PLATINUM OXIDE AS A CATALYST IN THE REDUCTION OF ORGANIC COMPOUNDS. VII. A STUDY OF THE EFFECTS OF NUMEROUS SUBSTANCES ON THE PLATINUM CATALYSIS OF THE REDUCTION OF BENZALDEHYDE[1]

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The writers have shown[3] that the presence of a very small amount of ferrous or ferric chloride enormously accelerates the platinum catalysis of the hydrogenation of aldehydes, and use has been made of this fact to develop a method[4] for the preparation of primary alcohols which is simple, reliable and rapid, requires only a very small amount of catalyst, and leads to practically quantitative yields.

This catalytic hydrogenation reaction is extremely sensitive toward the iron salt, and the latter may be regarded as a promoter of perhaps unusual power. Very few examples of promoter action in catalytic hydrogenation with noble-metal catalysts have hitherto been adduced,[5] and the subject has been thought worthy of further study. In this paper are described some of the results of an investigation of the effects of numerous substances on the platinum catalysis of the hydrogenation of benzaldehyde.

The apparatus and general procedure have already been described.[3,6]

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[2] This communication is abstracted from a thesis submitted by W. H. Carothers in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Carothers with Adams, THIS JOURNAL, **45**, 1071 (1923).

[4] Carothers with Adams, *ibid.*, **46**, 1675 (1924).

[5] Paal [*Ber.*, **44**, 1013 (1911)] and some of his students [Paal and Karl, *Ber.*, **46**, 3069 (1913); Paal and Windisch, *Ber.*, **46**, 4011 (1913); Sieke, *Dissertation*, Leipzig, 1914] studied various metals and metallic oxides, etc., as supports for platinum and palladium catalyst in the hydrogenation of certain olefinic compounds. Most of the substances used were anti-catalytic. Platinum deposited on nickel, however, was found to be a good catalyst, and the presence of alkalies in proper amounts accelerated the reaction.

Rideal [THIS JOURNAL, **42**, 749 (1920)], in a study of the hydrogenation of sodium phenyl-propiolate using a colloidal platinum catalyst, found that palladium accelerated the reaction.

Outside of the field of catalysts of the platinum metal group, a number of examples of promoter action in hydrogenation reactions are known. See Pease and Taylor, *J. Phys. Chem.*, **24**, 241 (1920); Kitu and Mazume, *Mem. Coll. Eng. Kyoto Imp. Univ.*, **3**, 81 (1923); Armstrong and Hilditch, *Proc. Roy. Soc. London*, **102A**, 21 (1922); **103A**, 586 (1923).

[6] (a) Voorhees and Adams, THIS JOURNAL, **44**, 1397 (1922). For the preparation of the catalyst see (b) Adams and Shriner, *ibid.*, **45**, 2171 (1923).

In the experiments discussed here, it was usually desired that the only variable from one experiment to the next should be the nature or the amount of some added substance. A standard procedure was, therefore, adopted and adhered to quite rigorously except in those experiments where some other variable was to be tested.

A solution of 21.2 g. of benzaldehyde (purified and stored as previously described[3]) in 50 cc. of 95% alcohol was introduced into the reaction bottle, a definitely known amount of the substance (in a suitable solvent) whose effect was to be observed was added from a capillary pipet, and then 0.1725 g. of the platinum oxide catalyst.[7] The catalyst was prepared from especially purified chloroplatinic acid by the method previously described.[3,6] The reaction bottle was attached to the hydrogen reservoir, the air was withdrawn, and hydrogen was admitted. After thermal equilibrium had been established, the hydrogen pressure was adjusted to a certain definite value (approximately 2.3+ atmospheres in excess of atmospheric pressure), the time was noted and the shaking was started.

Subsequent observations of the time and pressure were made at suitable intervals. The pressure readings having been converted by means of an experimentally determined factor into moles of hydrogen absorbed, the data thus obtained gave a measure of the reaction velocity. It is to be observed that two successive reactions were here involved. The first was the reduction of the brown platinum oxide to platinum black. During the course of this reaction, the amount of hydrogen absorbed was too small to be measured with the instruments used and the period of this reaction, called the induction period, is represented by an initial horizontal line on the reaction-velocity curve. The end of the induction period and the beginning of the reduction of the aldehyde were marked by complete change of the color of the reaction mixture to black, and by the beginning of measurable absorption of hydrogen. This method then gave data on the effects on two reactions, of the foreign substances used—the reduction of the platinic oxide and the catalytic reduction of the aldehyde.

This procedure was occasionally modified. Thus when it was desired to eliminate the first reaction, the platinic oxide was reduced by shaking with water or alcohol under hydrogen before the other materials were added. When it was not possible to dissolve in a neutral solvent the substance of which the effect was to be studied, a weighed amount of it was usually ground with the platinic oxide in an agate mortar.

Concerning the substances added, it may be said that the samples used were the purest commercially available (c. p. or analytical grade of purity). There is little probability that the nature of the results here described was significantly affected by such small amounts of un-

[7] It is to be observed that in the experiments described previously (Ref. 3) a somewhat larger amount, namely, 0.23 g. of catalyst, was used.

known impurities as would be present in substances of such a degree of purity.

