211. *Catalytic Toxicity and Chemical Structure. Part II. The Influence of Chain Length in the Alkyl Sulphide and Thiol Series.*

By Edward B. Maxted and Herbert C. Evans.

In a previous paper (this vol., p. 603), the relative toxicity of a number of sulphur compounds towards platinum and nickel hydrogenation catalysts was examined. It was found that, in general, the toxicity per unit of sulphur increases with the complexity of the inhibiting molecule of which the sulphur forms part, even if the remainder of this molecule contains no elements or groups which normally act as catalyst poisons; and the effect of the permanent attachment, at one point, of a complex molecule containing—in addition to a poisonous element or group responsible for the permanent linkage—a normally non-toxic chain or ring was discussed. It was pointed out that, even if the structure of the residual chain were such that—in the absence of the anchor effect introduced by the presence of the poisonous element proper—it would be freely adsorbed and evaporated from the catalytic surface, it should, by virtue of its permanent proximity to the surface, be in a preferential position for further attachment and thus, as a result of this preferential adsorption, it might act as if it were itself toxic.

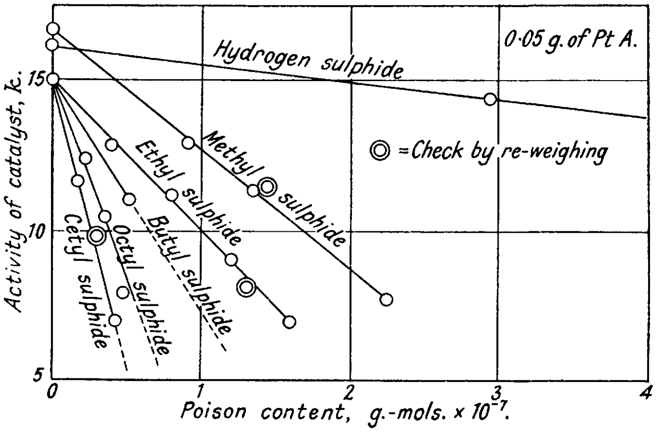
The subject has now been examined more systematically by measuring the increase in toxicity induced by the attachment to a sulphur atom of simple chains of known length; and this paper relates to relative toxicities in the alkyl sulphide and alkyl thiol series towards platinum in catalytic hydrogenation. It was found that the molecular toxicity—*viz.*, the toxicity expressed, as before, per g.-mol. of inhibitant or per unit mass of sulphur—increases, within both series of poisons, continuously with the chain length. The rate of increase in toxicity with each additional chain unit decreases, however, as the length of the chain becomes greater. This would be expected from the gradual recession of the anchor effect.

If poisoning is assumed to be caused by the obstructive coverage of potentially active surface, the increase in toxicity or covering power brought about by the attachment to sulphur of a chain of known length, and consequently of known maximum range of action, is of great interest in connection with the existence of special catalytically active points in the surface, since it allows an estimate to be made of the distance separating catalytically active surface elements and the comparison of this distance with that between the normal elements of the surface lattice. This point is dealt with in greater detail later. In view of the effect of even short chains on the toxicity, these distances are apparently identical; and it consequently seems probable that all surface elements can act catalytically. This homogeneity of a metallic catalysing surface is in agreement with evidence put forward from other standpoints (J., 1933, 502; 1934, 26, 672; 1935, 393).

EXPERIMENTAL.

The procedure employed in measuring toxicity was as described in the previous paper, to which reference should be made. In the case of each inhibitant, the activity of the catalyst at various known stages of poisoning was plotted against the poison content; and, from the slope of the poisoning graph, the poisoning coefficient, α, which is a measure of the toxicity, was calculated by means of the relationship $k_c = k_0(1 - \alpha c)$, in which k_c is the activity of the catalyst in the presence of a quantity, c, of the poison, and k_0 is its original, unpoisoned activity. As before, the rate of hydrogenation of crotonic acid in acetic acid solution was employed as a convenient standard hydrogenation reaction for the measurement of the catalytic activity, and platinum was taken as the catalyst throughout. A sufficient stock of the same standard preparation of platinum-black as had been used in the measurements previously described remained available for use throughout the alkyl sulphide series. For the measurements involving alkyl thiols, a fresh stock of platinum-black was prepared. These two standard preparations are indicated, respectively, by Platinum A and Platinum B. The system taken for hydrogenation in each case consisted, as before, of 0·05 g. of platinum, 10 c.c. of a *N*-solution of crotonic acid in glacial acetic acid, and the known quantity of poison dissolved in a further 10 c.c. of acetic acid, hydrogenation being carried out in a mechanically shaken reaction pipette, at 27°, with the previously described precautions for the standardisation of conditions.

FIG. 1.



