[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF GEORGETOWN (KENTUCKY) COLLEGE]

THE EFFECT OF TEMPERATURE ON THE REDUCTION RATE OF FURFURAL WITH THE CATALYST FROM $PtO_2 \cdot H_2O$

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Several investigators have noted a decrease in the catalytic activity of platinum black and sponge for hydrogenations when these are heated to a high temperature.[1] Others have noted that temperature affects reduction rates, both with[2] and without[3] the use of a solvent. However, little work has been done on a quantitative study of reduction rate, with platinum black, at temperatures slightly above and below room temperature, which is used generally in such reductions.

This paper deals with the effect of temperature on the reduction rate of furfural, in 95% alcohol, at 0, 20, 40 and 60°, with platinum black from $PtO_2 \cdot H_2O$[4] as catalyst. Using the same catalyst, Carothers and Jones[5] noted that between 50 and 100° increase in temperature caused increased speed in the reduction of aromatic nitriles. Tuley and Adams[6] observed that a rise in temperature caused an increase in the reduction rate of cinnamyl aldehyde, but a lowering of the yield of pure reduction product. Also, with this catalyst, it has been noted that the reduction rates of geraniol,[7] triphenylamine,[8] pyridine hydrochloride,[9] and aromatic nitro compounds[10] increase with rise in temperature, but these studies were not quantitative.

In this paper it is shown that increase in temperature from 0 to 40° causes a marked increase in the reduction rate of furfural, and at 60°, if sufficient catalyst is present, the initial reduction rate is much greater than at 40°. However, at 60° the catalyst is rendered inactive more readily than at 40°, so particularly if only a small amount of catalyst is present, the reduction will proceed faster at 40° than at 60°. Also, it

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[1] Vavon, *Compt. rend.*, **158**, 409 (1914); Wright and Smith, *J. Chem. Soc.*, **119**, 1683 (1921); Lemoine, *Compt. rend.*, **162**, 657 (1916).

[2] Paal and Gerum, *Ber.*, **40**, 2209 (1907); Willstätter and Waldschmidt-Leitz, *ibid.*, **54B**, 113 (1921); Böeseken, van der Weide and Mom, *Rec. trav. chim.*, **35**, 260 (1915); Hiers and Adams, *Ber.*, **59B**, 162 (1926).

[3] Zelinsky and Turowa-Pollak, *Ber.*, **58B**, 1298 (1925); Escourrou, *Parfums de France*, No. 26, p. 86; Zelinsky and Borisoff, *Ber.*, **57B**, 150 (1924).

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

[5] Carothers and Jones, *ibid.*, **47**, 3053 (1925).

[6] Tuley with Adams, *ibid.*, **47**, 3066 (1925).

[7] Adams and Garvey, *ibid.*, **48**, 480 (1926).

[8] Hiers and Adams, *ibid.*, **49**, 1101 (1927).

[9] Hamilton and Adams, *ibid.*, **50**, 2261 (1928).

[10] Adams, Cohen and Rees, *ibid.*, **49**, 1094 (1927).

is shown that, although furyl alcohol is formed readily and quantitatively, without activation of the catalyst, the same catalyst, without activation, will not add hydrogen to the formed furyl alcohol.

Experimental Part

The apparatus used in this work was essentially the same as that used by Vorhees and Adams,[11] except that it was arranged so that the temperature could be kept constant. In order that the results might be comparable, in each case 9.6 g. (0.1 mole) of furfural, dissolved in 75 cc. of alcohol, was reduced in the presence of catalyst from the same batch and 1 cc. of freshly prepared 0.1 *M* ferrous sulfate, with hydrogen at about 2 atmospheres pressure. Runs were made with 0.122 (see Fig. 1) and 0.244 g. (see Fig. 2) of $PtO_2 \cdot H_2O$[12] at 0, 20, 40 and 60°. In all of these reductions the catalyst was activated at the end of each hour by shaking it for ten minutes with oxygen.[13] The effect on the reduction rate may be noted from the upward trend of each curve at the beginning of the hour, in Figs. 1 and 2.

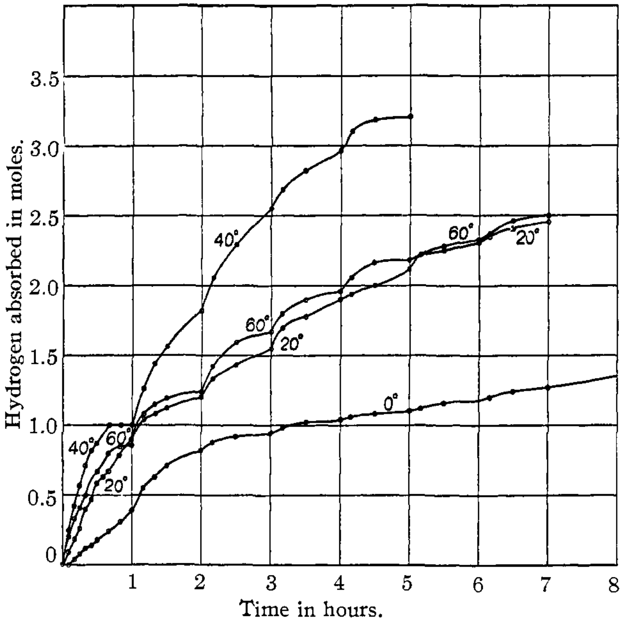

Fig. 1.—Reduction of 0.1 mole of furfural; 0.122 g. of catalyst; 1 cc. of *M*/10 ferrous sulfate.

Furyl alcohol was formed quantitatively by the addition of 1 mole of hydrogen to furfural. Kaufmann and Adams[13] showed that with the catalyst used for this work, on complete reduction, furfural yields tetrahydrofuryl alcohol, pentanediol-1,5, pentanediol-4,5 and *n*-amyl alcohol.

