[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 113]

The Effect of Certain Peroxides and Acids on the Reduction of Olefins in Alcohol Solution with Platinum Oxide Catalyst

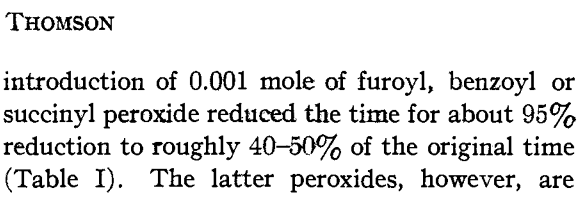
BY GEORGE THOMSON

In certain cases of hydrogenation using $PtO_2 \cdot 2H_2O$ as a catalyst it is necessary to reactivate the catalyst frequently by shaking with air, or, better, with oxygen. This is especially true when reducing aldehydes.[1,2] On the other hand, olefins reduce rather easily but, according to Adams, if the platinum catalyst contains iron and the olefin is pure the reduction is inhibited. If the olefin is impure and the catalyst contains iron, the reduction may be accelerated.[3] The work reported in this paper was undertaken to determine why olefins when impure are thus able to offset the poisoning effect of iron.

Kern, Shriner and Adams concluded that the impurities in allylbenzenes which caused this acceleration were aldehydes. Since, however, the catalytic activity of platinum catalysts for hydrogenation has been ascribed to the presence of a platinum peroxide[4,5,6] and since olefins on standing in contact with air readily form peroxides which, in the case of pentene-2 at 100° under pressure, will oxidize lead to litharge, it was thought these might be the impurities which caused the acceleration by oxidizing some of the platinum to platinum peroxide.

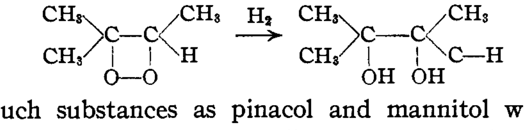
It was found that when using a catalyst containing iron, and a sample of trimethylethylene freshly distilled over sodium and boiling at 38.3–38.4° ("International Critical Tables," 38.4°), reagent alcohol[7] as a solvent, the reduction stopped after the absorption of 27% of the theoretical amount of hydrogen. The percentage reduction could be increased according to the length of time the olefin *alone* was shaken with air before being hydrogenated. If the catalyst does not contain so much iron as to stop completely the reaction after a small fraction is reduced, then the shaking with air or addition of peroxides has the effect of shortening the time required for a definite percentage reduction. The introduction of 0.001 mole of furoyl, benzoyl or succinyl peroxide reduced the time for about 95% reduction to roughly 40–50% of the original time (Table I). The latter peroxides, however, are probably reduced in the experiment to the corresponding acids and it was found that the addition of 0.002 mole of furoic, benzoic or succinic acid had an equally marked effect. Two drops of concentrated hydrochloric acid or glacial acetic were even more effective, the time for 91% hydrogenation being reduced from twenty minutes to about five minutes.

It seems probable, therefore, that when the olefin is shaken with air, the peroxide formed decomposes to give, in the case of trimethylethylene, acetone and acetaldehyde. The aldehyde is then oxidized by the air or olefin peroxide to acetic acid which counteracts the poisoning effect of the iron.



If a sample of trimethylethylene which has been exposed to the air is tested for peroxide with potassium iodide and starch solution and allowed to stand overnight, the blue color disappears and a precipitate of iodoform is found in the bottom of the test-tube, indicating the peroxide breaks up in the above manner. The addition of acetaldehyde itself had no appreciable effect on the hydrogenation but if the aldehyde was first added to some trimethylethylene containing peroxide and allowed to stand for ten minutes, there was a noticeable decrease in the time of reduction twenty minutes to fifteen minutes.

The olefin peroxide might also be reduced to a glycol.



Such substances as pinacol and mannitol were found to have but a small effect compared with that of acids or peroxides.

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(1) Carothers and Adams, THIS JOURNAL, **45**, 1071 (1923).

(2) Kaufmann and Adams, *ibid.*, **45**, 3035 (1923).

(3) Kern, Shriner and Adams, *ibid.*, **47**, 1147 (1925).

(4) Willstätter and Jaquet, *Ber.*, **51**, 767 (1918).

(5) Willstätter and Leitz, *ibid.*, **54**, 113 (1921).

(6) Rocasolano, *Compt. rend.*, **173**, 41, 234 (1921).

