# 634. *Metallic Salts as Promoters in Hydrogenation with Platinum Oxide Catalysts.*

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The effect of adding small quantities of various metallic chlorides to liquid-phase hydrogenation systems in the presence of platinum oxide catalysts has been studied. If this addition is made before the reduction of the platinum oxide to metal, promotion effects involving an increase in the hydrogenation rate up to over ten times its unpromoted value and a continuous hydrogenation path have been obtained for the reduction of valeraldehyde and acetone.

It is known that many metallic ions which are toxic towards platinum-metal catalysts in the liquid-phase hydrogenation of unsaturated C–C bonds are capable of acting as promoters in the reduction of aldehydes, ketones, or certain acid anhydrides if platinum oxide, initially unreduced, is used as the catalyst.[1] In addition to a large rise in the hydrogenation rate, a suppression of the series of halts which recur in the hydrogenation of aldehydes or the like, as a result of the elimination of traces of oxygen from the system, may also occur. Ferric chloride was in this earlier work found to be the most active promoter of a large number of substances tested.

This effect has now been studied in greater detail, mainly in order to try to extend the range of the promoters examined. It has been found that stannous chloride, which does not appear to have been previously used, possesses at its optimum concentration a very much higher promoting power than that given by ferric salts. Further, very appreciable promotion has also been obtained, both with stannous chloride and to a lesser degree with ferric chloride, in the hydrogenation of ethyl cinnamate with a platinum oxide catalyst.

## Experimental

The catalyst used throughout the present work was taken from a stock of platinum dioxide, containing 83·5% of platinum. Liquid-phase hydrogenation, usually of valeraldehyde, was carried out, at atmospheric pressure and at 20°, in a hydrogenation shaker operating under standardised conditions. In view of the known effect [2] of traces of oxygen on the rate of hydrogenation, the electrolytic hydrogen employed, which had originally an oxygen content of less than 50 parts per million, was further purified by passage over heated platinum immediately before its employment for hydrogenation. The metallic chlorides, in general, were applied in ethyl alcohol solution.

*Promoting Effect of Various Metallic Chlorides in the Reduction of Valeraldehyde.*—As a preliminary survey, the relative effect of a constant small amount ($10^{-5}$ mole) of a number of the more active metallic chlorides on the hydrogenation rate of 1 c.c. of valeraldehyde, in 9 c.c. of alcohol, by 0·025 g. of stock platinum oxide is shown in Fig. 1. In order to avoid overcrowding in the curves of this Figure, the effects of some less active promoters are given separately in Table 1.

Table 1.

| Promoter | None | $ZnCl_2$ | $CrCl_3$ | $CuCl_2$ | $MnCl_2$ | $AlCl_3$ |
|---|---|---|---|---|---|---|
| $H_2$ absorbed (c.c.) in 1 hr. | 12 | 34 | 29 | 27·5 | 25 | 23·5 |

It will be seen that stannous chloride is, under the conditions used, by far the most effective promoter tested, 127 c.c. of hydrogen being absorbed in an hour, compared with 92 c.c. for ferric chloride and only 12 c.c. in a blank run without a promoter. The relatively small promoting effect of stannic chloride, compared with that of the stannous salt, is to be noted. This point is of interest in connection with Carothers and Adams's observation [1] of no effective

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[1] Carothers and Adams, *J. Amer. Chem. Soc.*, 1925, **47**, 1047.

[2] Willstätter and Jacquet, *Ber.*, 1918, **51**, 767.

difference between the promoting activities of ferrous and ferric chlorides in the hydrogenation of benzaldehyde. In view of the lower promoting effect of stannic chloride than of the stannous salt, solutions of the latter gradually lose accelerating power on storage. Accordingly, in order to minimise oxidation, alcohol through which nitrogen had been passed was used in the preparation of the stannous chloride solution; and, with this precaution, any fall in the promoting power of a solution of stannous chloride only became noticeable after about 4 days. The low promoting power of $Cr^{3+}$ and of $Zn^{2+}$ should also be noted. With magnesium chloride some turbidity in the solution hydrogenated was observed, owing probably to slight hydrolysis; and the small increase in the hydrogenation rate may be due to a support effect since both the promotion and the turbidity disappeared on addition of a small quantity of hydrochloric acid.

The promoting effect of stannous chloride appears to be specially high for hydrogenation in alcoholic solutions. Thus, on changing the solvent to ethyl acetate, promotion by $10^{-5}$ mole of stannous chloride led to a hydrogen absorption of 52 c.c. in an hour, compared with 12 c.c. in a corresponding blank run. These figures should be contrasted with those given in Fig. 1 for the increase in the velocity obtained for the hydrogenation of valeraldehyde in alcohol.

