE⁺ was obtained. The assigned coupling constants are $a_N = 4.85 \pm 0.01$ (four equivalent N¹⁴ nuclei), $a_H = 2.84 \pm 0.01$ (twelve equivalent protons), $a_H = 3.28 \pm 0.01$ G. (twelve equivalent protons). The nitrogen coupling constant is discussed in relation to coupling constants for other nitrogenous cation radicals. Observation of two different methyl proton coupling constants is rationalized in terms of restricted rotation about the C-N(CH₃)₂ bond.

Introduction

Recent characterization of tetrakis(dimethylamino)ethylene (TDE) as a strong electron donor and the preparation of salts of the corresponding dication²



TDE⁺², strongly suggest that the paramagnetic monocation TDE⁺ should exist, at least as a transient species. The formal resemblance of TDE⁺ to the cation radical of N,N,N',N'-tetramethylphenylenediamine (Wurster's blue) is of considerable interest. We report here the electron spin resonance spectrum of the remarkably stable radical TDE⁺ as well as electrochemical parameters for the TDE system.^{2a}

(1) On leave from Osaka University, Osaka, Japan.

(2) N. Wiberg and J. W. Buchler, *Angew. Chem.*, **74**, 490 (1962); *Angew. Chem. Intern. Ed. Engl.*, **1**, 406 (1962); *Chem. Ber.*, **96**, 3223 (1963).

Experimental

Tetrakis(dimethylamino)ethylene, as prepared by the method of Pruett,³ *et al.*, was obtained from Chemical Intermediates and Research Laboratories, Cuyahoga Falls, Ohio. Since the compound is sensitive to moisture and oxygen, it was stored in a serum bottle and handled with a syringe. Tetrakis(dimethylamino)ethylene dibromide, TDE⁺²(Br⁻)₂, is precipitated when ether solutions of bromine and TDE are mixed.^{3,4} It may also be prepared by controlled potential electrooxidation of TDE at -0.1 v. *vs.* aqueous saturated calomel electrode (s.c.e.) in acetonitrile or dimethylformamide with 0.1 M tetraethylammonium bromide

(2a) NOTE ADDED IN PROOF.—The above authors² have informed us that they observed the orange color of TDE⁺ when alcoholic solutions of TDE were exposed to oxygen (J. W. Buchler, Doctoral Dissertation, University of Munich, 1963, p. 41). The mass spectrum of TDE obtained at an ionization voltage of 6.5 v. showed a small parent peak (mass 200). Above an ionization voltage of 9 v. fragmentation occurred. No TDE⁺² was formed by electron impact [N. Wiberg and J. W. Buchler, private communication; see also *Angew. Chem.*, **75**, 1112 (1963)].

(3) R. L. Pruett, K. E. Rapp, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *J. Am. Chem. Soc.*, **72**, 3646 (1950).

(4) Pruett, *et al.*,³ actually prepared this compound in 1950 and noted that the compound dissolved in water and that silver bromide was precipitated upon addition of silver nitrate. However, characterization as an ionic salt was not done.