52. *Catalytic Toxicity and Chemical Structure. Part V. Simple Anions containing Toxic Elements.*

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The usual catalytically toxic character of elements such as sulphur, selenium, tellurium, or phosphorus is, in general, lost if the structure of the molecule containing the normally poisonous atom is such that this poison atom is associated with a completely shared electron octet. Special interest is attached to the toxicity of phosphite and hypophosphite ions from this standpoint, in view of the apparent inability of covalently linked hydrogen to exercise this shielding effect.

It is a matter of general experience that not all molecular structures containing normally toxic elements are poisonous. For instance, although sulphur in most forms is strongly toxic towards metallic catalysts in catalytic hydrogenation, no poisoning occurs if the sulphur is present as an alkali sulphate.

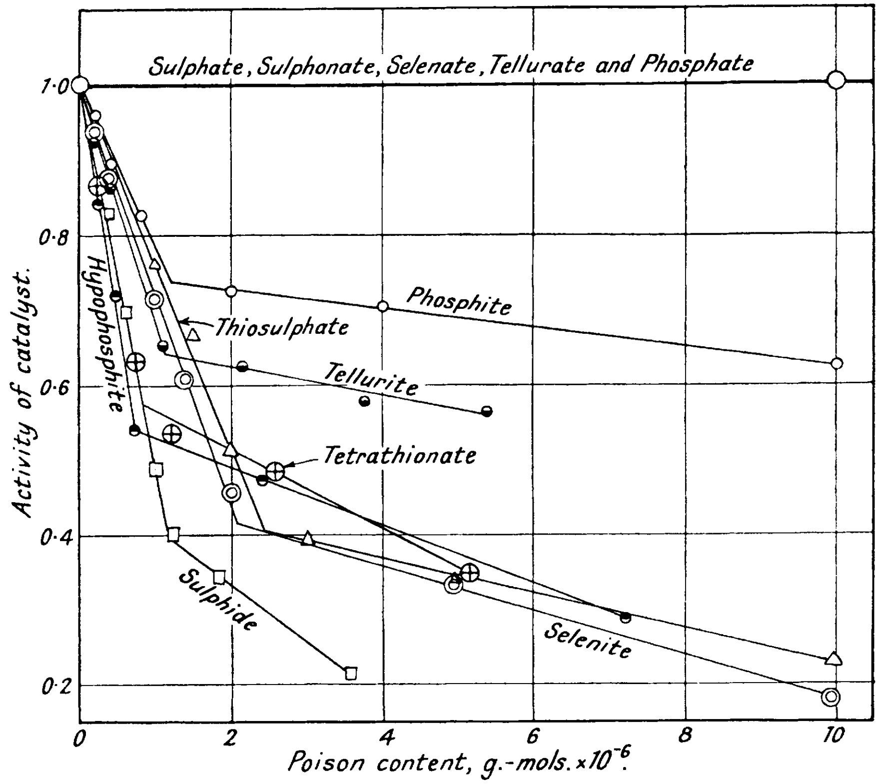
On the whole, however, little is known with regard to the type of structure necessary to shield a normally poisonous element, such as sulphur or phosphorus, in such a way that it no longer exerts its characteristic toxic properties; and it has been considered of interest, as an approach to this problem, to examine systematically the relative toxicities, in catalytic hydrogenation, of a number of simple anions containing, severally, sulphur, selenium, tellurium, or phosphorus. The subject of shielding a toxic element is of considerable practical importance, since, in preparing an impure substance for hydrogenation, it may be more convenient—as an alternative to the often difficult removal of any poison present—to convert the poisons either into a less toxic form or, better still, into a molecular form in which the inherently poisonous element is completely shielded.

The principal regularity found in the present work is one which would be expected from the dependence of catalytic toxicity on the ability of the toxic element to become linked to the catalyst to form a strongly held adsorption complex having a relatively long life, by virtue of which the surface elements of the catalyst become obstructively occupied by the poison in place of remaining free for normal catalysis. It seems probable, in chemisorption of the type involved, that the poisonous element is attached directly to the surface by ordinary covalent linkages; and, accordingly, the toxic nature of, for instance, sulphur or phosphorus should disappear if the electronic configuration of the molecule containing the toxic element is such that this element already has a completely shared electron octet, whereas the toxicity which is normally characteristic of the element in question should be shown if the element still contains unshared electron pairs. This view has been confirmed by the present work, in which the relative toxicities of sulphide, sulphite, sulphate, sulphonate, thiosulphate, tetrathionate, selenite, selenate, tellurite, tellurate, hypophosphite, phosphite, and phosphate ions, in each case towards platinum in catalytic hydrogenation, have been measured. As will be seen from the numerical results, all these ions are strong poisons with the exception of sulphates, sulphonates, selenates, tellurates, and phosphates. Since the form in which the potentially poisonous element is present must be stable under the conditions of testing, it is not possible to examine in this way the non-toxicity of substances such as the arsenates or antimonates, which, in the presence of catalytically activated hydrogen, are reduced to toxic arsine or stibine; but it was observed in earlier work that sodium arsenate was not effectively poisonous towards platinum in the decomposition of hydrogen peroxide.