(7) Reagent alcohol—95% ethyl, 5% methyl alcohol, negative test for aldehyde.

TABLE I

USING 0.1 G. OF CATALYST CONTAINING IRON, 10 CC. OF FRESHLY DISTILLED TRIMETHYLETHYLENE (38.3–38.4°), 150 CC. OF REAGENT ALCOHOL AND SHAKING AT A RATE OF 300 PER MINUTE

Trimethylethylene		Promoter, mole	Reduced, %[b]	Time, min.	Rate on linear part of curve, cc./min.
Olefin		None	91–92	19–20	400
Olefin	+	Furoyl peroxide,[a] 0.001	94.5	12	372
Olefin	+	Benzoyl peroxide, 0.001	94.5	8	457
Olefin	+	Succinyl peroxide, 0.001	92	6	457
Olefin	+	Furoic acid, 0.002	95	9.5	430
Olefin	+	Benzoic acid, 0.002	95	9	430
Olefin	+	Succinic acid, 0.002	93	6	486
Olefin	+	Glacial acetic acid (two drops)	91	6	430
			95	8	
Olefin	+	Mannitol (0.033 g. = 0.00017)	91	13	457
Olefin	+	C. P. hydrochloric acid (two drops)	91.0	5	515
Olefin		Iron-free catalyst + 4 drops 2 N $FeSO_4$	97.5	33	No linear portion
Olefin	+	As above, + C. P. concd. HCl (two drops)	96.2	10	315
E.K.C. Amylene		None	90	12	486
distd. over sod.		Succinyl peroxide	92	6	515

[a] The author is indebted to Dr. N. A. Milas for the peroxides.

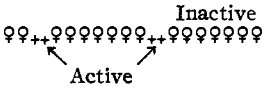
[b] The percentages reported do not mean that the reduction stopped at this point. Since the remainder of the reduction proceeded very slowly, these figures are used for convenience of comparison.

Kern, Shriner and Adams[3] found the addition of anisaldehyde to a solution of anethole decreased the time for reduction when using a catalyst in the presence of iron salts. The other oxidation product of anethol, acetic acid, was not considered. The addition of three drops of glacial acetic acid decreased the time for 92% reduction of the anethol from forty-one minutes to twenty-six minutes.

This effect of the acid might be explained as a dissolving from the surface of the catalyst of a film of ferrous hydroxide precipitated by the alkali included in the catalyst. While it may be that addition of alkali would cause poisoning by such a mechanism, if this were true, one would have to admit that the iron salts in the hydrogenation mixture are not poisonous to the platinum catalyst. Furthermore, such a simple explanation of the poisoning effect of iron salts would make them a universal poison whereas they accelerate the reduction of aldehydes and ketones. The catalyst was warmed with dilute C. P. hydrochloric acid several times and finally washed free of acid and dried. This catalyst behaved exactly as before when ferrous sulfate was added.[8,9]

It will be noted on examination of the curves that the addition of traces of acid or peroxide increases the time interval during which the rate of absorption of hydrogen is constant, whereas, when the catalyst is poisoned by iron salts, the rate deviates from the straight line much sooner. According to Taylor, linear curves indicate that[10] the catalyst surface was, initially and for a prolonged period of time, completely saturated with reactants and that the deviations from the straight line in the later stages of the reaction are due in part to the competition of the reaction products for the catalyst surface. If this is true, the addition of traces of acid must either prevent the adsorption of the reaction products, or create new active centers, or enlarge those already present to make up for the loss of those made inactive by iron poisoning or reaction products.

The following picture is suggested to show how hydrogen ions might maintain the activity of a catalyst although the above data are in no way considered to be proof of this mechanism. Suppose an inactive surface to be one covered with a layer of electrons whose charges are neutralized by the positive charges on the platinum atoms beneath them. An active spot would then be a small section, not covered by electrons, where the positive charges of the platinum atoms are exposed or not neutralized.[11]



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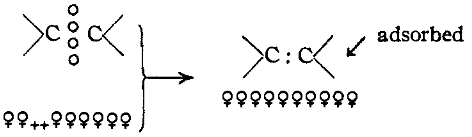
[8] Adams and Shriner, THIS JOURNAL, **45**, 2171 (1923).

[9] Wöhler and Martin, *Z. Elektrochem.*, **15**, 132 (1909).

[10] Taylor, "Treatise on Physical Chemistry," Vol. II, p. 1038.

