Discussion

A plot of the Shedlovsky function was made

$$\Lambda_0' = \frac{\Lambda + 60.27\ c}{1 - 0.2294\ c}\ vs.\ c$$

for each salt. The lower end of these plots is shown in Fig. 1. As is seen, the data for potassium bromate deviate from the straight line at low concentrations in a manner analogous to those of potassium nitrate.[9] This behavior is typical of polyvalent salts but is usually absent from uni-univalent electrolytes. Since the Shedlovsky function did not yield a straight line, the Λ_0 value for potassium bromate was obtained from the Onsager limiting equation using the data on those solutions whose concentration was less than 0.005 molar. The method of least squares applied to these data yielded a straight line with an intercept of 129.31 and a slope of −89.10. The theoretical slope is −89.93. The estimated error is ±0.05 reciprocal ohms.

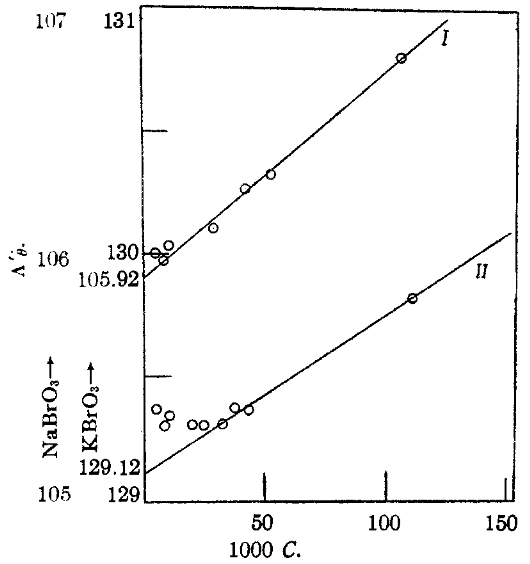

Fig. 1.—Plot of Shedlovsky function; Curve I, NaBrO$_3$; Curve II, KBrO$_3$.

The Shedlovsky plot for sodium bromate was a straight line up to concentrations of about 0.06 molar. The intercept was 105.92. The Onsager limiting equation for solutions of concentration less than 0.006 molar yielded a straight line with an intercept of 105.86 and a slope of −79.22. The average of these figures, 105.89, is accepted as the Λ_0 value for sodium bromate. The estimated error is again ±0.05 reciprocal ohm.

The Conductance of the Bromate Ion.—The conductance of the potassium ion at infinite dilution and 25° is 73.52, and that of the sodium ion is 50.11 (on Jones and Bradshaw standard). If the value of Λ_0 for potassium bromate is taken as 129.31 ± 0.05, the conductance of the bromate ion would be 55.79 ± 0.05. The value for Λ_0 of sodium bromate yields a conductance value for the bromate ion of 55.78 ± 0.05. These values are in good agreement, and the average value of 55.78 ± 0.05 is assigned as the conductance of the bromate ion at 25° and infinite dilution.

Summary

1. The conductance of aqueous solutions of potassium bromate at 25° has been measured over the concentration range of 0.0005–0.15 molar, and that of sodium bromate from 0.0005–0.5 molar.
2. The densities of sodium bromate from 0.0005–0.3 molar have been determined at 25°.
3. The conductance of the bromate ion at 25° and infinite dilution has been calculated from the conductance of sodium and potassium bromates and the known conductances of the sodium and potassium ions.

Bloomington, Indiana Received March 6, 1944

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[9] Shedlovsky, This Journal, **54**, 1409 (1932).

[Contribution from the Department of Chemical Engineering of Illinois Institute of Technology]

The Action of Chromia Catalyst on Aliphatic *Iso*-alcohols and *Iso*-aldehydes

By V. I. Komarewsky and L. G. Smith

It was shown recently that primary straight chain aliphatic alcohols[1] when subjected to the action of chromia (Cr_2O_3) catalyst at atmospheric pressure and 400° underwent a combined *condensation–dehydrogenation* reaction resulting in the production of ketones with $2n - 1$ carbon atoms. The reaction was found to go through an aldehyde-aldol formation. This mechanism was supported by the fact that aldehydes and aldols gave the same reaction with higher yields in the above-mentioned order.

Straight chain aldehydes subjected to the action of the same catalyst but at super-atmospheric pressures underwent a combined *condensation–dehydration* reaction resulting in the formation of olefin hydrocarbons with $2n - 1$ carbon atoms.[2]

The present investigation extends the application of these reactions to isoalcohols and isoaldehydes. The following compounds were subjected to the action of chromia catalyst: isobutyl alcohol, 2-methylpentanol-1, isomyl alcohol, 2-ethylhexanol, isobutylaldehyde, isoamyl-

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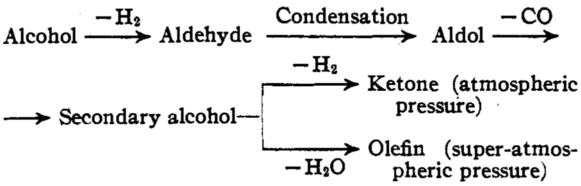
(1) Komarewsky and Coley, This Journal, **63**, 700 (1941). Komarewsky and Coley, *ibid.*, **63**, 3269 (1941).

(2) Komarewsky and Kritchevsky, *ibid.*, **65**, 547 (1943).

aldehyde and 2-ethyl butyl aldehyde. In addition the reactions with mixture of *n*-butylaldehyde and isomylaldehyde were carried out.