EXPERIMENTAL.

The method of measuring and expressing toxicity has already been described (J., **1937**, 603, 1004). Platinum black, weighed out as required from the same stock preparation throughout the series, was used as the catalyst; and crotonic acid (or ethyl crotonate in the case of unstable ions for which it was necessary to avoid acid) was taken as a convenient standard unsaturated substance. The charge employed in the hydrogenation pipette for each test consisted of 0·05 g. of platinum, 5 c.c. of a 2N-solution of crotonic acid in glacial acetic acid—or of ethyl crotonate in alcohol—and a further 5 c.c. of solvent containing the poison. The solvent used (acetic acid or alcohol) depended on the solubility and general stability of the particular poison being investigated: for example, the degree of toxicity of sulphate and other stable ions can obviously be tested in acetic acid solution without danger of decomposition and with the advantage of a more rapid reaction, whereas, with less stable ions (*e.g.*, thiosulphates), free acid cannot be present, and, for these, alcohol and ethyl crotonate were used. Where alcohol was employed, it was, with some of the poisons, necessary to dilute this with water in order to get the poison into solution. In such cases, all the measurements with the poison in question, including the initial

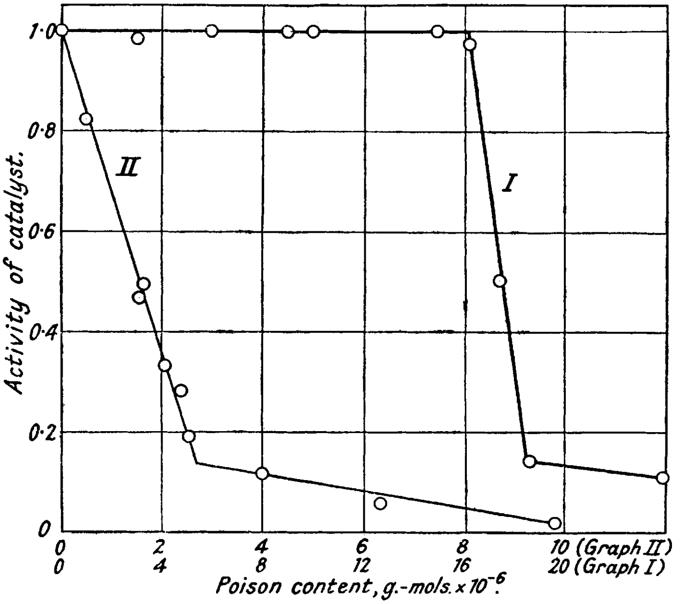
FIG. 1.



determination of the activity of the catalyst in the absence of poison, were made with alcohol of the same degree of dilution, and, in any case, the same solvent was taken both for the poison and for the unsaturated substance. It had previously been confirmed that, although the absolute hydrogenation rates are, of course, dependent on the solvent and on the substance hydrogenated, the value of the poisoning coefficient, α, which expresses the toxicity of a given poison—and is merely the fractional depression of the original activity per unit of poison present—is not affected by a change from crotonic acid to ethyl crotonate, or from acetic acid to alcohol or alcohol–water as the solvent. The temperature of hydrogenation was 25° throughout.

The very dilute solutions used for poisoning were made, by repeated dilution, from a weighed amount of the sodium salt of the anion to be tested, the sodium ion in such salts being non-toxic. In making a sulphonate solution suitable for testing in this way, it is necessary to start with a substance free from other forms of sulphur. For this reason, substances such as benzenesulphonic acid—in view of the liability of the original benzene to contain traces of thiophen and other toxic impurities—are less suitable than sulphonates of substances which are not likely to contain difficultly removable sulphur impurities. In the present case, the sodium salt of camphorsulphonic acid was used.

FIG. 2.



In order to allow a rapid general survey, the results of the measurements have been collected in Fig. 1, which includes all the anions tested with the exception of sulphites, which are discussed below. All the poisoning graphs are of the usual flexed linear form, the point of inflexion varying considerably with the nature of the ion. It will be seen that sulphates, sulphonates, selenates, tellurates, and phosphates are non-toxic; and this was also observed to be the case even with concentrations far beyond the range of the figure, *e.g.*, with concentrations of 60 × 10^{-6} g.-mol. in the 10 c.c. taken.

