519. *Studies of the Strength of Poison-to-catalyst Bonds. Part I. Heats of Adsorption of Ethyl Sulphide and Thiophen on Platinum.*

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The differential heat of adsorption of diethyl sulphide and of thiophen on platinum has been studied at temperatures at which this adsorption is reversible. Values for the initial adsorption heat of 65—70 kcal. per mole for ethyl sulphide, and of about 33 kcal. for thiophen, have been obtained. Thiophen, unlike ethyl sulphide, is known to be stabilised by a resonance energy of about 31 kcal.; and this observed difference of about 35 kcal. in the respective adsorption heats, which is of the same order as the resonance energy of thiophen, may support the view that thiophen, on its adsorption on platinum, loses its resonance structure, as has also been suggested for benzene.

APART from a general inference that the bonds formed between metallic hydrogenation catalysts and typical poisons, such as toxic sulphur compounds, are chemisorptive in character and that the strength of the poison-to-catalyst links must be high, little is known as to their actual bond strength. The chemisorptive nature of the bonds follows from the specificity of poisoning, in that toxicity towards platinum or similar catalysts is limited to specific structures in the poison molecule, including, in the case of a molecule containing sulphur or another inherently toxic element, the possession of a suitable electronic configuration in its valency shell.[1] The probable relatively high strength of the bond to the catalyst, compared with the bond strength of an ordinary reactant—such as an unsaturated substance in catalytic hydrogenation—may be inferred from the poisoning effect itself, since catalyst poisoning in its simplest form can be regarded as an extreme case of competitive adsorption in which what is usually a very small concentration of the poison competes effectively and obstructively for the occupation of catalyst surface with a far larger concentration of a normal reactant. On the other hand, recent observations of the reversibility of the adsorption of typical catalyst poisons, in that these can be desorbed rather unexpectedly easily into the liquid or gas phase,[2] suggest that the measured strength of poison-to-catalyst links will not be too high, otherwise poisons could not be easily desorbed. It should be noted that the above remarks apply only to poisoning at room or, at any rate, not too high temperatures, since poisoning at high temperatures may result in the decomposition of the adsorption complex. This is best known in the case of sulphur compounds on nickel, in which the rearrangement of the adsorption complex leads to the disappearance of this reversibility by the formation of nickel sulphide. All the present measurements have accordingly been made on platinum at temperatures not far removed

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[1] Maxted and Morrish, *J.*, 1940, 252, and succeeding papers.
[2] Maxted and Ball, *J.*, 1952, 4284; 1953, 3153; 1954, 2778; Maxted and Josephs, *J.*, 1956, 264.

from room temperatures and under conditions which are known from previous work to correspond to an easy and complete reversibility.

Heats of adsorption provide a convenient basis for a preliminary assessment of the order of magnitude of such bond strengths, since they represent, in a reversed sense, the energy required for the rupture of the poison-to-catalyst bond in the absence of complicating factors such as intramolecular changes in the nature of bonds within the poison molecule itself or in the bonding of the metallic surface element or elements involved to the remainder of the metallic lattice.

In the work now described, adsorption heats, on platinum, for diethyl sulphide and thiophen have been studied, these two substances being chosen as typical sulphur-containing poisons which are known to be reversibly adsorbed. An interesting secondary point also arises with these two poisons, since thiophen,[3] unlike ethyl sulphide, has a resonating structure stabilised by a resonance energy of about 31 kcal. The point in question may be developed as follows. It has been suggested tentatively by Smith, Alderman, and Nadig,[4] on the basis of regularities in the relative hydrogenation rates of a series of compounds containing a benzene ring, that the resonance in this ring is destroyed on its adsorption on platinum. If this is the case, and if the same effect occurs in the adsorption of thiophen, the experimentally determined apparent heat of adsorption of thiophen on platinum should (an approximately equal strength being assumed for the sulphur-to-platinum adsorptive bond in the case of both thiophen and of ethyl sulphide) be lower than the measured heat of adsorption of ethyl sulphide—which has no resonance complication—by a value equal to the resonance energy of thiophen since, with thiophen, 31 kcal. of the real adsorption heat would be absorbed in raising the thiophen from its more stable, and consequently lower, energy level corresponding to its stabilisation by resonance and would accordingly not appear as a rise in temperature. This effect would be somewhat similar in character to that observed by Kistiakowsky *et al.*[5] in their well-known work on the heat of hydrogenation of benzene; and the observation of such a difference between the measured heat of adsorption of ethyl sulphide and of thiophen would indicate this presumed loss of resonance by thiophen on its adsorption on platinum and would indeed constitute additional evidence for the reality of resonance itself. It was found in the present work that the initial differential heat of adsorption, *i.e.*, the heat for the first small increment of poison put on to the metal, was 65—70 kcal. for ethyl sulphide and about 33 kcal. for thiophen, the difference being about 35 kcal., which is of the same order as the resonance energy of thiophen.