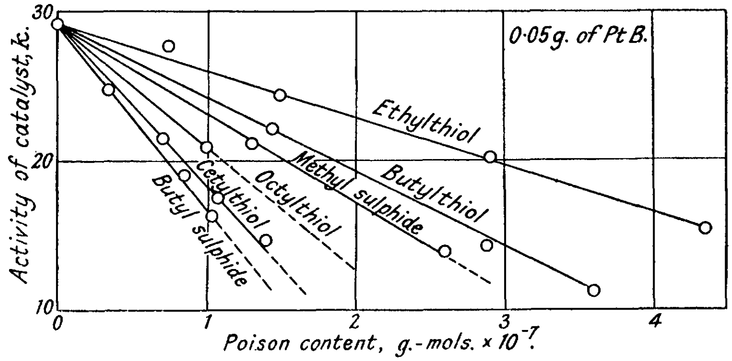
Relative Toxicity of the n-*Alkyl Sulphides*.—As representative sulphides of various chain lengths, methyl, ethyl, butyl, octyl, and cetyl sulphides were taken. These were prepared—by suitable dilution—in the form of very dilute standard solutions in acetic acid. The effect of varying quantities of these inhibitants on the activity of 0·05 g. of Platinum A is summarised in Fig. 1, in which, for purposes of comparison, has also been included the early part of the poisoning graph for hydrogen sulphide previously determined for the same preparation of platinum.

The quantity of poison present has been expressed, as before, in g.-mols. of the sulphide, equivalent to g.-atoms of sulphur. In view of the exceedingly small quantities (0·0025—0·05 mg.) of poison involved, confirmatory determinations, requiring the independent weighing out and dilution of a fresh small quantity of the inhibitant, were also made. These agreed well with the main determinations, as will be seen from the diagram, on which check measurements are indicated. As before, care was taken to limit the concentration of poison employed to that which was completely adsorbed by the platinum. The method of verifying the completeness of the adsorption, by testing the supernatant liquid, after allowing the platinum to settle, for freedom from poison by means of independent hydrogenation measurements has been referred to in the previous paper. The values of α, calculated from the slope of these graphs by means of the expression already given, are collected below.

Inhibitant.	$\alpha \times 10^{-5}$.	Relative toxicity.	Inhibitant.	$\alpha \times 10^{-5}$.	Relative toxicity.
Hydrogen sulphide	3·4	1	*n*-Butyl sulphide	51·2	15·1
Methyl sulphide	24·2	7·1	*n*-Octyl sulphide	87·7	25·8
Ethyl sulphide	34·0	10·0	Cetyl sulphide	116	34·1

Relative Toxicity of the n-*Alkyl Thiols.*—The corresponding poisoning graphs for ethyl-, *n*-butyl-, *n*-octyl- and cetyl-thiols are in Fig. 2. Since 0·05 g. of Platinum B was used for this series, in place of Platinum A, the poisoning of this second preparation of platinum by methyl sulphide and butyl sulphide was also measured in order to allow a comparison between the poisoning power of the sulphides and of the thiols; and these sulphide graphs with Platinum B are also included in the figure. The graph for octylthiol is probably less accurate than the rest, since there remained, when dealing with this poison, only sufficient of the standard materials for the determination of one point. The values of α, derived from these graphs, are given below.

FIG. 2.



Inhibitant.	$\alpha \times 10^{-5}$.	Inhibitant.	$\alpha \times 10^{-5}$.	Inhibitant.	$\alpha \times 10^{-5}$.
Ethylthiol	11·0	*n*-Octylthiol	28·6	Methyl sulphide	20·4
n-Butylthiol	17·0	Cetylthiol	37·0	*n*-Butyl sulphide	42·0

It has previously been found that, although the general sensitivity of a catalyst to poisoning may vary greatly with its physical condition—for instance with its degree of subdivision—relative toxicity, *viz.*, the ratio of the toxicity of one poison to that of another, is not changed appreciably on changing from one stock of catalyst to another. This is illustrated by the approximate constancy of the ratio between the experimentally determined values of α for methyl sulphide and butyl sulphide both for Platinum A and Platinum B :

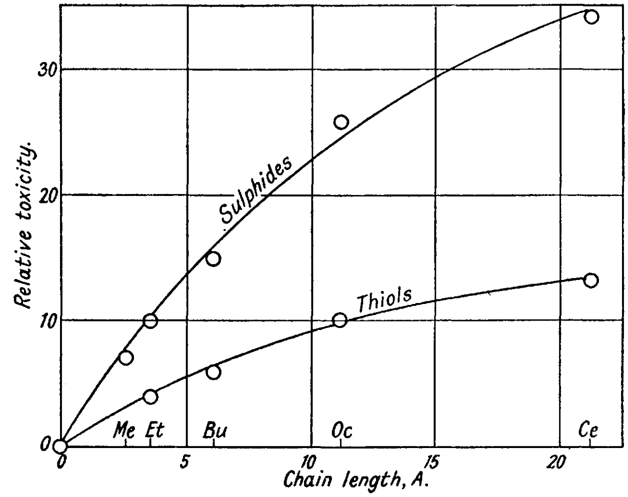
Inhibitant.	Platinum A.		Platinum B.	
	$\alpha \times 10^{-5}$.	Ratio.	$\alpha \times 10^{-5}$.	Ratio.
Methyl sulphide	24·2	2·12	20·4	2·06
Butyl sulphide	51·2		42·0	

