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Abstract

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HYDROGENOLYSIS OF FURAN HOMOLOGUES ON A PLATINUM CATALYST

In 1923, Kaufmann and Adams (1) used a platinum catalyst promoted with iron salts for the hydrogenation of furfural and some of its derivatives in the liquid phase at ordinary temperature. The authors found that under these conditions the principal reaction is hydrogenation of the double bonds in the furan ring, as a result of which tetrahydrofuran derivatives are formed. However, in the hydrogenation of furfural, together with tetrahydrofuryl alcohol, small amounts of products from hydrogenolysis of the furan ring at the C—O bonds were obtained—pentanediols-1,2 and -1,5 and *n*-amyl alcohol. In the authors' opinion, the formation of these compounds cannot proceed through the stage of tetrahydrofuryl alcohol, since the latter, under the experimental conditions, does not undergo hydrogenolysis in appreciable amounts.

Pierce and Adams (2) investigated the hydrogenation of ethyl- and butylfurylcarbinols under the conditions described above and arrived at analogous results: in addition to alkyltetrahydrofurylcarbinols, products of ring cleavage—alkanediols and alkanols—were obtained.

Smith and Fuzek (3), studying the hydrogenation of furan and its nearest homologues, as well as furyl alcohol and pyromucic acid, in the liquid phase in the presence of Adams' platinum catalyst at elevated temperatures, found that under these conditions the principal reaction is hydrogenolysis of the ring at the ether bond, leading to the formation of compounds of the aliphatic series. It was established that, other conditions being equal, the nature of the side group exerts a decisive influence on the direction of hydrogenolysis of the furan ring. Thus, sylvan and furyl alcohol are cleaved at the C—O bond 1—5 with formation, respectively, of pentanol-2 and pentanediol-1,2, whereas hydrogenolysis of the ring in the molecule of pyromucic acid proceeds at the ether bond adjacent to the carboxyl group (bond 1—2). With regard to the mechanism of hydrogenolysis of the furan ring, Smith and Fuzek, as a result of a comparative study of the hydrogenolysis of furan and tetrahydrofuran, came to the same conclusions as Kaufmann and Adams.

Hydrogenolysis of furan homologues in the liquid and vapor phases proceeds differently. In the hydrogenation of sylvan on copper chromite in the liquid phase under hydrogen pressure, the furan ring is cleaved to almost the same extent at the C—O bonds 1—2 and 1—5 (^{4}). In the vapor phase, on nickel (^{5}) and copper (^{6}) catalysts, the furan ring in sylvan is cleaved only in the direction of the C—O bond not adjacent to the side group.

Hydrogenolysis of furan homologues in the vapor phase on a skeletal Ni—Al catalyst proceeds in a very distinctive way (^{7}). This catalyst, in contrast to other catalysts, possesses a remarkable ability to carry out hydrogenolysis of the furan ring both at C—O and at C—C bonds (thus

the so-called “conjugated” hydrogenolysis), as a result of which aliphatic alcohols and ketones with a shortened carbon chain are formed from furan homologs. All furan homologs having an alkyl or alkenyl substituent in the α-position undergo hydrogenolysis in three directions, as is seen from the following scheme:

$$\text{furan ring with } R \text{ in position 2} \quad \begin{array}{l} \xrightarrow{\text{cleavage of bond 1–5}} CH_3CH_2CH_2{-}C(=O){-}R \quad \text{I} \\ \xrightarrow{\text{cleavage of bonds 1–5 and 4–5}} CH_3CH_2{-}C(=O){-}R \quad \text{II} \\ \xrightarrow{\text{cleavage of bonds 1–5 and 3–4}} CH_3{-}C(=O){-}R \quad \text{III} \end{array}$$

The hydrogenolysis reaction of furan homologs on a Ni—Al catalyst becomes predominant at temperatures above 150°. Below this temperature alkylfurans are converted in high yields into the corresponding alkyltetrahydrofurans. The direction of hydrogenolysis of the ring in α-alkylfurans depends substantially on temperature. At 175° and lower temperatures the furan ring is cleaved almost exclusively in directions I and II, whereas at higher temperature also in direction III. In this case the relative stability of the carbon—carbon bonds 3—4 and 4—5 changes with temperature in the opposite order: with increasing temperature the stability of the 4—5 bond increases, while that of the 3—4 bond decreases. As on the platinum catalyst, hydrogenolysis of the furan ring in the presence of a skeletal Ni—Al catalyst does not proceed through the stage of hydrogenation of the double bonds in the ring, since tetrahydrofuran homologs under comparable hydrogenation conditions prove to be more stable than alkylfurans (^{8}).

Such a mechanism of hydrogenolysis of the furan ring should apparently be regarded as general, since on other catalysts as well (copper chromite (^{4}), nickel (^{5})) the same relative stability of the furan and tetrahydrofuran rings is observed.

The investigations mentioned above make it possible to conclude that hydrogenolysis of the furan ring generally depends on the nature of the catalyst, the character of the side substituent, the temperature, and the method of carrying out the reaction (liquid or vapor phase).