Experimental Results

During the course of this study many data have been collected. Most of these are not presented here, but in Table I a few of the typical and more important data are collected, where the amount of hydrogen absorbed since zero time (the beginning of the experiment) is expressed in molecular equivalents $\times$ 10^{-3}. Actual observations were not made at such regular intervals as those recorded in the table. Instead, the intervals were adjusted to the rapidity of the reaction in such a way as to give a better picture of the shape of the reaction-velocity curve. Hence, many of the data of the table have been obtained by graphic interpolation. Regarding the accuracy of the data, it may be said that the conditions which would have to be defined in order to reproduce them are too numerous to justify the claim of any absolute quantitative significance for them. But they do have comparative significance. So far as the accuracy of the instruments used is concerned, the probable error of the data of the table is $\pm$ 10 in the units in which they are expressed. The most fruitful source of error in experiments of the kind here described is the presence of impurities. The effect of these is nearly always positive (that is, accelerating). The necessity for excluding impurities was kept constantly in view. Many of the results expressed in the table of data have been tested by repeated duplication, and probably none of them is in serious relative error.

If these data are represented graphically, it will be observed that the presence of comparatively small amounts of various substances is capable not only of profoundly modifying the reaction velocity, but also of changing its apparent order and its end-point.

Regarding the frequency with which different types of curves were encountered, it may be mentioned that when the reaction was very rapid, the curve was nearly always approximately linear over most of its course, and that when the reaction was slow, the linear type of curve was very rarely met.

Pure Catalyst.—Expt. 1 is typical of the pure catalyst in this reaction. The induction period was less than one minute. The reaction began fairly rapidly, but the velocity fell off very quickly so that in 180 minutes, only about 10% of the calculated amount of hydrogen (1 molecular equivalent) had been absorbed, of which amount 60% had been absorbed during the first five minutes. The initial activity of the catalyst could be restored by shaking with air, but was lost again just as quickly as before when hydrogen was readmitted.

Effect of Ferrous Chloride.—In the presence of 0.1 millimole of ferrous chloride, the platinum suffered no loss of activity and the reaction was completed in about 25 minutes (Expt. 2). The effects of variations in

the amount of ferrous or ferric chloride have already been discussed.[3] Certain other pertinent observations may be mentioned.

1. The greatly enhanced activity (here called permanent activity) of the catalyst due to the presence of ferrous chloride gradually diminishes and is ultimately lost when the catalyst is used for a long time in the reduction of aldehydes. It is more or less completely restored by shaking with air the mixture in which the catalyst is suspended.

2. When ferrous chloride (or ferric chloride) is added to completely exhausted catalyst (that is, pure catalyst which has been shaken under hydrogen with aldehyde until it ceases to catalyze the hydrogenation) its catalytic powers are not modified in the slightest degree. It remains completely inactive. When, however, the mixture is shaken with air either before or after the addition of the ferrous chloride, a part of the initial activity of the catalyst is restored and the restoration is permanent.

3. Small amounts of ferrous chloride somewhat diminish the induction period.

Iron and Its Compounds.—Ferric oxide was prepared by fusion of c. p. ferric chloride with sodium nitrate. It was thoroughly washed, dried, and ground with the platinic oxide in an agate mortar. The accelerating effect produced was somewhat irregular from one experiment to another, depending apparently upon such factors as fineness of subdivision, intimacy of mixing, etc., but under optimum conditions accelerations (Expt. 3) were produced which approached the highest obtainable with ferrous or ferric chloride. Rather remarkable is the fact that the ferric oxide underwent no color change during the course of the reaction, indicating that in this case most of the iron remains in the ferric condition.

Ferrous hydroxide (10 millimoles) caused considerable acceleration at first but the velocity soon fell off and shaking with air restored very little of the original activity. On the other hand, the addition of hydrochloric acid without shaking with air restored the original activity almost completely. Taken in conjunction with the facts that shaking with air reactivates promoted catalyst, that ferrous chloride alone restores none of the activity to exhausted catalyst, and that hydrochloric acid has a depressing effect on promoted catalyst, this behavior indicates that the gelatinous hydroxide had surrounded the catalyst mechanically and thus greatly diminished its efficiency. Ferric hydroxide behaved similarly.

Using 0.1 millimole of ferric acetate as a promoter, the reaction was very rapid: 0.9 mole-equivalent of hydrogen was absorbed in ten minutes, and the reaction-velocity curve up to that point was practically linear (Expt. 6). Using 1 millimole of ferric acetate (Expt. 7) the reaction was less rapid, and with 0.01 millimole (Expt. 5) still slower. With ferrous sulfate, also, the maximum accelerating effect was obtained when 0.1 millimole of the salt was used (Expt. 9). But here as with ferrous chloride

increasing the amount up to 1 millimole (Expt. 10) had no significant (further) effect on the velocity.

The behavior of ferric nitrate was rather peculiar (Expts. 11, 12, 13). The accelerations were of the same order as those produced by ferric chloride, ferrous sulfate, etc.; but when 0.1 or 1 millimole of the salt was used, the reaction stopped before it was complete, and unchanged aldehyde was found in the mixture at the end. Using 10 millimoles, however, the reaction proceeded far beyond the calculated extent, with the formation of toluene. It is interesting to observe that of the salts, ferric chloride, ferrous sulfate, ferrous chloride, and ferric acetate, the maximum acceleration was, in each case, observed when 0.1 millimole of the salt was used. Moreover, the reaction velocities, when that amount of each of these salts was used, were very nearly the same.