[11] Finch and Ikin, *Proc. Roy. Soc.* (London), **A145**, 551 (1934), find that there is a relation between catalytic activity and the charge on a surface. Electrically neutral films were inert as catalysts for the combination of H_2 and O_2.



If such an active spot were occupied by one or more adsorbed olefin molecules and if there were no additional active space for the adjacent adsorption of hydrogen, or if the neighboring previously active surface were occupied by adsorbed ferrous ion, no reduction would take place. According to such a picture, molecular hydrogen could not react at this particular spot but if hydrogen ions were in the immediate vicinity and could attach themselves adjacent to the olefin molecule, reduction would take place. After the detachment of the reaction product the active spot is now larger and capable of adsorbing both molecular hydrogen and olefin and the reduction proceeds in the normal way.

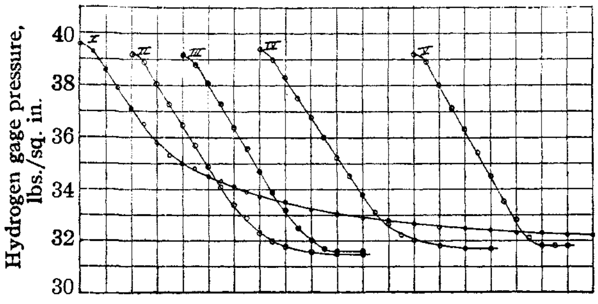
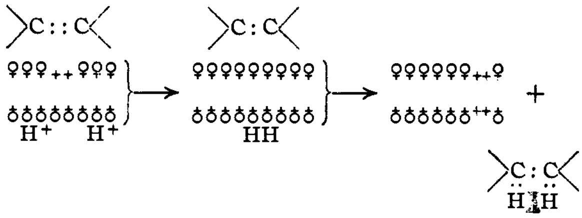
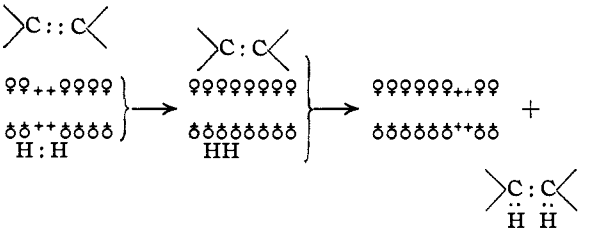


Fig. 1.—Reduction of trimethylethylene in alcohol solution using iron-containing platinum oxide–platinum black as a catalyst. 1 lb. decrease in H_2 pressure = 286 cc. H_2 (atm. press., 25°) absorbed. Curve I, nothing added; Curve II, 0.026 g. of benzoyl peroxide added; Curve III, 0.025 g. of succinic acid added; Curve IV, 2 drops of glacial acetic added; Curve V, 2 drops of concd. C. P. hydrochloric acid added. The catalyst in each case was from the same batch of platinum oxide. The iron content was not determined but the amount in 0.1 g. of catalyst must have been less than that in 4 drops of 2 N $FeSO_4$ (see Table I).



When iron free catalyst is used, the addition of acid is without effect either on the rate or total percentage of olefin reduced. In view of this fact, the above explanation involves the assumption that there is possible only a certain amount of active surface per unit weight of catalyst. Otherwise, the addition of small amounts of acid should increase the active surface of iron-free catalyst according to the above mechanism. It may be that an active spot soon becomes hemmed in by adsorbed hydrogen so that the adjacent adsorption of olefin and hydrogen then becomes possible only in the center of the active area. The diminishing of the active area by this hemming-in process may account for the fact that suspensions of platinum black become totally inactive after being shaken for a long time with hydrogen.[12]



Another possible explanation of the effect of the addition of acid is that the suspension of platinum is stabilized.

Packendorff,[13] using a platinum catalyst on active carbon for the reduction of compounds such as levulinic acid, phthalimide, etc., found that whenever the reaction came to a stop, it could be started again by the successive addition of small portions of concentrated hydrochloric acid. Since iron affects this type of reduction, it is of importance to know whether the added hydrochloric acid was chemically pure or not and this was not stated.