Toxicity of Sulphites.—If measurements of the toxicity of sulphites are made in the ordinary way, poisoning graphs of the unusual form shown in Graph I of Fig. 2 are obtained. In these, the activity of the catalyst remains completely unaffected until the concentration of sulphite passes a limiting value, whereupon normal poisoning occurs. In this case, some factor is obviously present which neutralises the toxicity of the sulphite when this is present in small quantities only; and it was thought that the initial horizontal portion in this type of variation might be due to the irreversible catalytic oxidation of sulphite to non-poisonous sulphate by oxygen contained in the platinum black or even by traces of oxygen in the hydrogen. If this is the case, the sulphite solution used will, as is actually observed, only begin to exercise its normal toxic action when the amount added is in excess of that which can be rendered inactive by the oxygen present.

This view was confirmed in two ways. First, the initial oxidation of sulphite should be prevented by using oxygen-free platinum black; and, accordingly, a series of measurements was carried out in which the charge of platinum used as the catalyst was allowed to remain in contact with hydrogen before the remainder of the system, including the unsaturated compound and the poison, was added, any oxygen in the platinum being thus converted to water before coming into contact with the sulphite. The hydrogen employed both for the initial removal of oxygen from the platinum and for the actual hydrogenation of the ethyl crotonate was carefully freed from traces of oxygen; and a special type of hydrogenation pipette was used which permitted the addition of the remainder of the system to the oxygen-free platinum without access of air. All the solutions used were made up with recently boiled solvents, which had been allowed to cool in hydrogen; and, to prevent a possible loss of activity by the platinum, through sintering, during the removal of the oxygen, the charge of metal was first of all covered with a small quantity of water. On working with an oxygen-free system in this way, a normal form of poisoning graph (see Graph II of Fig. 2) was obtained.

Secondly, the above explanation of the non-toxicity of small quantities of sulphites under ordinary conditions was also confirmed by an opposite procedure, *viz.*, by the observation that even a relatively concentrated sulphite solution could be rendered completely non-poisonous by first of all shaking this with air in the presence of platinum.

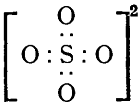
Relative Toxicities.—Since the graphs given in Figs. 1 and 2 merely represent effective toxicities, *i.e.*, the variation of the catalytic activity with the total poison present, rather than with the poison actually adsorbed on the catalytic surface (see J., **1938**, 2071), no attempt will be made for the time being to discuss the dependence of the relative toxicity, and of the position of the point of inflexion, on the size and valency of the ions. However, since the relative poisoning effect exerted by various bulk concentrations of the various ions under comparable conditions is of practical interest, these effective toxicities have been summarised in the table. The non-poisonous ions are omitted.

	Toxicity.			Toxicity.	
Ion.	$\alpha \times 10^{-5}$.	Relative toxicity.	Ion.	$\alpha \times 10^{-5}$.	Relative toxicity.
Phosphite	2·27	1·00	Sulphite	3·23	1·42
Thiosulphate	2·38	1·05	Tetrathionate	5·13	2·26
Selenite	2·86	1·26	Sulphide	5·13	2·26
Tellurite	3·12	1·37	Hypophosphite	6·25	2·75

The above values relate to the slope of the first linear portion of the poisoning graphs, this portion—with the exception of the phosphites and, to a lesser degree, the tellurites—covering the poisoning effect down to the loss by the catalyst of about one half of its original activity; α is the poisoning coefficient, derived in the manner described in earlier papers.

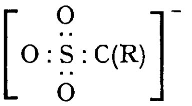
DISCUSSION.

On the whole, the results need little comment from the standpoint of the main object of the paper, *viz.*, the dependence of toxicity on the electronic configuration. It will at once be seen that, in all the non-toxic ions, the poisonous element possesses a completely shared electron octet of the type (I), in which sulphur may be replaced by selenium or tellurium, or, with a change in the valency, by phosphorus, this saturation being sufficient to prevent the central element from attaching itself to the platinum and exercising its normal toxic properties. A similar shielding is observed with the non-toxic sulphonate ion (II).



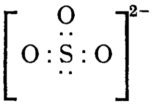
$$\left[\begin{matrix} & O & \\ O & :\overset{..}{\underset{..}{S}}: & O \\ & O & \end{matrix}\right]^{2-}$$

(I.)