Metallic iron (1 g. of U. S. P. Iron by Hydrogen, Merck) not intimately mixed with the catalyst, but simply thrown into the same bottle with it, exerted a considerable accelerating effect. The reduction was 95% complete in 80 minutes (Expt. 14). Reduction then stopped and unchanged aldehyde was found in the reduction mixture. When 0.015 g. of metallic iron was ground with the catalyst, the reduction was 93% complete in 40 minutes.

From these experiments it appears that promotion occurs when iron or one of its ions is present. The (initial) nature of the ion (whether ferrous or ferric), the nature of the anion (if any) and the solubility of the substance are factors of only secondary importance.

Manganese, Nickel and Cobalt.—The data of the table (Expts. 15–32) show the effects of manganese, nickel and cobalt acetates and chlorides. All of these salts had an accelerating effect and in the case of manganese and cobalt acetates, this effect was nearly as great as that produced by iron salts. The acetates were more effective than the corresponding chlorides. Concerning the relative activity of the three metals the order was for the acetates $Mn > Co > Ni$, and for the chlorides, $Co > Ni > Mn$. Variations from this order appear, since the relative increase in velocity produced by the same increase in concentration varied considerably with different salts. Regarding the effect of increase in concentration of the different salts, it will be observed that the velocity was usually much higher with 0.1 millimole of the salt than with 0.01 millimole, but that increasing the amount to 1 millimole either caused very little further increase or caused a decrease in reaction velocity. In this connection it will be observed that ferrous chloride produced its maximum accelerating effect when 0.1 millimole was present, and that larger amounts produced no further effect.[3] The behavior of ferrous sulfate was similar.

Titanium, Vanadium and Chromium.—Since neutral solutions of simple titanium salts are not available, it was necessary to use the titanium

in an insoluble form. Titanic oxide, thoroughly mixed with the platinic oxide, was without effect on the reaction velocity in the amount used (0.0098 g.). On the other hand, vanadium in a similar form (as the oxide) had a slight, though appreciable, accelerating effect (Expt. 33, 34). Chromium in solution as chromic chloride (Expts. 35–37) was almost as effective as cobalt. Sodium chromate (0.1 millimole) (Expt. 52) acted as a rather strong promoter, but 1 millimole of the same salt inhibited the reduction of the platinic oxide and almost completely suppressed the reaction (Expt. 53).

Copper and Zinc.—Copper as the chloride had a slight depressing effect, whereas the acetate appeared to have a very slightly accelerating effect. The behavior of zinc was very peculiar. Zinc is recognized as a strong catalyst poison for hydrogenation with noble-metal catalysts. Using 1 millimole of zinc acetate, this poisoning effect appeared (Expt. 40); the reaction was almost completely suppressed. On the other hand, 0.1 millimole of the same salt greatly accelerated the reaction (Expt. 39). The effect was equal to the maximum produced by manganese acetate and greater than that produced by the salts of any other metals than manganese, palladium and iron. Finally, 0.01 millimole of zinc acetate was practically without effect (Expt. 38).

These results are perhaps worthy of more extended study. In the first place, they contradict, or at least, restrict the applicability of Maxted's linear poisoning law.[8] In the second place, they show how complex and various may be the effects of a single added salt, and they suggest that where two reducible groups are present it may be possible simultaneously to accelerate the reduction of one of them and to inhibit the reduction of the other.

Molybdenum, Palladium and Silver.—Molybdenum (standing just below chromium in the periodic table) was practically without effect in the form used (0.0144 g. of molybdic acid ground with the catalyst). Palladium (standing just under cobalt) considerably increased the reaction velocity (Expts. 41–43). As to whether the palladium functions here as a promoter or acts independently, it is not possible definitely to decide from the data. In Expts. 42 and 43 it is observed that the reduction proceeds beyond the alcohol stage (though slowly) without any break in the reaction-velocity curve. This tendency is characteristic of palladium as a catalyst.[9]

Silver nitrate (0.1 millimole or 1 millimole) was without effect on the reaction velocity.

Tungsten, Osmium, Iridium and Gold.—Tungsten as W_2O_5 was without effect in the amount used (0.77 g.). Another compound of tungsten

8 Maxted, *J. Chem. Soc.*, **121**, 1760 (1922).

9 Shriner and Adams, THIS JOURNAL, **46**, 1683 (1924).

tried, silico-tungstic acid, was also without effect.   This acid is easily re-
ducible, for example, by warm alcohol with the formation of lower, colored
oxides of tungsten, but there was no evidence of such reduction when it was
shaken with hydrogen and benzaldehyde in the presence of platinic oxide.

Osmium was introduced as "osmic acid" solution.   In the proper con-
centration it accelerated the reaction.   Using 1 millimole of the acid
(Expt. 45), the reaction was complete in three hours and the curve was
roughly linear throughout its whole course.   The only other case in which
an approximately linear curve was observed when the reaction was not
very rapid was in Expt. 52 where sodium chromate was used as a promoter.

Iridium was of especial interest in view of Faillebin's statement[10] that
it aids the reduction of aldehydes and ketones when added to the chloro-
platinic acid from which platinum black is prepared by the formaldehyde
reduction.   In the present work it was found that iridium added as sodium
chloro-iridate to the reduction mixture had comparatively little effect on
the reaction velocity.   Using 0.01 millimole or 0.1 millimole of the salt,
there was no acceleration; using 0.5 millimole, there was a slight increase
in velocity (Expt. 46).   The iridium salt used in the present work was
prepared from ammonium chloro-iridate of highest purity furnished by
the United States Bureau of Standards.

