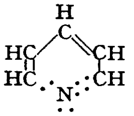
217. *Studies in the Detoxication of Catalyst Poisons. Part VII. The Self-poisoning Effect in the Hydrogenation of Pyridine.*

By E. B. Maxted and A. G. Walker.

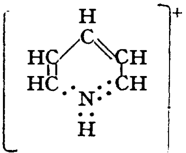
The influence of the electronic state of the nitrogen atom in pyridine and in quaternary pyridinium compounds as a factor in inducing, respectively, a relatively low or a relatively high hydrogenation velocity has been considered from the standpoint of catalytic toxicity; and it has been shown that the low hydrogenation rate of free pyridine is probably a self-poisoning effect which tends to vanish if pyridinium ions are hydrogenated, owing to the shielded state of the nitrogen atom. This conception of nitrogen as a potentially toxic element seems to predict the catalytic toxicity of dry ammonia; and it has been found that very carefully dried ammonia dissolved in a water-free non-ionising solvent such as *cyclo*hexane acts as a poison towards a platinum catalyst in the liquid-phase hydrogenation of *cyclo*hexene.

PYRIDINE, even when free from sulphur, is known to undergo catalytic hydrogenation at a considerably lower rate than, for instance, benzene under similar conditions; and, since the nature of its unsaturated bonds does not differ greatly from those in aromatic hydrocarbons, it appears probable that its low hydrogenation rate may be an effect connected with the influence of its nitrogen atom. It has also been noticed by various workers that the successful hydrogenation of substances containing basic nitrogen has in some cases been facilitated by using an acidic catalyst.

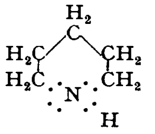
The present paper deals with this effect from the standpoint of the electronic conditions which are known to govern catalytic toxicity or non-toxicity in compounds of sulphur or other inherently toxic elements (*J.*, 1940, 252; 1941, 132; see also previous papers of the present series), namely, the correspondence of toxicity with the presence of free electron pairs in the outer or valency orbits of the toxic atom or, on the other hand, the disappearance of toxicity if the derivative has a shielded structure. Although nitrogen is not generally regarded as an inherently toxic element like the remaining members of its periodic group (phosphorus, arsenic, antimony and bismuth), it will be seen that, if the possession of a free electron pair by a suitably combined nitrogen atom is sufficient to lead to a strong adsorption by a metallic catalyst, then free pyridine or piperidine might be to some degree toxic, whereas the corresponding quaternary compounds generally, including pyridinium or piperidinium ions, should be less strongly adsorbed and accordingly non-toxic :



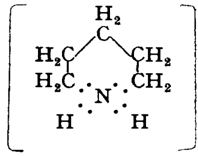
Pyridine (toxic).



Pyridinium ion (non-toxic, shielded structure).



Piperidine (toxic).



Piperidinium ion (non-toxic, shielded structure)

On these grounds, the slow rate of hydrogenation of free pyridine might be a self-poisoning effect due to the obstructively long adsorbed life—which is characteristic of all poisons—of piperidine on the catalytic surface : further, if the hydrogenation is carried out in acid solution, such that non-toxic pyridinium and piperidinium ions are present in place of the free bases, the self-poisoning effect should disappear and the hydrogenation of pyridine should proceed at the much higher rate which would be expected from the nature of its unsaturated bonds.

The above views have been confirmed experimentally. It has been shown that: (i) Free pyridine is an effective catalyst poison in the hydrogenation of unsaturated substances generally; *e.g.*, small quantities of sulphur-free pyridine added in the hydrogenation of *cyclo*hexene exert a toxic effect the magnitude of which is of the order of one-tenth of that exerted by the addition of an equivalent quantity of thiophen. Pyridine would accordingly be expected to act as a poison in its own hydrogenation. (ii) The rate of hydrogenation of sulphur-free pyridine can be raised to over eight times its normal value by the addition of a regulated quantity of an aqueous acid in such a way as to provide a pyridinium ion for the hydrogenation in place of free pyridine. Curves have been obtained showing the conditions required for a maximum hydrogenation velocity.