FIG. 1 *Activation of* $PtO_2$ *catalyst by metallic salts.*

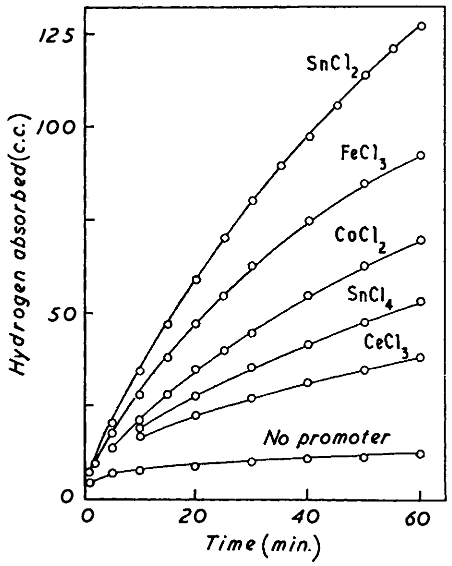
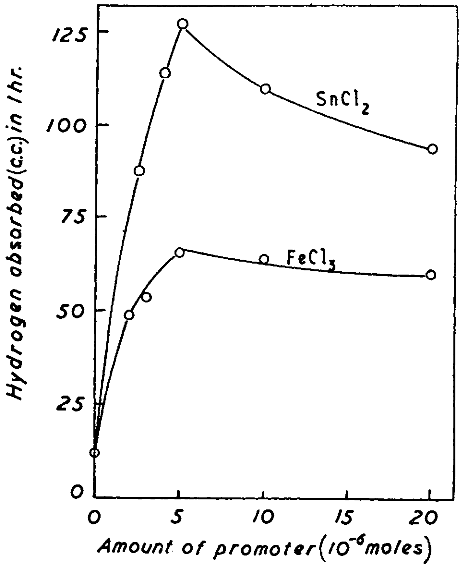


FIG. 2.



*Conditions for Maximum Promotion.*—The observed variation of the promoting effect with the concentration of stannous and ferric chlorides is given in Fig. 2, the hydrogenation being, however, carried out with a stock of valeraldehyde which was not identical with that used for Fig. 1. It will be seen that maxima in the promotion occur, with both promoters, at a concentration of about $5 \times 10^{-6}$ mole and that, at this optimum concentration, the reaction rates correspond with the absorption of 125 c.c. of hydrogen per hr. for stannous chloride and 68 c.c. for ferric chloride, the unpromoted value being 10·5 c.c. per hr. The position of these maxima will of course change with the nature and concentration of the unsaturated substance and with the area of the catalyst surface, in each case on account of changes in the distribution of the unsaturated substance between the adsorbed and the free liquid phases.

*Effect of Mixed Promoters.*—The effect of a given molecular quantity of two promoters was in general intermediate between that exercised by the same quantity of each promoter separately. Thus a hydrogenation system, as used for Fig. 1 but containing $10^{-5}$ mole of both stannous and ferric chlorides, absorbed 109 c.c. of hydrogen in the first hour, compared with adsorptions of 127 and 92 c.c., respectively, with stannous chloride and ferric chloride alone. A similar intermediate absorption was also obtained for stannous and manganous chlorides and their mixture. This is shown in the first part of Table 2. The second part of this table contains figures for the hydrogen absorption obtained with mixtures of stannous and cerous chlorides, the amount of the stannous salt being kept constant at its optimum value and the concentration of cerous chloride being varied.

TABLE 2.

| Promoter (moles) | Hydrogen absorption (c.c.) in 1 hr. | Promoter (moles) | Hydrogen absorption (c.c.) in 1 hr. |
|---|---|---|---|
| $10^{-5}$ $SnCl_2$ | 127 | $5 \times 10^{-6}$ $SnCl_2$ | 123 |
| $10^{-5}$ $MnCl_2$ | 25 | $5 \times 10^{-6}$ $CeCl_3$ | 33 |
| $10^{-5}$ $SnCl_2$ + $10^{-5}$ $MnCl_2$ | 88 | $5 \times 10^{-6}$ $SnCl_2$ + $5 \times 10^{-6}$ $CeCl_3$ | 94 |
| | | $5 \times 10^{-6}$ $SnCl_2$ + $10^{-5}$ $CeCl_3$ | 46 |
| | | $5 \times 10^{-6}$ $SnCl_2$ + $2 \times 10^{-5}$ $CeCl_3$ | 38 |

*Promotion in Other Hydrogenation Systems.*—In addition to the above work, the use of stannous chloride in the hydrogenation of a ketone, ethyl cinnamate, and cyclohexene was studied.

Ketones are known to be hydrogenated rather slowly by platinum oxide at room temperature. Thus a charge containing 1 c.c. of acetone, 9 c.c. of alcohol, and 0·025 g. of platinum oxide underwent hydrogenation, in the absence of a promoter, at a very low and gradually decreasing rate, only 7·6 c.c. of hydrogen being absorbed in 20 min., by which time the reaction had almost stopped. However, after the addition of $10^{-5}$ mole of stannous chloride to a similar charge, absorption of hydrogen took place at an approximately constant rate of 3 c.c. per min. until 200 c.c. had been absorbed, following which the rate gradually fell until approximately the theoretical volume of hydrogen had been taken up in about 4 hr. There was, in the presence of the promoter, no intermediate halt, and no reactivation was necessary.

