[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

SELECTIVE REDUCTION OF CITRAL BY MEANS OF PLATINUM-OXIDE PLATINUM BLACK AND A PROMOTER. XII[1]

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The use of an iron salt as a promoter to platinum-oxide platinum black in the catalytic reduction of aldehydes has recently been applied to the reduction of an α,β-unsaturated aldehyde, cinnamic aldehyde.[1j] It was found possible to reduce the aldehyde group first and completely to an alcohol before the olefin linkage was attacked, although other catalytic methods caused the reduction of the olefin to take place before the aldehyde. This paper describes a study of the reduction of citral in order to determine whether the course of the reduction of other α,β-unsaturated aldehydes may be directed and controlled by poisoning or promoting the catalyst.

No satisfactory reducing reagents other than catalytic have been used with citral. Enklaar,[3] using finely divided nickel as a catalyst with temperatures of 130–140°, obtained a mixture of geraniol (II), citronellol (III), a hydrocarbon and cyclic alcohol. Even a more complex mixture was obtained with copper as a catalyst.

Skita[4] using colloidal palladium obtained a mixture of citronellal, citronellol and a considerable amount of a dimolecular aldehyde, which are analogous products to those obtained by reduction of other α,β-unsaturated aldehydes.

Ipatiew,[5] using palladium black, efficient stirring, a high pressure and temperature, obtained an excellent yield of the saturated alcohol tetrahydrogeraniol.

Armstrong and Hilditch[6] report the reduction of citral with nickel at 150°, obtaining first citronellal, second citronellol and finally tetrahydrogeraniol. Although detailed experiments were not given, presumably

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[1] For previous articles in this field, see (a) Voorhees with Adams, THIS JOURNAL, **44,** 1397 (1922). (b) Carothers with Adams, *ibid.*, **46,** 1071 (1923). (c) Adams and Shriner, *ibid.*, **45,** 2171 (1923) (preparation of catalyst). (d) Kaufmann with Adams, *ibid.*, **45,** 3029 (1923). (e) Carothers with Adams, *ibid.*, **46,** 1675 (1924). (f) Shriner with Adams, *ibid.*, **46,** 1684 (1924). (g) Carothers with Adams, *ibid.*, **47,** 1047 (1925). (h) Pierce with Adams, *ibid.*, **47,** 1098 (1925). (i) Kern and Shriner with Adams, *ibid.*, **47,** 1147 (1925). (j) Tuley with Adams, *ibid.*, **47,** 3061 (1925).

[2] This communication is an abstract of a portion of a thesis submitted by B. S. Garvey in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at the University of Illinois.

[3] Enklaar, *Ber.*, **41,** 2084 (1907).

[4] Skita, *Ber.*, **42,** 1639 (1909).

[5] Ipatiew, *Ber.*, **45,** 3218 (1912).

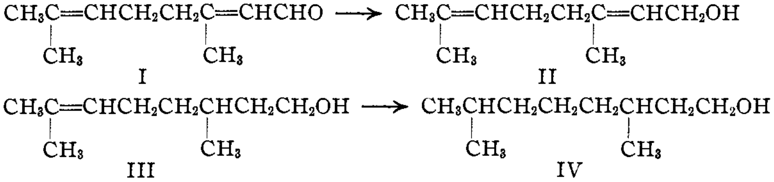
[6] Armstrong and Hilditch, *Chimie et Industrie*, **12,** 211 (1924); *J. Soc. Chem. Ind.*, **44,** 708 (1925).

each molecular equivalent of hydrogen was absorbed at one group quantitatively before the next group was attached.

Escourrou[7] used nickel at 190° and employed diminished pressure, thus effecting a reduction to citronellal.

It is obvious that wherever the reduction has been carried in steps the olefin adjacent to the aldehyde has reduced first, then the aldehyde and finally the second olefin group. No procedure has been found for satisfactory reduction of citral (I) to geraniol (II), that is, a method by which the aldehyde group is reduced first.