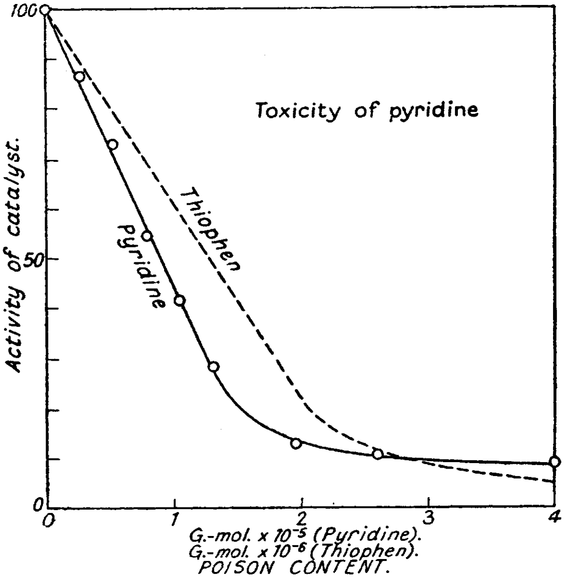
This conception of the toxic nature of nitrogen in free pyridine also raises the interesting question of the toxicity of free ammonia. Ammonium salts, as well as solutions of ammonia in water and the ammonium ion generally, are of course known to be non-toxic to metallic hydrogenation catalysts; but it has now been shown that carefully dried ammonia in a water-free non-ionising solvent such as *cyclo*hexane acts as a fairly strong catalyst poison in the hydrogenation of a non-acidic unsaturated substance such as *cyclo*hexene. The catalytic toxicity of dry free ammonia, contrasted with the known non-toxicity of the ammonium ion, agrees respectively with the non-shielded and the shielded electronic configuration of the nitrogen atoms and appears to confirm the inherently toxic nature of unshielded nitrogen in compounds of suitable structure.

EXPERIMENTAL.

Pyridine as a Catalyst Poison.—In order to establish the toxic nature of pyridine as an ordinary catalyst poison in a reaction involving the hydrogenation of a further unsaturated substance, the pyridine used must obviously be free from sulphur compounds and other extraneous poisons : accordingly, a stock of sulphur-free pyridine was prepared from the purest available pyridine (containing originally 0·015% of total sulphur) by the adsorption-column method described in Part VI (preceding paper). For the determination of toxicity *cyclo*hexene was taken as a convenient unsaturated substance, small known quantities of the pure pyridine, in *cyclo*hexane solution, being added to a standard hydrogenation system which consisted in each case of 5 c.c. of a 2N-solution of *cyclo*hexene in *cyclo*hexane, 0·05 g. of stock platinum catalyst, and a further 5 c.c. of *cyclo*hexane, including that added with the poison. The hydrogenation tests were carried out in a shaker at 27°.

It will be seen from the results plotted in Fig. 1, in which for purposes of comparison a corresponding toxicity curve for thiophen has also been included, that pyridine acts as a catalyst poison of moderate strength, its toxicity being of the order of one-tenth of that of thiophen. This difference in the order of the toxicity of pyridine and of thiophen, when applied to the hydrogenation of the poisons themselves, explains why pyridine can be hydrogenated without great difficulty, even if the reaction is rather slow, whereas thiophen is hydrogenated far more slowly unless an unusually large proportion of catalyst is used (Mozingo *et al.*, *J. Amer. Chem. Soc.*, 1945, **67**, 2092) so that a relatively large fraction of the thiophen taken is present in an adsorbed state (see also Part V). The difference in the order of the toxicity also explains why pyridine can be successfully freed from sulphur poisons by filtration through a column of platinum-black.

FIG. 1.

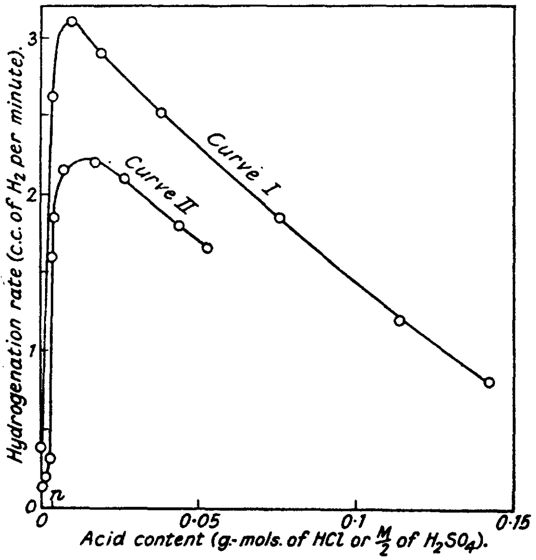


Hydrogenation of Pyridine.—The low hydrogenation rate of pyridine compared with that of benzene is shown in the following table, which refers to comparative tests with specimens of pyridine and benzene which had previously been freed from sulphur and other extraneous poisons with platinum-black. The hydrogenation rate of sulphur-free *cyclo*hexene is also included in order to show the still higher hydrogenation rate of an ethylenic bond, in a substance of similar structure, compared with that of the aromatic bonds in benzene. The tests were carried out in a shaker, at 27° and at atmospheric pressure, with similar charges consisting in each case of 10 c.c. of a N-solution of the unsaturated substance and 0·05 g. of stock platinum catalyst.