The hydrogenation of ethyl cinnamate by platinum oxide differs from that of aldehydes and ketones since it proceeds smoothly to completion without intermediate reactivation of the catalyst. Thus a standard charge containing 1 c.c. of ethyl cinnamate absorbed 55 c.c. of hydrogen in 30 min. This absorption was raised to 68 c.c. in 30 min. by the inclusion of $10^{-5}$ mole of ferric chloride, and up to 96 c.c. by the same quantity of stannous chloride.

With cyclohexene and platinum oxide a far higher hydrogenation velocity is reached and an approximately linear course is followed. In this case, a slight promotion was obtained if $10^{-5}$ mole of stannous chloride was included in the system (1 c.c. of cyclohexene, 9 c.c. of alcohol, 0·025 g. of $PtO_2$), but a slight poisoning effect for a similar addition of the same quantity of ferric chloride, the times for complete hydrogenation being 12 min. in the blank run, 10 min. in the run promoted by stannous chloride, and 13·5 min. for ferric chloride. These figures correspond to about 17% acceleration and to 12% retardation, respectively.

Pre-reduced platinum black, on the other hand, was poisoned both by stannous chloride and by ferric chloride. Thus, in the reduction of 1 c.c. of cyclohexene in alcohol, by 0·025 g. of metallic platinum, the volume of hydrogen absorbed after 10 min. was 225 c.c. in the blank run, the corresponding values being 208 and 15 c.c. with $10^{-5}$ mole of stannous and ferric chloride respectively.

*Variation of the Promotion Effect with Temperature.*—This was studied for the hydrogenation of valeraldehyde in a system containing 0·025 g. of platinum oxide, 1 c.c. of valeraldehyde, 9 c.c. of alcohol, and, in the promoted series, $10^{-5}$ mole of stannous chloride. The hydrogen absorption after 30 min., at temperatures between 0° and 35°, is shown in Table 3, the volumes being corrected to N.T.P.

TABLE 3.

| Temp. | | 0° | 20° | 25° | 30° | 35° |
|---|---|---|---|---|---|---|
| C.c. of hydrogen absorbed in 30 min. | Unpromoted system | 9·3 | 10·6 | 11·1 | 8·3 | 8·5 |
| | Promoted system | 42·0 | 79 | 82 | 69·0 | 60 |

In addition to the rather large promotion effect in the second series, the hydrogenation rate passes in both cases through a maximum at 25°. About 5 c.c. of the above volumes correspond in each case to hydrogen required for the reduction of the platinum oxide. Accordingly, the smallness of the net absorption probably accounts for the reversal in sequence in the absorption at 30° and 35° in the unpromoted series.

*Discussion.*—It is known that, if platinum black is deprived of oxygen by use in the catalytic hydrogenation of aldehydes or acid anhydrides such as phthalic anhydride, the activity of the catalyst becomes reduced to a low order, but can be restored by treatment with oxygen: [2] complete hydrogenation of such substances usually necessitates a series of alternate hydrogenations and revivals with oxygen. This revival with oxygen has been found by us also to apply in the hydrogenation of unsaturated C–C bonds, *e.g.*, in the hydrogenation of ethyl cinnamate with platinum black which had previously been freed from oxygen by its use in the hydrogenation of phthalic anhydride (unpublished work). Similar effects in oxygen-free systems also occur in hydrogenation with platinum oxide catalysts,[3] and the necessity for reactivation by treatment with oxygen can be delayed or eliminated by the addition of suitable promoters. It may be noted that the promoters used are in all cases very small quantities of metallic salts known to be toxic in catalytic hydrogenation on platinum; and it appears probable that the action takes place by retarding the autocatalytic reduction of the platinum oxide to metal in such a way as to prolong the period during which highly active nascent platinum is being produced. Further, since the reduction of the platinum oxide to metal is an exothermic process, this should present continuously, during the reduction, freshly produced platinum having a localised temperature higher than that of the surrounding liquid. Moreover, after the reduction of the platinum oxide to metal, the poison should reduce the activity of the metallic platinum in such a way as to induce a reaction path which curves gradually towards the time axis, as was in most cases obtained.

On rise of the gross reduction temperature, the time of this production of highly active platinum is decreased, so that the period of greater activity is shortened, *i.e.*, the volume of hydrogen taken up by the valeraldehyde after a given time decreases with temperature, as was shown in Table 3. This decrease is, however, superimposed on the ordinary increase in the hydrogenation velocity with temperature. By reason of these opposed factors, the amount of hydrogen taken up after a given time passes through a maximum as the temperature is increased, and this rise and subsequent fall should be more pronounced in a promoted than in an unpromoted system. Further factors in this subsequent fall in the reaction rate are to be found in the decrease with temperature of the solubility of hydrogen in the solvent and of its adsorption on the catalyst.

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[3] Vorhees and Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 1397.