By using platinum-oxide platinum black and a small amount of promoter such as an iron salt, it was possible to reduce the aldehyde group first and quantitatively without reduction of either of the olefin linkages, thus producing geraniol (II) as a product. Further absorption of hydrogen gave citronellol (III) and finally tetrahydrogeraniol (IV).



$$\mathrm{CH_3\underset{CH_3}{C}{=}CHCH_2CH_2\underset{CH_3}{C}{=}CHCHO} \longrightarrow \mathrm{CH_3\underset{CH_3}{C}{=}CHCH_2CH_2\underset{CH_3}{C}{=}CHCH_2OH}$$

I II

$$\mathrm{CH_3\underset{CH_3}{C}{=}CHCH_2CH_2\underset{CH_3}{C}HCH_2CH_2OH} \longrightarrow \mathrm{CH_3\underset{CH_3}{C}HCH_2CH_2CH_2\underset{CH_3}{C}HCH_2CH_2OH}$$

III IV

Citral, like all other aldehydes studied in previous investigations, when reduced with hydrogen and platinum-oxide platinum black absorbs only a small amount of hydrogen (about 40% of one molecular equivalent) before the reaction stops completely. The time required for this absorption is less, the greater the amount of catalyst used. If the catalyst is reactivated with air or oxygen the reduction proceeds considerably further but

TABLE I

REDUCTION OF 15.2 G. OF CITRAL IN 50 CC. OF ALCOHOL (95%) AND FERROUS SULFATE

Catalyst, g.	$FeSO_4$, millimoles	Time in minutes Moles of hydrogen I	II	III	Product
0.05	0.1	180[a]	..	..	Geraniol; n_D^{20}, 1.4668
.05	($FeCl_2$) 1.0	180	..	..	Geraniol; $n_D^{27.5}$, 1.4705
.10	0.1	28	55	52	Tetrahydrogeraniol; $n_D^{27.5}$, 1.4380
.20	.5	20	24	26	Tetrahydrogeraniol; n_D^{20}, 1.4390
.20	.5	19	23	28	Tetrahydrogeraniol
.20	.1	17[b]	..	..	Geraniol; $n_D^{27.5}$, 1.4711
.20	.1	15	12[c]	..	Citronellol; $n_D^{27.5}$, 1.4510

[a] The reaction practically stopped after one molecular equivalent of hydrogen had been absorbed.

[b] The reaction was stopped after one molecular equivalent of hydrogen had been absorbed.

[c] The reaction was stopped after two molecular equivalents of hydrogen had been absorbed.

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[7] Escourrou, *Les Parfums de France*, **26**, 86 (1925).

not completely to tetrahydrogeraniol since the catalyst tends to coagulate after successive reactivations and loses its catalytic action.

The addition of a small amount of iron salt as a promoter causes the reduction of the citral to go rapidly and completely to tetrahydrogeraniol; no reactivation of the catalyst is necessary (Table I).

By stopping the reaction after successive equivalent proportions of hydrogen are absorbed, practically pure geraniol, citronellol or tetrahydrogeraniol can be obtained, as determined by boiling point, indices of refraction and odor. Traces of citral, for example, could not be detected in geraniol by the boiling point or index of refraction, but could be noted very readily by the odor. Since the readings for the absorption of hydrogen were accurate only to about 2–5%, the degree of purity might vary by this amount. In preparing pure geraniol by this procedure, all traces of citral disappeared when slightly more than the calculated amount of hydrogen was allowed to react.

The variation in the amount of iron salt used had very little effect on the speed of reduction (Table I). Increase in the amount of catalyst, however, had a marked effect in increasing the speed. With very small amounts of catalyst (0.05 g. to 15.0 g. of citral) the reduction almost stopped after one molecular equivalent of hydrogen was absorbed. With larger amounts (0.1 g.) the reduction proceeded until 3 molecular equivalents of hydrogen had been absorbed, but the first molecular equivalent was more rapidly absorbed than the second or third; with still larger amounts (0.2 g.) the time of absorption for each of the three molecular equivalents of hydrogen differed only slightly.

A similar study with zinc acetate as a promoter gave results which might be predicted from previous experiments with other aldehydes. Small amounts had a promoter effect just like the iron salts, but an increase in the amount slowed up the reduction so that the two or three molecular equivalents were only absorbed with great difficulty. Finally, with still larger amounts the catalyst was entirely poisoned so that reduction did not even start (Table II).