Gold chloride like silver nitrate was practically without effect in the
amounts used (0.1 and 1 millimole).

Mercury and Lead.—Mercury and lead, free or in almost any state of
combination, are recognized as powerful catalyst poisons.   Mercury and
lead acetates were also found to act as poisons in the reaction studied here.
The amounts of these salts required to produce complete suppression of
catalytic activity is surprisingly great.   Neither salt, when present to the
extent of 0.1 millimole, had any considerable depressing effect (that is,
the reaction velocity was practically the same as with pure catalyst).
This is rather remarkable in view of the fact that most salts which accelerate
the reaction exhibit their maximum promoting effect when present to the
extent of approximately 0.1 millimole.   Even as much as 0.6 millimole
of mercuric acetate only partially suppressed the reaction.   Of course,
the suppression became practically complete with large amounts (1.0
millimole) of either salt.

Uranium.—Uranium as uranyl acetate mixed and ground with the
catalyst had a considerable accelerating effect (Expts. 44, 45).

Alkalies.—Amounts of sodium hydroxide up to 0.1 millimole had little
or no effect on the reaction.   Such small amounts of alkali did not cause
any considerable alkalinity in the mixture (about 0.08 millimole of sodium
hydroxide was required to make the reduction mixture alkaline to phenol-
phthalein).   As soon as enough alkali had been added to make the reaction

10 Faillebin, *Compt. rend.*, **175**, 1077 (1922).

mixture distinctly alkaline, the reaction became more rapid. Thus, 0.2 millimole had a distinctly accelerating effect (Expt. 49). In the presence of 1 millimole of sodium hydroxide the reaction became quite rapid. Reduction to the alcohol was 90% complete in 20 minutes (Expt. 50). A further increase (to 10 millimoles) in the amount of sodium hydroxide did not cause much change in the velocity of the main part of the reaction (Expt. 51). Besides accelerating the main part of the reaction, alkali somewhat inhibited the reduction of platinum oxide to platinum black, and the resulting lengthening of the induction period became continuously (slightly) greater with increasing amounts of alkali. Hence, in the presence of considerable amounts of alkali the first part of the reaction appears to be autocatalytic, and the main part of zero order. The last part of the reaction is also peculiar in the abruptness with which the velocity changes toward the end, and in certain cases, in the slowness with which the last few per cent. of aldehyde are reduced.

The power to accelerate the reaction was found to be common to all the alkalies examined, namely, to potassium hydroxide, barium hydroxide, sodium carbonate and calcium oxide. The effect of these alkalies differed from the effect of sodium hydroxide only in degree.

Aluminum.—Aluminum in solution as the chloride (0.1 or 1 millimole) or ground with the catalyst as the oxide (0.007 g.) had no effect on the reaction velocity. This is of interest in connection with Faillebin's statement[10,11] that in his experiments the presence of aluminum chloride in the chloroplatinic acid from which platinum black was prepared by the formaldehyde reduction produced the same kind of result as iron.

Sodium Salts.—The effect of certain salts of sodium was of interest, because of the fact that small amounts of such salts are present in the platinum oxide catalyst,[6b] and also because certain alkali salts inhibit the auto-oxidation of benzaldehyde.[12] Sodium chloride, sodium bromide, and sodium iodide all increased the length of the induction period. Thus in the presence of 10 millimoles of sodium chloride, the induction time was nine minutes, in the presence of 10 millimoles of sodium bromide it was ten minutes, and in the presence of 10 millimoles of sodium iodide, about 50 minutes. Aside from lengthening of the induction period, the chloride and bromide were practically without effect. The iodide, however, acted as a poison, though rather a weak one, the reaction being partially suppressed in its presence. This poisoning effect is probably to be referred to the presence of free iodine rather than to the iodide ion, since the color of the solution after the addition of the aldehyde was distinctly yellow, and the intensity of the yellow color increased on the addition of the platinum oxide.

[11] Faillebin, *Compt. rend.*, **177**, 1118 (1923).

[12] Moureu and Dufraisse, *Compt. rend.*, **176**, 797 (1923).

Sodium nitrate increased the induction period very slightly and perhaps exerted a slightly depressing effect on the reaction.

Ten millimoles of sodium nitrite completely inhibited the reduction of the platinum oxide, so that at the end of 200 minutes the catalyst was still dark brown and no absorption of hydrogen had occurred. With 1 millimole of sodium nitrite the suppression was almost as complete as with 10 millimoles. With 0.1 millimole there was practically no effect. The action of sodium nitrate, nitrite and chloride is particularly interesting because these are the alkali salts which would naturally be present as impurities in the oxide catalyst.

Sodium sulfate in the concentration used (1 millimole) had little or no effect. The same was true of sodium chlorate.

Sodium cyanide, as would be expected, acted as a poison. As with the acetates of lead and mercury, however, this poisoning effect did not appear until more than 0.1 millimole of the salt was used.

Acids.—Large amounts (10 millimoles) of hydrochloric, sulfuric and nitric acids had practically no effect on the induction period or the reaction velocity.