EXPERIMENTAL

Apparatus.—The calorimeter used is shown in Fig. 1. It consists of two sections which, for clearness, are drawn separately. In Section I, *A* is a calorimeter bulb which, in the measurements, contained about 12 g. of platinum black, this bulb being blown as thin in the wall as possible in order to have a minimum heat capacity, and the remainder of the apparatus being of thicker glass in a manner similar to that previously used in an earlier calorimeter for the determination of the heat of adsorption of ethylene.[6] The adsorption bulb was surrounded by a vacuum jacket *B*, for thermal insulation during a heat measurement. This jacket could, alternatively, also be filled with air at atmospheric pressure when thermal conductivity was required in the initial adjustment of the platinum to the temperature of the thermostat bath in which the calorimeter was immersed, the bulb *A* being filled with helium and both the air in the jacket and the helium in the adsorption bulb being removed by high-vacuum pumping before the adsorption-heat measurement, for which the platinum has of course to be thermally insulated from the thermostat. In this evacuation process, it was necessary at all times to avoid appreciable pressure differences between *A* and *B* in order to preclude a possible collapse of the thin adsorption bulb. An extension *C* carried a closed tube into which was inserted the cold junction of the thermocouple system used for measuring the rise in temperature during an adsorption of a known small increment of poison.

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[3] Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, New York, 1939, p. 130.

[4] Smith, Alderman, and Nadig, *J. Amer. Chem. Soc.*, 1945, **67**, 272.

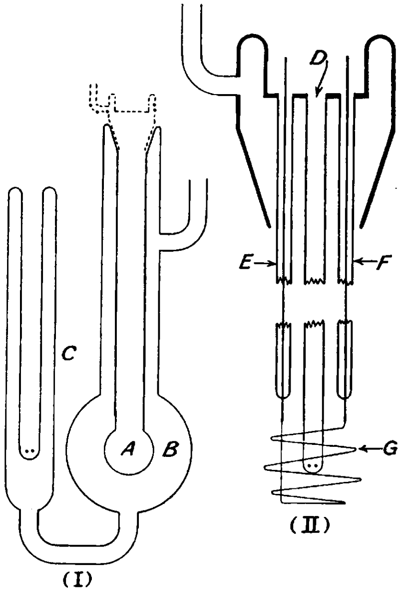
[5] Kistiakowsky, Ruhoff, Smith, and Vaughan, *ibid.*, 1935, **57**, 876; 1936, **58**, 137, 146.

[6] Maxted and Moon, *Trans. Faraday Soc.*, 1936, **32**, 1375.

Section II (drawn on a larger scale), which was inserted as a stopper into Section I, carried three tubes, closed at the lower end. Of these, the central tube *D* served as a thermocouple pocket and was thin-walled for about an inch from its lower end which, when in position, occupied a position within the spherical adsorption bulb containing the platinum in such a way that the hot junction of the thermocouple was situated centrally within this bulb. Both couples, *i.e.*, both the hot and the cold junctions, consisted of twin, series-coupled copper–constantan units, the rise in temperature during an adsorption being measured by means of a reflecting galvanometer, the original high sensitivity of which was amplified by the optical projection of the image of cross-wires on to a distant recording drum.