TABLE II

REDUCTION OF 15.2 G. OF CITRAL IN 50 CC. OF ALCOHOL (95%) WITH 0.2 G. OF CATALYST AND VARIOUS AMOUNTS OF ZINC ACETATE

$ZnAc_2$, millimoles	Time in minutes Moles of hydrogen I	II	III	Product
0.1	20	95	Half complete in 11 hours	Mixture
.2	85[a]	..	....	Geraniol; n^{31}_{D}, 1.4668
.4	..	..	....	....

[a] Reaction practically stopped after one mole of hydrogen was absorbed.

As pure reduction products were obtained by using iron salts and stopping the reduction after successive molecular equivalents of hydrogen were absorbed, only a few experiments were made which parallelled those with cinnamic aldehyde, using a mixture of iron and zinc salts in such a proportion that the reduction would stop completely after one molecular equivalent or after two molecular equivalents of hydrogen had been absorbed. These experiments indicated that conditions could readily be found for causing the reduction to stop either at geraniol or citronellol. It was noticeable, however, that amounts of zinc or iron salts necessary to cause the stopping of the reaction completely after one or two molecular equivalents of hydrogen were absorbed caused a much slower rate of reduction (Table III).

Table III

Reduction of 15.2 G. of Citral in 50 Cc. of Alcohol (95%) with 0.2 G. of Catalyst, 0.1 Millimole of $FeSO_4$ and $ZnAc_2$

$ZnAc_2$, millimoles	Time in minutes Moles of hydrogen			Product
	I	II	III	
0.075	20	25	28	Tetrahydrogeraniol
.10	23	125[a]	..	Citronellol; n_D^{33}, 1.4515
.12	60—very slowly after one mole			Geraniol
.15	60[b]			Geraniol; n_D^{33}, 1.4669

[a] The reaction stopped almost completely after two molecular equivalents of hydrogen had been absorbed.

[b] The reaction stopped almost completely after one molecular equivalent of hydrogen had been absorbed.

It is obvious that citral behaves similarly to cinnamic aldehyde in these catalytic reductions and the probability is that other α,β-unsaturated aldehydes will act in the same way.

Other investigators[8] who have studied the reduction of citral have also studied the reduction of geraniol, and since geraniol is an intermediate product in the complete hydrogenation of citral, a few experiments have been made which gave the expected results. Using platinum-oxide platinum black (0.2 g. and 15.4 g. of geraniol) the reduction took place so rapidly that much heat was evolved and there was very little difference in the rate of reduction of the first and second olefin groups (five minutes for each). It seems likely, however, that this rapid reduction of the second olefin group is due chiefly to the heat evolved by the reduction of the first group. The use of smaller amounts of catalyst made the reduction proceed more slowly and the increased rate of hydrogenation of the first olefin over the second olefin was noticeable. In a previous study of the reduction of various olefins both iron and zinc salts were found to poison the catalyst, the latter salt being the more effective. The same results were found in the reduction of geraniol. Moreover, the reduction of the second olefin linkage became very much slower than the first under these conditions.

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[8] Grignard and Escourrou, *Bull. soc. chim.*, **38**, 546 (1925). Previous papers are cited in this reference.

In all cases the reaction product after absorption of one molecular equivalent of hydrogen proved to be practically pure citronellol (Table IV).

TABLE IV

REDUCTION OF 15.4 G. OF GERANIOL IN 50 CC. OF ALCOHOL (95%)

Catalyst, g.	Millimoles of salt	Time in minutes Moles of hydrogen I	II	Product
0.01	...	300[a]	..	Citronellol
.05	...	15	80	Tetrahydrogeraniol
.2	...	5	5	Tetrahydrogeraniol; $n_D^{27.5}$, 1.4378
.2	...	5[b]	..	Citronellol; $n_D^{27.5}$, 1.4545
.2	0.1 ($FeSO_4$)	6	18	Tetrahydrogeraniol; $n_D^{27.5}$, 1.4380
.2	.1 ($ZnAc_2$)	10[a]	..	Citronellol

[a] The reaction stopped after one molecular equivalent of hydrogen had been absorbed.