The Effect of Various Substances on Promoted Catalyst.—It was thought to be of interest to examine the effects of certain substances on promoted catalyst. In these experiments the standard procedure was followed and, in addition to the substance mentioned, 0.1 millimole of ferrous chloride was added. The reaction-velocity data are to be compared with those of Expt. 2.

One millimole of hydrochloric acid lengthened the reaction time to 30 minutes and also caused the reaction to proceed (slowly) beyond the alcohol stage. Twelve millimoles of the same acid exerted a very powerful depressing effect. Sodium nitrate (1 or 10 millimoles) had very little effect on the reaction velocity but, curiously enough, caused some acetal formation. Sodium chloride (1 or 10 millimoles) had very little effect on the reaction velocity, but caused the reaction to proceed (slowly) beyond the alcohol stage. Ten millimoles of sodium nitrite inhibited the reduction of the oxide so completely that the catalyst was still brown at the end of 140 minutes when the experiment was interrupted. When 1 millimole of the salt was used, the induction time was 170 minutes. One-tenth millimole of the same salt had very little effect. When the platinic oxide was first reduced to platinum black before adding the other materials, 1 millimole of sodium nitrite was found to have a considerable though not large depressing effect on the reaction velocity.

The Nature of the Reduction Products.—Whether a promoter is present or not and regardless of the nature of the promoter, benzyl alcohol appears to be the exclusive first product of the reduction of benzaldehyde by the procedure here described. Where the reduction went to completion

TABLE I

RESULTS

Expt.	Amount in millimoles of substance added	Time in minutes 1	2	3	5	10	15	20	30	50	75	100	150	200
							Molecular-equivalents $\times 10^3$ of hydrogen absorbed from zero time							
1	None	0	20	45	75	80	...	...	85	..	100	...	...	110
2	Ferrous chloride, 0.10	45	150	255	405	780	940	995	1000	1005	...	...	...	1005
3	Ferric oxide, 0.06 g	20	85	150	245	440	630	770	940	995	1000	1000	...	1000
4	$PtO_2.H_2O$ 0.043 g.; Fe_2O_3 0.24 g	0	10	35	115	200	255	280	320	350	380	410	440	460
5	Ferric acetate, 0.01	0	35	70	105	135	160	185	220	260	280	300	340	350
6	Ferric acetate, 0.10	45	160	250	460	930	980	990	995	...	...	1000	...	...
7	Ferric acetate, 1.0	20	60	95	130	200	240	270	315	390	470	550	670	...
8	Ferrous sulfate, 0.01	30	95	160	230	330	420	485	605	735	845	920	950	960
9	Ferrous sulfate, 0.10	65	170	265	490	780	940	960	985	990	995	995	1000	1000
10	Ferrous sulfate, 1.0	55	170	245	400	750	920	960	1000	...	...	1000	1005	...
11	Ferric nitrate, 0.1	30	105	185	340	685	880	930	945	945	...	...	...	945
12	Ferric nitrate, 1.0	30	115	200	370	735	835	845	...	...	...	860	...	...
13	Ferric nitrate, 10.0	0	20	65	180	450	675	840	1000	1080	1120	1140	1170	...
14	Fe, 1 g	20	130	170	240	390	420	630	755	880	935	950	955	955
15	Manganous chloride, 0.01	20	45	60	85	115	130	150	170	200	225	255	280	310
16	Manganous chloride, 0.1	10	30	50	100	160	200	230	265	310	360	405	475	530
17	Manganous chloride, 1.0	0	20	35	80	160	200	240	280	330	380	420	475	530
18	Manganous acetate, 0.01	30	60	80	120	170	190	210	225	250	270	290	320	340
19	Manganous acetate, 0.10	20	70	120	220	460	670	820	980	...	...	1010	...	...
20	Manganous acetate, 1.0	0	20	30	60	140	200	260	360	520	680	800	940	1005
21	Nickel chloride, 0.01	10	40	60	80	100	110	120	130	140	155	170	180	190
22	Nickel chloride, 0.10	20	60	80	105	170	200	235	280	345	400	440	530	610
23	Nickel chloride, 1.0	0	30	60	100	180	220	265	330	440	530	610	730	790
24	Nickel acetate, 0.01	45	65	80	100	130	140	160	180	220	255	280	340	400
25	Nickel acetate, 0.10	10	60	110	190	290	380	430	520	620	700	760	840	890
26	Nickel acetate, 1.0	20	60	100	190	310	400	470	580	740	860	950	990	1000

TABLE I (Concluded)