The remaining tubes *E* and *F* carried an electrical heating unit, *G*, by means of which the heat generated during the adsorption of a known increment of poison could subsequently be simulated and assessed by releasing, within the platinum, an adjustable and accurately known quantity of electrically generated heat. This unit consisted of a thin platinum heating filament, coiled into the form of a hollow spherical shell having half the radius of the adsorption bulb and, when in position, disposed concentrically within this bulb in such a way that the length of the path to be travelled by the heat to the thermocouple during an electrical simulation was equal to the average length of path travelled in an adsorption, on the assumption that adsorption occurs uniformly within the mass of platinum black, which assumption is, however, not quite true. The coils of this spherical heating filament were carefully covered with the thinnest possible coating of glass, applied by high-temperature painting, for insulation from the platinum black; and the ends of the heating coil were welded on to thicker copper leads passing through the sealed lower ends of the tubes *E* and *F*, in order to concentrate the production of this electrical heat into the region within the platinum black.

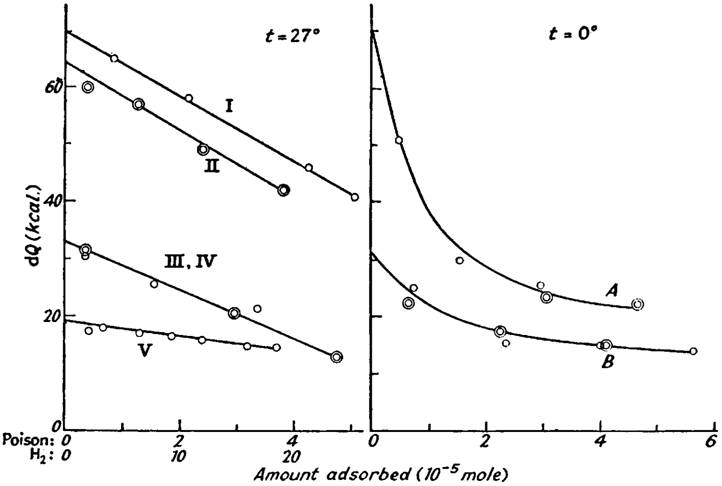
Fig. 1.



The calorimeter was immersed in a thermostat bath; and, in addition, all pertinent sections of the apparatus, including the calorimeter and its thermostat, were enclosed in a large constant-temperature box for further temperature control. The complete apparatus included provision for the addition of known volumes, at known pressures, of the vapour of the poisons used, the course of the adsorption being followed by the change in pressure indicated by a sensitive Bourdon-type spiral pressure gauge, the movement of which was, as in the temperature-measuring system, projected optically on to a distant scale, the changes in pressure and temperature in the course of each determination of an adsorption heat being measured simultaneously. The apparatus could, when required, be evacuated by a normal high-vacuum pumping system; and a limb, which could be cooled in liquid air, was also provided for "cold limb" pumping. The latter method of pumping was known to be very effective for the removal of poison from the platinum black, in the manner already described in our previous paper, and it was used when this removal was required before starting a fresh set of heat measurements.

Hydrogen diluted with nitrogen was used, followed by re-evacuation, for the necessary initial removal of adsorbed oxygen from the platinum as first placed in the apparatus. Helium was employed both for the initial calibration of the volume of various sections of the apparatus and in order to bring the gas conductivity within the adsorption bulb—during an electrical simulation of an adsorption heat—up to approximately the same value as the average conductivity during the previous adsorption run. Reservoirs containing krypton and nitrogen were sealed to the apparatus for the measurement of the surface area of the platinum by the B.E.T. method. Where mercury-filled pressure gauges were used, and also in connection with the mercury diffusion pump, possible access of mercury vapour to the platinum black was prevented by means of traps containing gold leaf and cooled in liquid air. The surface area of the platinum black used as the adsorbent was found to be 6·59 m.^{2}/g. in B.E.T. measurements with krypton and 7·05 m.^{2}/g. with nitrogen, in each case at −182°. This difference is not unexpected, since estimated areas based on nitrogen adsorption are known usually to be somewhat greater than those based on krypton.

FIG. 2. FIG. 3.



I, II, *Ethyl sulphide.* III, IV, *Thiophen.* V, H_2. *A, Ethyl sulphide. B, Thiophen.*

Heats of Adsorption of Diethyl Sulphide and Thiophen.—Before measurements were started with poisons, the general working of the apparatus was tested by determining the heat of adsorption of hydrogen. These measurements gave an initial adsorption heat of from 18 to 20 kcal. in a number of runs, in conformity with the accepted value.