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[11] Vorhees with Adams, This Journal, **44**, 1403 (1922).

[12] Note: 0.122 g. of catalyst is 0.005 mole, assuming its formula to be $PtO_2 \cdot H_2O$. Calcd. for $PtO_2 \cdot H_2O$: Pt, 79.95. Found: Pt, 79.73.

[13] Kaufmann with Adams, This Journal, **45**, 3029 (1923).

As can be seen from the figures, the catalyst becomes active and the absorption of hydrogen becomes rapid much more quickly in the higher temperature than in the lower temperature reductions. $PtO_2 \cdot H_2O$ is brown and the active catalyst is black, so the change in color from brown to black is an indication of the formation of the active catalyst. Usually, in the 60° runs, the catalyst became black in less than forty-five seconds, while in the 0° runs it sometimes took ten minutes or over for the catalyst to become completely black.

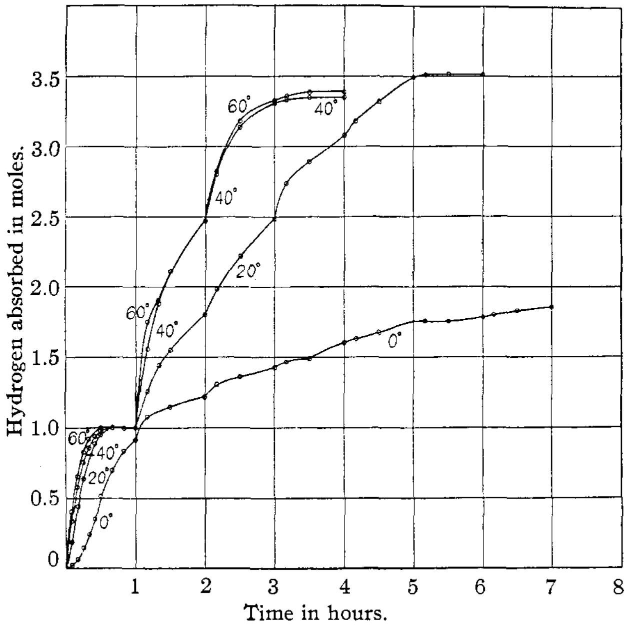

Fig. 2.—Reduction of 0.1 mole of furfural; 0.244 g. of catalyst; 1 cc. of $M/10$ ferrous sulfate.

It was noted that in no case was over 1 mole of hydrogen added to furfural until the catalyst was activated. Attempts were made to cause more to be absorbed by increasing the amount of catalyst and lengthening the time of shaking the reaction mixture. Although 0.122 g. of catalyst at 40° caused 1 mole of hydrogen to be added smoothly in forty minutes, at the same temperature 0.976 g. or eight times as much catalyst caused no more to be added (if a correction is made for the hydrogen required to reduce the $PtO_2 \cdot H_2O$ to the active catalyst, as determined in a control test), although the reaction mixture was shaken for one hour after hydrogen ceased to be absorbed. These facts seem to indicate that the platinum black which has been used as a catalyst for the reduction of furfural is not a catalyst for the reduction of furyl alcohol, and that the only way it can be made to add more hydrogen to the latter compound is to change its surface by activation.

Summary

1. Curves are given for the reduction rate of furfural at 0, 20, 40 and 60°.
2. Activation of the catalyst is necessary to add more than 1 mole of hydrogen to furfural.

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

THE PREPARATION OF MERCURY DIPHENYL[1] BY USE OF THE GRIGNARD REAGENT

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The reactions that may take place in the preparation of mercury diphenyl by the Grignard reagent are as follows

$$\begin{aligned} HgX_2 + 2C_6H_5MgBr &= Hg(C_6H_5)_2 + 2MgBrX \qquad (1)\\ HgX_2 + C_6H_5MgBr &= Hg(C_6H_5)Hal + MgBrX\\ Hg(C_6H_5)X + C_6H_5MgBr &= Hg(C_6H_5)_2 + MgBrX\\ HgX_2 + Hg(C_6H_5)_2 &= 2Hg(C_6H_5)X \end{aligned}$$

HgX_2 may be the iodide, bromide or chloride. Laszczynski[2] measured the solubility of mercuric iodide and chloride in absolute ether at 0° and found it to be 0.62 and 5.98%, respectively. Measurements made on mercuric bromide at 0° gave the solubility as 4.82 g. per 100 g. of solution, using absolute ether. Due to the insolubility of the iodide experiments were made with the bromide and chloride only. The yields as given in Table I show some difference between the bromide and chloride for the same concentration but not sufficient to say that one is much better than the other.

Table I shows that 85 mole per cent. of mercuric halide gives the best yield with the methods used. From published data[3] the yield of the Grignard reagent from bromobenzene is about 94%, which gives an excess over the mercuric halide used of about 9%; this is not too much considering the fact that it must be transferred before using.

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[1] For the different methods of preparation of mercury diphenyl see "Organic Syntheses," Vol. IX, John Wiley and Sons, Inc., New York, **1929**, p. 54. One later method is described in *Ber.*, **62**, 1018 (1929). The method in "Organic Syntheses" uses a 3% sodium amalgam. Better yields can be obtained with an 8% amalgam (Michaelis and Loesner, *Ber.*, **27**, 264 (1894)) which has been checked by the authors. If a large quantity of mercury diphenyl is wanted this method is recommended over the Grignard. It should always be remembered that the vapors of mercury diphenyl are toxic.

[2] Laszczynski, *Ber.*, **27**, 2285 (1894).

[3] Gilman, Zoellner and Dickey, THIS JOURNAL, **51**, 1584 (1929).