It thus becomes possible, in spite of the change in the preparation of platinum, to compare the toxicities of the thiols with those of the sulphide series generally by reducing the poisoning coefficients to a common basis. This has been done in the following table, in which M is the molecular weight. In calculating the chain lengths, which are also included in the table, a value of 1·54 A. has been taken for the –C–C– link, resulting, by virtue of the alternating effect introduced into the flexed and reflexed chain by the tetrahedral valency angles, in a linear increment of about 2·52 A. in chain length for each two carbon atoms added. The chain lengths are those measured from the centre of the sulphur atom, the atomic radius of sulphur being taken as 1·04 A.

Inhibitant.	*M.*	Chain length (A.).	Relative toxicity.	Inhibitant.	*M.*	Chain length (A.).	Relative toxicity.
Hydrogen sulphide	34	—	1	Methyl sulphide	62	2·58	7·1
				Ethyl sulphide	90	3·50	10·0
Ethylthiol	62	3·50	3·9	Butyl sulphide	146	6·08	15·1
Butylthiol	90	6·08	6·0	Octyl sulphide	258	11·12	25·8
Octylthiol	146	11·12	10·1	Cetyl sulphide	482	21·20	34·1
Cetylthiol	258	21·20	13·1				

In addition to the general increase in toxicity within each series with increasing molecular weight or chain length, it will be seen from the above table that the ratio of the toxicity of a given sulphide—which contains two hydrocarbon chains—to that of the corresponding thiol, containing only one chain of the same length, has an approximately constant value of 2·5—2·6 : the ratios of the toxicity of ethyl, butyl, octyl, and cetyl sulphide to that of the corresponding thiol are 2·56, 2·52, 2·55, and 2·60, respectively.

FIG. 3.



Special interest is attached to the relatively great increase in toxicity brought about by the attachment to a sulphur atom of even short chains. Superimposition of a scale model of the inhibitant on a scale model of a platinum lattice—which is of the face-centred cubic type having a lattice constant of about 3·91 A., the atomic radius of platinum being about 1·38 A.—shows that there cannot at the most be more than about 9 platinum surface elements within the range of possible cover of methyl sulphide attached to the surface by its sulphur atom : yet the relative toxicity of methyl sulphide compared with that of hydrogen sulphide is, on the basis of the above experimental figures, about 7. Consequently, at least 7 potentially catalytically active surface elements must lie within the range of possible cover; in other words, at least 7 out of the 9 available elements must be catalytically active; and, since the effectiveness of the cover of surface lying within its range by a mobile chain anchored at one end is never complete, it appears probable that all the surface elements of a metal such as platinum are capable of acting catalytically. Little is known of the number of platinum surface elements covered by a molecule of adsorbed hydrogen sulphide (which, since it possesses the lowest observed toxicity, is taken as the unit in the toxicity scale); but, from the well-known molecular dimensions, both hydrogen sulphide and the sulphur head of a hydrocarbon chain are each of approximately sufficient size to cover one platinum surface element. If the adsorption of a sulphur head were shared by more than one platinum surface element, it would become more difficult to account for the observed relative toxicity of short-chain compounds even on the basis of the catalytic activity of all the surface elements within range; and this difficulty would be intensified if more than one sulphur head is assumed to be adsorbed on a single platinum surface element. It accordingly appears probable that the sulphur head is adsorbed on a single surface element, and that the maximum possible area within which there is a time-probability of the occupation of surface elements by the chain is a circle of radius equal to the chain length.

With longer chains, a lesser degree of effectiveness of cover of surface lying within the range of the chain would—in view of the recession of the anchor effect—be expected than for shorter chains; and the toxicity should, as has been found, increase less rapidly than the square of the chain length : further, the effectiveness of the cover of a sulphide should, as is also the case, be greater than that of the isomeric thiol containing the same number of carbon atoms, in virtue of the presence of the sulphur anchor in the centre, in place of at the end, of the hydrocarbon chain.

The general form of the variation of toxicity with chain length is shown graphically in Fig. 3.

UNIVERSITY OF BRISTOL.

[*Received, April 27th,* 1937.]