[b] The reaction was stopped after one molecular equivalent of hydrogen had been absorbed.

A possible explanation for the promoter action of certain salts in the reduction of aldehydes with platinum-oxide platinum black was previously discussed. It was suggested that the aldehyde was so highly absorbed that the active points of the catalyst were poisoned and only for a very short time after a fresh surface of catalyst was available would reduction take place. Agitation of the catalyst with oxygen caused reactivation by burning off the adsorbed layer. The promoter in turn was assumed to prevent poisoning of the catalyst by aiding the desorption of the aldehyde.

Other mechanisms, however, are possible which agree with the experimental facts. It has been well established that the power of adsorption alone is not sufficient to make a substance a catalyst. As a consequence, it might be assumed that a promoter is actually the activating agent of the substance to be reduced. The promoter must be used in very definite amounts since it may in addition to its activating action also be adsorbed by the catalyst and poison it.

Applying this assumption to the reduction of aldehydes it might be said that the aldehyde is not activated for reduction by the platinum but by the promoter. It is a fact that the promoters which have been found for aldehydes, especially the iron and zinc salts, are substances which are known to catalyze various aldehyde reactions, such as acetal formation, diacyl formation, oxidation, etc. The iron salts are apparently not so readily adsorbed by the platinum as the zinc salts and consequently do not poison the catalyst when used in proportionately large amounts.

This explanation of the promoter action in reduction of aldehydes, however, cannot be so simple, since it has been repeatedly confirmed that oxygen[9] is necessary for the reduction. The promoters do not function

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[9] See Waldschmidt-Leitz and Seitz, *Ber.*, **58**, 563 (1925).

unless the oxygen is present. This suggests that perhaps the aldehyde itself is not activated by the platinum but that there is an intermediate oxygen-benzaldehyde compound which is readily activated by the catalyst and reduced. The iron or zinc salt promoters may then act as catalysts in the formation of the oxygen-aldehyde complex or perhaps may function as a carrier for the oxygen from the oxygen-benzaldehyde molecule after reduction, to another aldehyde molecule, thus slowing down very materially the reduction of the oxygen by the hydrogen.

Experimental Part

The catalyst and the iron and zinc salt solutions were prepared as described in a previous paper.[1j] The apparatus was the same that was employed in the other reduction investigations.

The procedure followed was to introduce the platinum oxide into the reaction bottle, then the alcohol and substanec to be reduced (50 cc. of 95% alcohol for 0.1 mole of compound, 100 cc. for 0.2 mole). When salts were added they were introduced at this time. The reduction of the platinum oxide and then of the substance was carried out as previously described.

The citral and geraniol were commercial C. P. samples. They were redistilled; the citral boiled at 108° (5 mm.), n_D^{20}, 1.4868; the geraniol boiled at 115° (6 mm.), $n_D^{27.5}$, 1.4670.

The products were isolated by filtering the platinum from the reaction mixture; the solvent was then distilled and the product fractionated under diminished pressure, using a modified Claisen flask with side-arm column.

Only a few of the more typical experiments are given in the tables. In all the experiments the geraniol, citronellol and tetrahydrogeraniol were collected over about a 3° range and the indices of refraction taken. The yields were practically quantitative. The boiling points agreed with those in the literature; geraniol, 115° (6 mm.); citronellol, 110° (10 mm.); n_D^{14}, 1.4514; tetrahydrogeraniol, 109–110° (13 mm.); n_D^{15}, 1.4438; citronellal, n_D, 1.4461. The observed indices of refraction are given in the tables.

Summary

1. Citral may be reduced quantitatively to geraniol by means of platinum-oxide platinum black and hydrogen in the presence of small amounts of promoters such as ferrous sulfate or zinc acetate.

2. When two molecular equivalents of hydrogen instead of one are absorbed, pure citronellol results. After three equivalents are absorbed tetrahydrogeraniol is obtained.

3. Geraniol is reduced to citronellol then to tetrahydrogeraniol. Promoters for the citral reduction act as poisons in this reduction.

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