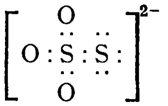
$$\left[\begin{matrix} & O & \\ O & :\overset{..}{\underset{..}{S}}: & C(R) \\ & O & \end{matrix}\right]^{-}$$

(II.)



$$\left[\begin{matrix} & O & \\ O & :\overset{..}{\underset{..}{S}}: & O \end{matrix}\right]^{2-}$$

(III.)



$$\left[\begin{matrix} & O & \\ O & :\overset{..}{\underset{..}{S}}: & \overset{..}{\underset{..}{S}}: \\ & O & \end{matrix}\right]^{2-}$$

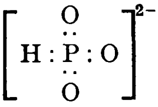
(IV.)

On the other hand, the possession of unsaturation, in the form of unshared electron pairs, by the potentially toxic atom leads at once to the free exercise of its ordinary poisonous character. For example, sulphite, selenite, or tellurite ions, which are of the type (III), also thiosulphates (IV), in which the additional sulphur atom is unsaturated, and the sulphide ion, $\left[:\overset{..}{\underset{..}{S}}:\right]^{2-}$, are all strongly toxic.

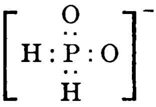
The toxicity of the tetrathionates would be expected from the presence of unsaturated sulphur in whichever of the alternative structures [Debus, J., 1888, **53**, 278; Calzolari, *Gazzetta*, 1907, (ii), **37**, 609; Riesenfeld and Feld, *Z. anorg. Chem.*, 1921, **119**, 225; Martin and Metz, *ibid.*, 1923, **127**, 82; Raschig, " Schwefel- und Stickstoffstudien," Leipzig, 1924, p. 305; Vogel, J., 1925, **127**, 2248] is accepted; but, in any case, tetrathionate ions are quickly reduced by hydrogen to thiosulphates (Thatcher, *Z. physikal. Chem.*, 1904, **47**, 691), and, actually, the observed toxicity of the tetrathionates is about twice that of the thiosulphates, which would correspond with the production, and presence at the time of the measurement, of two molecules of thiosulphate from one of tetrathionate.

Special interest is attached to the toxicity of the phosphites and hypophosphites. The usual dibasic character of phosphorous acid and the monobasic nature of hypophosphorous acid lead to the ionic structures (V) and (VI) (Lowry, *Phil. Mag.*, 1923, **45**, 1105), in which the phosphorus atom is apparently completely shielded and which should therefore, contrary to observation, not be poisonous.

(V.)



$$\left[\begin{array}{c}\mathrm{O}\\ \mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{P}}}:\mathrm{O}\\ \mathrm{O}\end{array}\right]^{2-}$$



$$\left[\begin{array}{c}\mathrm{O}\\ \mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{P}}}:\mathrm{O}\\ \mathrm{H}\end{array}\right]^{-}$$

(VI.)

Two views of this apparent anomaly seem possible. In the first place, the apparent inability of the probably covalently linked hydrogen atoms to protect the platinum catalyst from linkage with the phosphorus atom may lie in the bond-strengths of the linkages, namely, in the easily ruptured phosphorus–hydrogen bond, on the one hand, and in the strength of the potential link between phosphorus and platinum, by virtue of which poisoning occurs. The general weakness of such phosphorus–hydrogen bonds is shown by the actual evolution of hydrogen on treating a hypophosphite solution with platinum black or similar metals, as well as by the general reducing properties both of phosphites and of hypophosphites and by the production of so-called copper hydride (copper containing loosely attached hydrogen) by the action of hypophosphites on solutions of copper salts. It may be noted that a somewhat similar displacement of hydrogen covalently linked to a poison atom occurs if gaseous hydrogen sulphide is adsorbed by platinum or palladium (J., 1919, **115**, 1050; 1920, **117**, 1280; 1931, 2203), in that, on subsequent evacuation, the gas obtained consists of hydrogen rather than hydrogen sulphide, the sulphur remaining attached to the platinum.

Although the above point of view seems probably the correct one, the inability of hydrogen to shield a poisonous atom such as phosphorus may perhaps be considered from the standpoint developed by Bernal and Megaw (*Proc. Roy. Soc.*, 1935, *A*, **151**, 384) for the structure of the hydroxyl ion. They point out that, in consequence of hydrogen atoms possessing the unique property of having no inner electrons and consequently contributing nothing to repulsive forces, such atoms in combination occupy no space and in general lie *within* the effective radius of the atom to which they are bound by homopolar forces. Thus, the hydrogen atoms of the phosphite and hypophosphite ions may be regarded as lying within the *p* or valency shell of the phosphorus, which remains at any rate partly free for normal attachment, for instance to platinum.

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