Expt.		Time in minutes 1	2	3	5	10	15	20	30	50	75	100	150	200
27	Cobalt chloride, 0.01................	20	60	80	95	120	140	150	170	190	210	230	260	280
28	Cobalt chloride, 0.10................	20	80	130	200	320	430	520	630	750	830	890	980	...
29	Cobalt chloride, 1.0.................	30	80	130	200	340	460	560	690	820	920	970	995	1000
30	Cobalt acetate, 0.01................	20	50	80	110	140	160	170	185	190	195	200	210	220
31	Cobalt acetate, 0.1.................	20	60	130	260	310	690	790	900	970	990	995	...	...
32	Cobalt acetate, 1.0.................	10	30	60	130	220	300	370	500	720	850	970	1000	1000
33	Vanadic acid, 0.0109 g.............	10	50	65	75	90	110	120	140	175	210	230	270	320
34	Vanadic acid, 0.1090 g.............	0	35	70	90	110	125	140	150	170	190	200	230	250
35	Chromic chloride, 0.01..............	0	35	65	95	145	180	210	265	355	450	520	630	690
36	Chromic chloride, 0.1...............	20	30	65	105	200	280	335	405	500	590	660	770	820
37	Chromic chloride, 1.0...............	10	30	55	200	340	430	495	605	785	900	950	990	1000
38	Zinc acetate, 0.01..................	10	45	55	75	90	110	120	140	165	180	190	210	220
39	Zinc acetate, 0.10..................	10	35	75	170	310	480	610	790	950	995	1000	1000	1000
40	Zinc acetate, 1.0...................	0	0	0	10	10	10	10	15	...	...	...	...	20
41	Palladous chloride, 0.01............	55	85	100	110	150	190	220	280	380	480	545	640	670
42	Palladous chloride, 0.10............	85	150	175	220	350	450	560	710	910	1050	1130	1200	1220
43	Palladous chloride, 0.5.............	95	150	180	220	330	410	490	620	810	980	1120	1310	1420
44	Osmic acid, 0.10...................	30	65	75	90	95	100	105	110	120	140	150	175	185
45	Osmic acid, 1.0....................	20	35	45	65	100	130	155	210	330	490	650	935	1015
46	Sodium chloro-iridate, 0.5..........	0	10	55	85	120	160	190	240	320	370	400	440	450
47	Uranyl acetate, 0.0424 g...........	10	35	70	120	280	420	550	680	840	930	960	1000	1005
48	Uranyl acetate, 0.0042 g...........	65	120	185	300	480	600	660	720	795	930	955	...	...
49	Sodium hydroxide, 0.2..............	0	0	10	80	170	250	300	350	430	510	560	610	640
50	Sodium hydroxide, 1.0..............	0	0	0	0	120	600	850	970	985	990	995	995	995
51	Sodium hydroxide, 10.0.............	0	0	0	0	15	100	270	760	...	...	...	1000	1000
52	Sodium chromate, 0.10.............	0	0	10	75	130	175	210	285	420	570	700	920	1000
53	Sodium chromate, 1.0..............	0	0	0	0	0	0	0	15	20	25	30	40	...

(1 molecular equivalent of hydrogen absorbed) the reaction mixture was frequently characterized by fractional distillation and identification of the various fractions. In such cases, 85 to 95% yields of pure benzyl alcohol were isolated and identified by boiling point and refractive index. A method more frequently used and which was more nearly quantitative though less direct was the following. The measured hydrogen absorption (accurate to within 1%) indicated complete reduction to the alcohol. After completion of the reaction, a test with phenylhydrazine before and after boiling with a drop of dilute acid indicated the absence of unchanged aldehyde and of acetal. Benzyl alcohol was, therefore, the only product of the reaction (accurate to within 1%). Where the reaction was very slow and incomplete, the nature of the reduction product was of comparatively little interest and the process of analysis difficult and uncertain, owing to the large amount of unchanged aldehyde still present. Usually, in such cases, no attempt was made to analyze the reduction product. One such case, namely, where pure platinum oxide was used and no foreign substance was present, was examined in some detail. In one experiment, pure aldehyde in the presence of pure catalyst (0.23 g.) was caused to absorb 95% of the calculated amount of hydrogen by long shaking and repeated reactivation. In the reduction mixture a trace of toluene was detected by its odor, but none could be isolated. Benzyl alcohol was isolated in a yield of 80% of that calculated (or 84% of that calculated on the basis of the hydrogen absorbed) indicating that the amount of toluene formed must have been very small. Similarly, salicylaldehyde was reduced by means of pure catalyst and saligenin isolated in a yield of 82.5% of the calculated amount. In other experiments, it was attempted to determine the nature of the reduction product of benzaldehyde when pure catalyst is used and no attempt is made to force the reaction to completion by reactivation. Under these conditions about 10% of the calculated amount of hydrogen is absorbed. Aside from a very small amount of residue from the distillations, there was no evidence of the presence of any substances other than water, alcohol, benzaldehyde and benzyl alcohol in the reduction mixture.

In the aromatic series it was frequently observed that after completion of the first stage of the reaction (the formation of the alcohol), further reduction to the hydrocarbon occurred. This reaction was always slower than the first one. The tendency for this reaction to occur was more marked in absolute alcohol than in 95% alcohol and was specifically promoted by certain agents. Among these may be mentioned large amounts of ferric or ferrous chloride or sodium chloride or hydrochloric acid in the presence of ferrous chloride. The most powerful promoter for this reaction was palladium chloride. The formation of the hydrocarbon appeared always to be a subsequent, not a simultaneous, reaction. In the

aliphatic series this tendency was absent, and such aldehydes were not observed ever to absorb more than one molecular equivalent of hydrogen.

Discussion of Results

Regarding the mechanism of the effects described in this paper, it is given as an experimental fact that aldehydes very quickly deprive pure platinum black of its catalytic activity. Aldehydes, then, poison the platinum.[13]

Hence it appears that the function of the iron salt or other promoter is merely to eliminate or diminish the poisoning action of the aldehyde on the platinum. And in order to derive a partial explanation of the promoter action, it is necessary only to explain the poisoning action of the aldehyde.

Two possible explanations of the poisoning effect of the aldehyde were considered: (A) the aldehyde deprives the platinum black of the oxygen that is essential to its activity; (B) the aldehyde is very strongly or ir-reversibly adsorbed by the platinum.