The results obtained were in complete accord with the mechanism of reactions *outlined* in the previous work.



As is well known, the aldol condensation does not readily take place with the aldehydes which contain an α-substituted carbon.

Instead of undergoing the above-described reactions the α-substituted alcohols (isobutyl alcohol, 2-methylpentanol and 2-ethylhexanol) underwent simple dehydrogenation to corresponding aldehydes.

The α-substituted aldehydes (isobutylaldehyde and 2-ethylbutylaldehyde) with the exception of slight decomposition gave no reaction.

However isoamyl alcohol and isoamyl aldehyde, since they contained no α-substituent, underwent the above-described reaction with the production of ketones or olefins with $2n-1$ carbon atoms depending on the use of either atmospheric or superatmospheric pressure.

The mixture of *n*-butyl and isoamyl aldehydes produced the expected heptene-3, 2,6-dimethylheptene-3 and 6-methylheptene-2.

Experimental Part

Apparatus and Procedure.—The experiments at atmospheric pressure were carried out in the previously described catalytic furnace,[1] temperature 400°, space velocity 0.1. The experiments at superatmospheric pressure were carried out in a high pressure rotating autoclave.[2]

Material Used: Isobutyl alcohol, Eastman Kodak Co., b. p. 106–108°; isobutyl aldehyde obtained by catalytic dehydrogenation of isobutyl alcohol over copper catalyst at 300°, b. p. 64°; isoamyl alcohol, Eastman Kodak Co., b. p. 128–130°; isoamyl aldehyde by catalytic dehydrogenation of isoamyl alcohol over copper catalyst at 300°, b. p. 92°; 2-ethylbutyl aldehyde, Carbide and Carbon Co., b. p. 116–117°; 2-methylpentanol-1, Eastman Kodak Co., b. p. 147–148°; 2-ethyhexanol, Carbide and Carbon Co., b. p. 183–184°; *n*-butyl aldehyde, Eastman Kodak Co., b. p. 72–74°.

Chromia catalyst was prepared by precipitation of chromium hydroxide from a solution of chromium nitrate by sodium hydroxide, redissolving precipitated chromium hydroxide in excess of alkali. The chromite solution on standing gave a precipitate of chromium hydroxide gel, which was washed, dried and activated with hydrogen at 500°.

Analysis of the Products.—The liquid products of the reaction separated from water and dried over anhydrous sodium sulfate were fractionated on a 100-plate Podbielniak column. The olefin hydrocarbons were identified by physical constants, molecular weights and hydrogenation to corresponding paraffins. The ketones were identified by their physical constants and preparation of derivatives. Experimental results are presented in the tables.

TABLE I

EXPERIMENTS AT ATMOSPHERIC PRESSURE

Catalyst Cr_2O_3; 60 ml.; temperature 400°; space velocity 0.1.

Charging material	Yields of ketone with $2n - 1$ carbon atoms, % of calcd.	Yields of aldehydes obtained by simple dehydrogenation of alcohols, % of calcd.
Isobutyl alcohol	None	40.0[b]
2-Methylpentanol-1	None	36.0[c]
2-Ethylhexanol	None	30.0[d]
Isoamylalcohol	17.6[a]	
Isoamylaldehyde	29.9	

[a] Identified as diisobutyl ketone. m. p. 166°; 2,4-dinitrophenylhydrazone m. p. 92°; semicarbazone m. p. 120°. [b] Identified as isobutyraldehyde, b. p. 61–63°, semicarbazone m. p. 124°. [c] Identified as 2-methylpentanal, b. p. 119–121°; 2,4-dinitrophenylhydrazone, m. p. 182°. [d] Identified as 2-ethylhexanal, b. p. 163°.

TABLE II

EXPERIMENTS AT SUPERATMOSPHERIC PRESSURE

Charge 100 ml., catalyst Cr_2O_3, 12 g.; temperature 400°; time of contact two hours, initial pressure 20 atm. of N_2.

Aldehydes	Yields of olefins with $2n - 1$ carbon atoms, % of calcd.	Identification of olefins
Isobutylaldehyde	None	.....
2-Ethylbutylaldehyde	None	.....
Isoamylaldehyde	27.5	2,6-Dimethylheptene-3[a]
n-Butylaldehyde (50 ml.)		Heptene-3 (8%)[b]
Isoamylaldehyde (50 ml.)	30.0	6-Methylheptene-3[c] (15%)
		2,6-Dimethylheptene-3 (7%)[c]

[a] B. p. 130–131°, $n^{20}D$ 1.4105, hydrogenated to 2,6-dimethylheptane (b. p. 134°). [b] B. p. 95.8–96°, $n^{20}D$ 1.4039, hydrogenated to heptane (b. p. 98°). [c] B. p. 114–114.5%, $n^{20}D$ 1.4070, hydrogenated to 2-methylheptane (b. p. 117°).

Summary

1. Isoamyl alcohol at atmospheric pressure in the presence of a chromia catalyst undergoes a *condensation–dehydrogenation* with a production of di-isobutyl ketone.

2. Isoalcohols having an α-substituted carbon atom give no condensation-dehydrogenation reaction but a simple dehydrogenation to corresponding aldehydes.

3. Isoamyl aldehyde at superatmospheric pressure in the presence of a chromia catalyst undergoes a *condensation–dehydration* with a production of 2,6-dimethylheptene-3.

4. Isoaldehydes having an α-substituted carbon atom give no reaction under conditions studied.

5. The above facts support the aldol mechanism of these reactions.

CHICAGO, ILLINOIS

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