In the present work we investigated the hydrogenolysis reaction of α-substituted furan homologs in the vapor phase on platinum (15%), deposited on activated birch charcoal. Furan homologs with side-chain lengths from C_1 to C_5 were taken into the reaction, which made it possible to judge the influence of the length of the carbon chain of the side alkyl group on the character of hydrogenolysis of the furan ring. It was found that, irrespective of the length of the side substituent, the furan ring in α-alkylfurans on hydrogenation in the vapor phase on platinized carbon at 275° is completely cleaved at the C–O bond 1–5, not adjacent to the side group:

$$\text{-alkylfuran} \quad + \; H_2 \longrightarrow CH_3CH_2CH_2{-}C(=O){-}R$$

As a result of the reaction, aliphatic ketones are formed in yields of 90–95% of theoretical. At this temperature it was not possible to detect any appreciable amount of alkyltetrahydrofurans among the reaction products. However, at a lower temperature (230°), from the catalyst obtained by hydrogenation of α-*n*-propylfuran, in addition to heptan-4-one, α-*n*-propyltetrahydrofuran was also isolated in an amount of 16% of the weight of the catalyst.

Consequently, a lower temperature favors the course of the hydrogenation reaction of the double bonds in the furan ring, whereas an elevated temperature favors hydrogenolysis of the ether bond 1-5.

Experimental Part

Catalyst. Activated carbon was impregnated with a calculated amount of a solution of chloroplatinic acid and then reduced with hydrogen in the reaction tube at 200–250°. The catalyst contained 15% finely dispersed Pt.

Starting substances. Furan homologs were synthesized according to the following general scheme:

$$\text{(furfural)} \xrightarrow{\text{RMgX}} \text{(furylcarbinol)} \xrightarrow[350^\circ]{Al_2O_3} \text{(alkylfuran)} + \text{(alkenylfuran)}$$

$$\text{(alkenylfuran)} + H_2 \xrightarrow[20^\circ]{\text{Ni, Pd}} \text{(alkylfuran)}$$

Pure alkyl- and alkenylfurans were isolated from the dehydration products by distillation on a column with an efficiency of about 40 theoretical plates. In this way, α-ethyl-, α-*n*-propyl-, α-*n*-butyl-, and α-*n*-amylfurans were obtained. Pure sylvan was obtained from a commercial preparation by treating the latter with sodium and distilling on an efficient column. Table 1 gives the physical properties of the α-alkylfurans.

Table 1

Furan homologs	B.p., °C/mm Hg	d_4^{20}	n_D^{20}
Sylvan	63–64/750	0.9120	1.4321
α-Ethylfuran	91–91.5/750	0.9018	1.4402
α-n-Propylfuran	114–115/745	0.8876	1.4395
α-n-Butylfuran	139.5–140.2/750	0.8877	1.4468
α-n-Amylfuran	163.6–164/745	0.8835	1.4512

Experimental conditions. Hydrogenation of the furan homologs was carried out in a flow system at $275 \pm 3°$. The reactor was a quartz tube 120 cm long with an internal diameter of 18 mm. The temperature was measured with a chromel-alumel thermocouple in the middle of the catalyst bed. The starting substance was fed into the reaction zone at a space velocity of 0.1 hr^{-1}.

Analysis of the reaction products. The hydrogenation catalyzates obtained, after drying over potassium carbonate, were subjected to rectification on a column with an efficiency of 40 theoretical plates. The ketones were then identified through the corresponding semicarbazones. Table 2 gives yields and physical properties of the ketones obtained and the melting points of their semicarbazones.

Table 2

Hydrogenolysis products	Yield, %	B.p., °C	d_4^{20}	n_D^{20}	M.p. of semicarbazones, °C
2-Pentanone	95	101–101.5	0.8081	1.3912	110
3-Hexanone	90	123–124	0.8169	1.4006	110
4-Heptanone	93	142.5–143	0.8176	1.4085	132
4-Octanone	95	166.5	0.8190	1.4135	95
4-Nonanone	92	186–187	0.8236	1.4205	85

Conclusions

It has been found that, in the hydrogenation of α-alkylfurans in the vapor phase at 275° over platinized charcoal, selective hydrogenolysis of the furan ring at the

C–O bond 1–5 occurs, as a result of which aliphatic ketones are formed in high yields.

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References

1. W. Kaufmann, R. Adams, J. Am. Chem. Soc., **45**, 3029 (1923).
2. J. Pierce, R. Adams, J. Am. Chem. Soc., **47**, 1098 (1925).
3. H. Smith, J. Fuzek, J. Am. Chem. Soc., **71**, 415 (1949).
4. R. Connor, H. Adkins, J. Am. Chem. Soc., **54**, 4687 (1932).
5. C. Wilson, J. Am. Chem. Soc., **70**, 1313 (1948).
6. J. Bremner et al., Engl. pat. 63408 (1950); Chem. Abstr., **49**, 1175 (1955).
7. N. Chouikin, I. Belski, Bull. Soc. Chim., No. 11–12, 1556 (1956).
8. N. I. Shuikin, V. A. Tulupov, I. F. Belsky, ZhOKh, **25**, 1175 (1955).

Note: Figure translations are in progress. See original paper for figures.