The first explanation is that used by Willstätter and Waldschmidt-Leitz[14] to explain the poisoning effect of certain readily oxidizable substances such as glycerol on platinum black. It was also used as a guiding hypothesis in the early part of the present investigation. It involves the assumption that oxygen is associated in some way or other with active platinum black and that this oxygen is essential to its activity.

Although it is possible by means of this hypothesis to develop a fairly consistent explanation of the observed phenomena, some doubt has recently been thrown on the fundamental assumption on which it is based.[15] Moreover, salts of manganese, iron, and nickel are known to be powerful accelerators of the auto-oxidation of aldehydes, and it seems improbable that these salts would, even under the quite different conditions of the catalytic reduction, have the opposite effect on the oxidation of the alde-hyde by oxygen associated with the platinum. The hypothesis also led to certain predictions that could not be verified experimentally.

On the other hand, strong or irreversible adsorption (**B**) is supposed frequently to account for poisoning of catalysts. Aldehydes are among the more reactive types of organic compounds and it is, therefore, not sur-prising that they should be strongly adsorbed. Moreover, the existence of strong chemical forces between platinum and aldehyde is indicated by the tendency for the platinum to become permanently colloidal in the

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[13] In this connection it is to be observed that the reduction of the aldehyde starts rapidly, but soon stops. It may also be mentioned (unpublished results of Adams and Kern) that olefins containing a little aldehyde are reduced only very slowly with pure platinum, but rapidly when ferrous chloride is added or when the aldehyde is absent and no ferrous chloride is added.

[14] Willstätter and Waldschmidt-Leitz, *Ber.*, **54**, 113 (1921).

[15] Hofmann, *Ber.*, **55**, 573 (1922).

presence of aldehyde (in the absence of solvent). The fact that comparatively high concentrations of such poisons as mercuric acetate and potassium cyanide are required to suppress completely the activity of pure platinum in the presence of aldehyde may indicate that the surface of the platinum is almost completely covered with aldehyde. Reactivation of exhausted catalyst with air or oxygen may be explained by assuming that oxygen burns off the adsorbed aldehyde.

It seems probable that the poison is the aldehyde itself and not some possible oxidation or reduction product of it. A large amount of benzyl alcohol does not depress the activity of pure catalyst, and so far as observation has extended, benzaldehyde containing small amounts of benzoic acid behaves like pure aldehyde in this reaction.

Apparently, then, the function of the promoter is in some way to bring about a desorption of the aldehyde and so permit a renewal of the platinum surface. This may perhaps be brought about through the formation of a salt or complex between promoter and adsorbed aldehyde which subsequently dissociates in solution. Another possible mechanism of the promoting action of salts of elements of variable valence has already been discussed in detail.[16]

The physical condition of a catalyst is a very important factor in determining its activity. It is probable that the very unusual activity of the platinum oxide catalyst described in this series of papers is due partly to the fact that the platinum surface is produced in the reaction mixture and immediately before use. A perfectly clean and highly active surface is thus formed. In part, it may also be due to the favorable degree of subdivision of the platinum. The platinum oxide used is a powder sufficiently coarse to sink rather rapidly in still water. The degree of subdivision of the platinum produced from it depends upon such factors as the nature and relative amount of the solvent, the nature of the substance reduced, etc. By a proper regulation of conditions it is possible to obtain catalyst of almost any desired degree of subdivision whether a promoter is present or not.

A certain degree of subdivision was found to accompany maximum activity. This is such that the catalyst will remain suspended for several minutes in the quiet reaction mixture, but can readily be filtered off. More coarsely granular platinum (corresponding to ordinary platinum black) is less active. More finely divided, completely colloidal platinum is very much less active. To some extent the promoter affects the degree of subdivision of the catalyst. Thus the platinum shows somewhat less tendency to coagulate in the reduction of benzaldehyde when ferrous chloride is present than in its absence; but the difference in the degree of subdivision of the catalyst produced in the two cases is scarcely de-

tectable while the difference in reaction velocity is enormous. The platinum produced in the reduction of cinnamic aldehyde under certain conditions is completely colloidal either in the presence or absence of ferrous chloride. In both cases the reduction is slow, but it is very much slower in the absence of ferrous chloride than in its presence. Numerous facts of this kind show that however important may be the factor of subdivision, the presence or absence of a promoter is much more important in determining the velocity of the reduction of aldehydes, and that the promoter cannot possibly exercise its effect simply by stabilizing the catalyst suspension.

The Work of Faillebin.—The investigation of Faillebin on the effect of certain foreign substances on the platinum catalysis of the hydrogenation of aldehydes and ketones has been carried out concurrently with that of the writers, and quite independently. The methods used in the two investigations have been somewhat different. In his first communication,[10] Faillebin set forth the following results. Using 1 to 2 g. of platinum black as a catalyst, very little reduction was obtained with various aldehydes and ketones; for example, benzaldehyde and the products obtained consisted almost exclusively of the hydrocarbons. When ferric chloride was added to the solution of chloroplatinic acid from which the platinum black was prepared (by the formaldehyde-alkali reduction) quite different results were obtained. The hydrogenation took place with an excellent yield of the alcohol. The effect of iridium was similar to that of iron. In a second paper,[11] further experimental work apparently designed to furnish some insight into the mechanism of the reaction was described. Ethyl aceto-acetate was reduced. With pure platinum black the product was chiefly ethyl butyrate; with platinum containing iron, no ethyl butyrate was formed, but only ethyl β-hydroxybutyrate. The difference in the nature of the reaction under these two conditions was shown not to be due to a difference in the relative amounts of keto and enol form present; the formation of the hydrocarbon was shown to be a single reaction not involving intermediate formation of the alcohol. Platinum black prepared in the presence of aluminum chloride was found to behave like that prepared in the presence of ferric chloride; the difference was only one of degree.