The heat determinations with poisons were carried out at 27° and at 0°. The results obtained at these two temperatures are discussed separately.

(i) *Determinations at* 27°. The results at this adsorption temperature are summarised in Fig. 2. In this, curve I represents an initial series with ethyl sulphide on platinum which had not yet been brought into contact with poison. In determining the successive points on the curve, the poison vapour was added in successive small known increments, with concurrent measurements of the amount adsorbed and of the corresponding temperature rise, plotted in each case against the time. In general, the small increments used were rapidly and substantially completely adsorbed, within the limits of sensitivity of the spiral pressure gauge by means of which the course of the adsorption was followed. Individual subsequent electrical simulations of the heat effect produced by the absorption of the poison increment were used at each point on the curve. Curve II, also with ethyl sulphide, was determined after the completion of curve I, the poison absorbed during the previous series being first removed from the platinum by desorption *in situ* by cold-limb pumping. It will be seen that the points on this curve are consistently lower than those of curve I, probably owing to a not quite complete removal of the poison between the two series. When extrapolated back to zero, these two curves give values, respectively, of about 70 and 65 kcal. per mole of ethyl sulphide for the initial absorption heat, the former value being preferred since the poison may not have been completely removed.

In order to ensure the removal of poison before starting the measurements with thiophen, the platinum was taken out of the calorimeter and thoroughly revived by long-term desorption of the poison into the liquid phase according to a standard procedure which has been used for several years in this laboratory and is known with certainty to lead to complete removal of poison. The platinum treated in this manner, on being replaced in the calorimeter, gave heat values for the adsorption of thiophen shown in curves III and IV, these two representing two successive series of adsorption heat measurements, with prolonged desorption of the thiophen *in situ* by cold-limb pumping. It will be seen that, with this improvement in the removal of poison between series, the two successive curves are substantially identical and lead to an initial heat of adsorption of about 33 kcal. for thiophen.

Curve V represents a heat of adsorption series obtained with hydrogen as a reference gas.

(ii) *Determination at* 0°. Whereas the heat of adsorption plots at 27° had shown an approximately linear fall in the adsorption heat over the adsorption range studied, the plots both for ethyl sulphide and for thiophen, on lowering the adsorption temperature to 0°, were found to have an appreciable curvature from the start, with progressive increase of this curvature away from the heat axis with increasing coverage. This is shown in Fig. 3. The modified form of the plots at 0°, which represent the greatly increased weight of a curvature factor which may be present, although to a far less noticeable degree, in the very nearly linear plots at the higher temperature, does not lend itself to an accurate extrapolation of the heat values to initial poison concentrations; and these lower-temperature curves can accordingly only be regarded as providing secondary evidence for the value of the initial adsorption heat. Thus, as is shown in the Figure, these curves can reasonably be extrapolated back to the same initial heat values as have been found by the more satisfactory plots of Fig. 2.

In addition to the chemisorption which is responsible for the toxicity, the total adsorption even of a small increment of the vapour of a volatile poison almost certainly contains some van der Waals component, the weight of which increases with a decrease in the temperature and with an increase in the coverage: indeed, it is probable that the adsorption even of a small increment is primarily physical, this type of adsorption, which has no activation energy, undergoing a transition into chemisorption at a rate controlled by the activation energy of the chemisorptive form of bonding which, for many reasons, is that involved in true poisoning. This transition will occur more rapidly at higher temperatures and will indeed not be noticed if it is sufficiently fast. This may explain the curvature and the increased rate of fall of the adsorption heat with the coverage observed at 0°, since the heat of any physical adsorption is of course low. With this point in view, an attempt was made to determine the adsorption heats at 50°; but the apparatus, mainly on account of lubricated joints, was unsatisfactory for work at temperatures much above atmospheric, and modifications are being made which it is hoped will make possible the calorimetric study of higher-temperature poisoning. Excessively high temperatures, above the region of the complete reversibility of the adsorption of the poison, cannot of course be used on account of the decomposition of the poison under such conditions.

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