Experimental Part

The reductions were carried out in a standard Adams apparatus as sold by the Burgess–Parr Company, Moline, Ill. Most of the experiments were carried out with trimethylethylene obtained from *t*-amyl alcohol by dehydration with oxalic acid. The hydrocarbon was distilled over sodium immediately before using in a reduction and boiled at 38.3–38.4°. A new batch of olefin was always checked with the previous one, using the same sample of iron containing catalyst, before the effect of a particular acid or peroxide was tried out. For 91–92% reduction the time was nineteen to twenty minutes and the rate in the linear part of the curve was 400 cc. of hydrogen per minute. The experimental conditions were: 10

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(12) Willstätter, *Ber.*, **54**, 113–118 (1921).

(13) Packendorff, *ibid.*, **67**, 905 (1934).

cc. of trimethylethylene, 150 cc. of reagent alcohol, 0.1 g. of iron-containing catalyst, rate of shaking 300 per minute, initial gage pressure of hydrogen 39–40 lb. per sq. in.

In one experiment in which ferrous sulfate was added to an iron-free catalyst so that the time was extended to thirty-three minutes, the plot of hydrogen pressure against time was not linear except perhaps during the first minute.

The addition of two drops of C. P. concd. hydrochloric acid when using an iron-free catalyst made no difference in the activity, the data without the addition of acid being: 93% in seven minutes, linear rate 430 cc. of hydrogen per minute: with acid, 93% in eight minutes, linear rate 430 cc. of hydrogen per minute.

In the experiments with anethol the material was distilled under 2 mm. vacuum and it boiled at 79.5–80.5°; 15 cc. of this was taken, 0.05 g. iron-free catalyst, 150 cc. reagent alcohol, 8 drops of 2 *N* ferrous sulfate solution, 300 shakes per minute. The time for 92% reduction was forty-one minutes, whereas when 3 drops of glacial acetic acid were added, the time was reduced to twenty-six minutes for the same reduction.

Summary

1. It has been shown that the acid oxidation products of olefins are the impurities which offset the poisoning effect of iron on platinum catalysts used in the reduction of these olefins.

2. Benzoyl, furoyl, succinyl peroxides and benzoic, furoic, succinic, acetic, hydrochloric acids in small amounts offset this poisoning effect of iron.

3. A mechanism to explain this effect of small amounts of acids is suggested.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. XII. The Decomposition of Methane

BY F. O. RICE AND M. DENISE DOOLEY

Recently Kassel[1] has studied the thermal decomposition of methane and has concluded that the primary step is probably represented by the equation $CH_4 \longrightarrow H_2 + CH_2$ followed by the reaction[2] $CH_2 + CH_4 \longrightarrow C_2H_6$. Furthermore, Belchetz[3] has attempted to obtain a direct experimental proof of the first step of this proposed mechanism by passing methane in a rapid stream at low pressures over a platinum filament heated in the range 877–1027°; after leaving the filament the methane and any fragments which had been formed were passed over a tellurium mirror and through a liquid air trap, the contents of which were analyzed. Similar experiments were performed using mirrors of iodine. As a result of this work Belchetz concluded that the methylene radical was formed in the decomposition of methane and that it could be identified by its products of combination with the mirrors.

These experiments, however, are not in agreement with the results obtained when diazomethane is decomposed[4] and the fragments are passed over a tellurium mirror; the compound formed by the combination of the methylene radicals thus produced with tellurium has been shown to be a polymer of telluroformaldehyde, $(HCHTe)_n$, which is so involatile that it does not pass into the liquid air trap but deposits on the walls of the tube just beyond the tellurium mirror as a red solid. We decided therefore to investigate the products formed when methane was decomposed in a quartz furnace at low pressures according to a technique previously described.[5] When the gases leaving the furnace were passed over a tellurium mirror we obtained no trace of any telluroformaldehyde on the walls of the tube; instead we obtained a red solid in the liquid air trap; this substance melted sharply at −19.5°, showing it to be dimethyl ditelluride $CH_3TeTeCH_3$. The same results were obtained when the experiment was repeated with pieces of platinum foil in the furnace. In none of the experiments did we obtain any indication of the presence of methylene radicals.

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(1) Kassel, THIS JOURNAL, **54**, 3949 (1932).

(2) The ethane thus formed undergoes dehydrogenation to yield ethylene, acetylene and finally carbon.

(3) Belchetz, *Trans. Faraday Soc.*, **34**, 170 (1934).

(4) Rice and Glasebrook, THIS JOURNAL, **56**, 2381 (1934).

(5) Rice, Johnston and Evering, *ibid.*, **54**, 3259 (1932).