Certain important points of difference between these results and those found in the present investigation appear.

In the writers' experiments the most striking effect of the iron salt was the enormous increase in reaction velocity which it produced. One infers that this effect was not so noticeable in Faillebin's experiments, since he refers to it only indirectly.

Faillebin states that in the presence of pure platinum, the product of the reduction of aldehydes and ketones was chiefly the hydrocarbon.

So far as the ketone acetone is concerned this statement is confirmed in a qualitative way by experiments of the writers (not previously described). It was found that ferrous chloride had no accelerating effect on the reduction of acetone in glacial acetic acid or in alcohol or in the absence of a solvent, but that in the absence of ferrous chloride a considerable fraction of the product consisted of propane. On the other hand, the formation of any significant amount of hydrocarbon (except as a subsequent reaction) was never observed in the reduction of aldehydes even with pure platinum.

Concerning Faillebin's statement that the behavior of aluminum is similar to that of iron, it has already been mentioned that in the writers' experiments, aluminum as the chloride or the oxide had no effect on the velocity of the reduction of benzaldehyde, nor did ferrous chloride accelerate the reduction of acetone. One infers that the above statement was, perhaps, only intended to imply that aluminum prevents the reduction to the hydrocarbon. The writers can only reiterate that in their experiments, aldehydes showed no tendency under any circumstances to be reduced directly to the hydrocarbons. The highly interesting experiments of M. Faillebin are here compared with those of the writers in some detail because it appears that M. Faillebin has overlooked[17] a certain disparity in the experimental results of the two investigations. This disparity is doubtless due to differences in experimental conditions and it illustrates again the necessity for precise definition of experimental detail in work on catalysis.

Summary

In continuation of the study of the catalytic reduction of aldehydes and promoter action, the effect of a number of substances on the platinum catalysis of the hydrogenation of benzaldehyde has been studied.

1. When ferrous chloride is added to pure catalyst that has been completely deprived of its activity by shaking with aldehyde, none of the activity is restored to the platinum, but when the mixture which contains the exhausted platinum is shaken with air, either before or after the addition of the iron salt, the activity of the catalyst is partially restored and the restoration is permanent.

2. The power to accelerate the platinum catalysis of the reduction of benzaldehyde was found to be common to all the compounds of iron examined, namely, metallic iron, ferrous hydroxide, ferric hydroxide, ferric oxide, ferric chloride, ferrous chloride, ferrous sulfate, ferric acetate and ferric nitrate.

[17] Faillebin (Ref. 11). "Par quel mécanisme le platine-fer donne-t-il un alcool là où le platine pur donne le carbure correspondant? Carothers et Adams ont proposé une explication difficilement conciliable avec le fait que l'aluminium jouit ici de la même propriété que le fer au degré près." The reduction of benzaldehyde to benzyl alcohol using pure platinum was described in the paper referred to.

3. The effects of 36 other inorganic salts, acids and bases have been studied. Salts and oxides of elements of the transition series had various degrees of promoting power. All alkalies accelerated the reaction. Mineral acids had little effect.

4. The effect of some substances on the promoting power of ferrous chloride was examined. Large amounts of hydrochloric acid diminished its effectiveness. Sodium nitrate and sodium chloride had very little effect on the acceleration produced by the ferrous chloride, but the latter caused the reaction to proceed slowly beyond the alcohol stage to the hydrocarbon. Sodium nitrite caused a large increase in the induction time and slightly repressed the main part of the reaction.

5. Whether a promoter was present or not, and regardless of the nature of the promoter, the first product of the reduction of the aldehydes appeared always to be almost exclusively the corresponding primary alcohol. The formation of hydrocarbon was sometimes observed as a subsequent reaction, but it was always very slow.

6. Hypotheses which might account for the mechanism of the promoter effects observed are discussed.

URBANA, ILLINOIS

TWO FORMS OF NITROGUANIDINE[1]

BY TENNEY L. DAVIS, AVERY A. ASHDOWN AND HENRY R. COUCH

Nitroguanidine exists in two forms, both agreeing with published descriptions in being "asbestos-like," but differing in their appearance and crystal habit, and being definitely distinguished as different by their indices of refraction.

α-Nitroguanidine appears invariably to be produced when guanidine nitrate is dissolved in concd. sulfuric acid and the solution is poured into water. It has been prepared in this Laboratory more than 200 times by that procedure. It crystallizes from water in long, thin, flat, flexible, lustrous needles which resemble phthalic anhydride; $N_\alpha = 1.518$, N_β a little greater than 1.668, N_γ greater than 1.768, double refraction 0.250.

β-Nitroguanidine is produced in variable amount, usually along with some of the alpha compound, by the nitration of the mixture of guanidine sulfate and ammonium sulfate which results from the hydrolysis of dicyanodiamide by sulfuric acid. After many experiments at different con-