Related Thermal Data.—Table III lists the heats, entropies and free energies of formation at 298.16° K. of the two silicates from the elements and from the oxides. The entropy values are derived from the compilation of Kelley[13] and the work of Humphrey, King and Kelley,[14] and Todd and Bonnickson.[15]

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[13] K. K. Kelley, U. S. Bureau of Mines Bull. 477 (1950).

[14] G. L. Humphrey, E. G. King and K. K. Kelley, U. S. Bureau of Mines, Report of Investigations 4870 (June, 1952).

[15] S. S. Todd and K. R. Bonnickson, THIS JOURNAL, **73**, 3894 (1951).

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NOTES

The Effect of Sodium Oxide on the Chromium Oxide Catalyzed Conversion of Aldehydes to Ketones[1]

BY J. R. COLEY[2] AND V. I. KOMAREWSKY

RECEIVED MARCH 1, 1952

In the course of a study[3] of the action of metallic oxide catalysts on alcohols, it was found that alcohols and aldehydes of "n" carbon atoms undergo a complex dehydrogenation–condensation reaction when passed over a chromia catalyst at 400° to form ketones of "$2n - 1$" carbon atoms. It was noted that a sodium hydroxide precipitated catalyst was quite active in contrast to a comparatively inactive ammonia precipitated catalyst.

It has therefore been of interest to determine the effect of sodium content in a chromia catalyst upon this reaction.

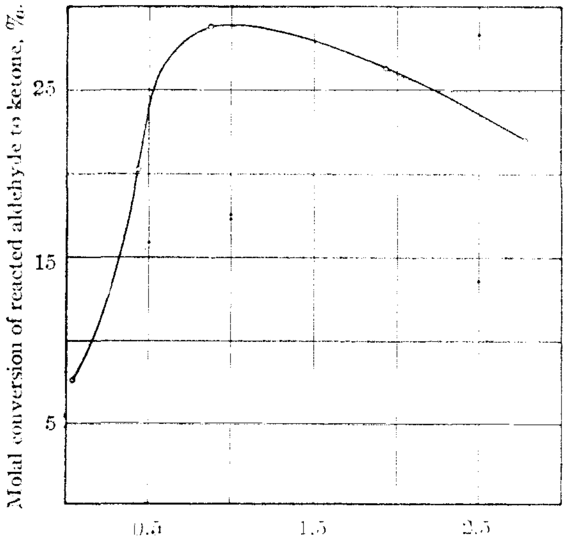

Fig. 1.—The effect of sodium oxide on the conversion of n-butyraldehyde to di-n-propyl ketone.

Experimental Part

Procedure.—The catalysts were prepared by redissolving a cold slurry of chromium hydroxide precipitate in cold excess sodium hydroxide. The chromite solution on standing overnight formed a chromium hydroxide gel. The gel was washed anion free, dried at 110°, screened to 8 mesh and heated in an atmosphere of hydrogen at gradually increased temperatures up to 500°. To vary the sodium content, portions of the catalyst, after washing but prior to drying, were agitated in sodium carbonate solutions of varying concentrations, filtered and dried. The method of sodium analysis was a modification of the triple acetate procedure devised by Kahane.[4]

The catalytic reaction procedure consisted of passing a three to one mixture of nitrogen and vaporized n-butyraldehyde over a granular (8–10 mesh) catalyst bed (volume 50 cc.), maintained at a temperature of 400° by an electrically heated furnace. A constant liquid space velocity of 0.1 was used for all runs. All products were distilled in a 20-inch super-cal Heli Grid Podbielniak Column.

Discussion of Results

The results obtained are given in Table I and Fig. 1.

TABLE I

DATA ON SODIUM CONTENT OF CHROMIA CATALYSTS *versus* YIELD OF KETONE

Weight % sodium	Molal conversion of reacted aldehyde to ketone,[a] %
0.04	7.6
.45	20.3
.88	28.8
1.93	26.3
2.79	22.1

[a] Dipropyl ketone, b.p. 144.18°.

These results indicate that the sodium content of a chromia catalyst has a definite effect on the catalytic activity for the dehydrogenation–condensation reaction discussed. This is consistent with the aldol mechanism proposed[3] for this ketone synthesis. The optimum sodium content was found to be approximately 1.0%.

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[1] From the Senior Problems of B. M. Joseph and S. C. Mikszta.

[2] Research Dept., Standard Oil Co. (Indiana), Whiting, Indiana.

[3] V. I. Komarewsky and J. R. Coley, THIS JOURNAL, **63**, 700 3269 (1941).

[4] E. Kahane, *Bull. soc. chim.*, **47**, 382 (1930).

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Preparation and Some Reactions of Indenyllithium

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In connection with a general project in this Laboratory concerned with the synthesis and reactions of cyclic ketones, methods of preparing β-(1-in-