Unsaturated substance.	Solvent.	Hydrogenation rate, in c.c. of H_2 per min.
*cyclo*Hexene	*cyclo*Hexane	22·1
Benzene	,,	4·2
Pyridine	,,	0·33
Pyridine	Water	0·39

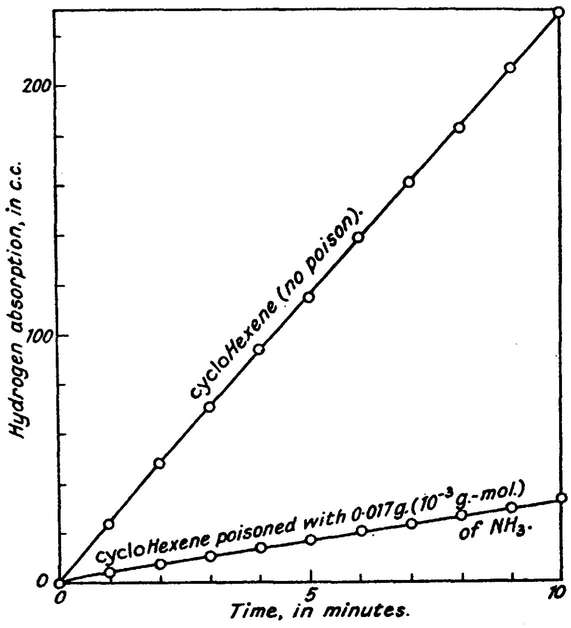
It will be noticed that, even in aqueous solution—in which there is some formation of pyridinium ions but still an appreciable concentration of free toxic pyridine—the hydrogenation rate of pyridine remains very low if no acid is present. It may also be noted that, in making up N-solutions of the various unsaturated substances for these comparative tests, the normality was, for equivalence in strength from a hydrogenation standpoint, based on the hydrogen value in such a way that the standard 10 c.c. hydrogenation charge required in each case the same volume (*ca.* 240 c.c.) of hydrogen for saturation. Accordingly, the N-*cyclo*hexene was molar, whereas the benzene and pyridine, both of which are capable of absorbing three molecules of hydrogen per molecule of unsaturated substance, were one-third molar. The question of relative strengths is however not of great importance, since all these hydrogenation reactions are approximately of zero order.

FIG. 2.



The suppression of the self-poisoning effect in the hydrogenation of pyridine was studied by adding various amounts of sulphuric or hydrochloric acid to aqueous pyridine solutions, the composition of the 10-c.c. hydrogenation charges used for the tests being as already given save that the solvent was water containing a known amount of acid. The form of the curve obtained by plotting the hydrogenation rate against the acid content is shown in Fig. 2. Curve I of this figure relates to the addition of sulphuric acid to sulphur-free pyridine. Curve II refers to a preliminary series of runs in which hydrochloric acid was added to a specimen of technical pyridine containing 0·024% of total sulphur. It will be seen that in each case the hydrogenation velocity rises very steeply as the acid present approaches the neutralisation point (marked *n* on the acid axis) but that the maximum velocity occurs

FIG. 3.



at an acid concentration which is considerably beyond that required for the neutralisation of the pyridine present. The general form of the curve shows, moreover, in addition to the expected rate-increasing effect of the addition of acid, the presence of an adverse factor, the weight of which increases continuously with an increase in the acid present. The nature of this adverse factor is not at present clear; and further work appears to be necessary before the subsequent fall in the rate can be explained. This should not have its origin in the presence of the increasing quantities of undissociated pyridinium or piperidinium sulphate or hydrochloride which would result from an increased acid content: moreover, the effect does not, as far as can be seen at present, seem to be due to the introduction of an extraneous poison with the acid; and the solutions are probably too dilute for the progressive cloaking of the catalyst by the deposition of an insoluble deposit. It is hoped to discuss this form of the curve further in a later paper.

Dry Ammonia as a Catalyst Poison.—It may be noted that gaseous ammonia, which has already been almost completely dried by passage through quicklime or solid sodium hydroxide, may be further dried with phosphoric oxide, since it is—unlike ammonia in the presence of water—a neutral gas when in a dry state. Accordingly, a solution of dry ammonia in *cyclo*hexane was made by passing into this solvent a current of pure ammonia, the final drying of which had been carried out with phosphoric oxide, the strength of this solution being adjusted so that 5 c.c. contained 0·017 g. (10^{-3} g.-mol.) of ammonia.

For the examination of the toxicity of this dry ammonia towards a platinum catalyst in the hydrogenation of a neutral unsaturated substance, the hydrogenation rate, at 27°, of a charge consisting of 5 c.c. of a N-solution of *cyclo*hexene in *cyclo*hexane, 5 c.c. of the *cyclo*hexane solution of ammonia, and 0·05 g. of stock platinum-black was compared with the rate for a similar charge containing no ammonia. The results of these comparative tests are shown in Fig. 3, from which the catalytic toxicity of the ammonia will be seen.

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