

changes which will be required to bring the theoretical calculation into agreement with experiment, several arbitrary adjustments were made in the values calculated by the above authors. This procedure is employed by Eyring and co-workers.

A 50% decrease in the normal frequencies of the activated complex is not enough to give the desired value and the ratio of the reaction rate constants is even less sensitive to changes in the frequency normal to the barrier, *i. e.*, that frequency leading directly to reaction. If however $E_{act.}$ for the two reactions is not the same then it is only necessary to have a difference of several hundred small calories to bring the ratios into agreement. This difference is somewhat less than the experimental error. It is thus apparent that more fundamental adjustments will be required in the theoretical calculation.

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Summary

The equilibrium constants for the dissociation of hydrogen and deuterium iodides have been determined for the temperature range 763.8 to 666.8°K. The results for the hydrogen iodide are in disagreement with the experimental work of Bodenstein. The slope of the $\log K$ vs. $1/T$ plot agrees with that calculated by Murphy and by correcting his equation for the new value of ΔE_0^0 for the dissociation, the curves are brought into coincidence. The data for deuterium iodide agree with the predictions based on the new ΔE_0^0 above and the zero point energies of the molecules concerned.

The ratios of the rate constants for hydrogen and deuterium, in both the combination and decomposition reactions, have been determined at 698.6 and 666.8°K. The results differ from those predicted by Wheeler, Topley and Eyring and from the experimental work of Geib and Lendle, while they are in agreement with that of Blagg and Murphy.

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III. Two-Component Gel Catalysts Containing Chromium Oxide for the Aromatization of *n*-Heptane

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Three types of material have been incorporated as a second component in chromium oxide gels: (a) the dehydrogenating metals copper, nickel and palladium, (b) the dehydrogenating metal oxides of manganese, zinc and molybdenum, (c) oxides such as silica, zirconia and stannic oxide, and these have been compared with standard chromium oxide gel.¹

Experimental Details

Catalyst Preparations.—Gels of chromium oxide with copper, nickel, zinc and manganese oxides, respectively, were obtained by addition of 0.166 *N* ammonium hydroxide solution to solutions 0.1 *N* in chromium nitrate and 0.1 *N* in the nitrate of the metal under study. For the molybdenum preparations the appropriate amount of ammonium paramolybdate was added to the chromic nitrate before precipitation with ammonia.

A 3% palladium-97% chromium oxide gel, by weight,

was prepared by immersing an equivalent amount of standard gel in the appropriate solution of palladium chloride. A chromium oxide-silica catalyst was prepared by stirring a 20% solution of sodium silicate into a 20% chromium nitrate solution containing ammonium acetate, the whole being brought to boiling and forming a jelly.

A group of gels containing 10% by weight of zirconia were prepared with the chromium oxide gel types examined in Part I. As typical of these ZrV was made by ethyl alcohol reduction of chromic acid solution with the requisite amount of zirconium oxynitrate added in three portions during the reduction process. In ZrIII the oxynitrate solution was added rapidly to the solution obtained by mixing concentrated solutions of ammonia and chromic acetate. ZrI was obtained by adding the gelatinous precipitate from ammonia and zirconium oxynitrate in three portions during the reduction of chromic acid with ethyl alcohol, stirring vigorously under reflux for several hours. The activity of zirconia alone was tested with a precipitate from zirconium oxynitrate (72 g./liter) with concentrated ammonia. Two catalysts incorporating 10% stannic oxide were tested to compare the effect of another Group IV oxide with that of zirconia.

(1) J. Turkevich, H. Fehrer and H. S. Taylor, *THIS JOURNAL*, **63**, 1129 (1. 41).

Experimental Results

The catalysts were tested by the standard procedure for gas yield and liquid products from normal heptane with 0.3 cc. charged per minute to 15 g. catalyst in the temperature range 425–500°. Typical data are presented in Table I.

TABLE I
DEHYDROGENATION OF HEPTANE ON VARIOUS TWO-COMPONENT GEL PREPARATIONS

Catalyst constituent with Cr ₂ O ₃ molar, %	Temp., °C.	Rate of gas evolution in cc./min. at <i>t</i>		Hydrogen content of gas, %	Liquid analyses			Liquid feed used in analysis in cc.
		min. = 20	min. = 60		d ²⁰ ₄	Olef. wt., %	Arom. wt., %	
Standard Cr ₂ O ₃ Gel	475	70	58	91	0.717	15	15	0-40
3 Wt. % Pd	475	45	27	95	.705	12	11	0-20
50% Ni	425	150	82	55	.694	4	8	0-30
50% Cu	475	50	40	92	.702	12	11	0-20
50% ZnO	475	31	16	83	.691	5	9	0-20
33% MoO ₃	475	120	46	89	.707	8	19	0-30
9% MoO ₃	475	33	26	92	.694	12	7	0-40
50% MnO	475	36	16	91	.692	3	6	0-30
50% SiO ₂	475	65	30	87	.696	8	4	0-30
10% ZrO ₂ (I)	475	110	80	94	.734	14	40	0-20
10% ZrO ₂ (III)	475	90	62	93	.722	14	27	0-30
10% ZrO ₂ (V)	475	95	24
100% ZrO ₂	475	27	21	..	.692	12	8	0-20
10% SnO ₂ (I)	475	90	63	94	.714	17	23	0-20
10% SnO ₂ (II)	450	40	48	..	.705	14	17	0-20

Discussion of Results

The palladium-chromium oxide yielded only that quantity of gas expected from the oxide content. The hydrogen content of the gas is increased but the conversion to aromatics is below the standard yield. The nickel preparation gave cracking as shown by the high hydrocarbon content of the gas. The copper-chromium oxide gel gave rates higher than those deduced from the chromium oxide content, lower than those with an equal quantity of standard gel. The gaseous product was higher in hydrogen content than standard and the aromatic content of the liquid lower.

Of the hydrogenating metal oxides incorporated, the zinc oxide differs from the others in that the hydrogen content of the gas was lower than standard. The liquid product shows, however, an interesting feature common also to both the manganese and molybdenum oxide preparations, namely, the aromatic content of the liquid is some two- or threefold the olefin content which is much lower than with the chromium oxide alone. The molybdenum oxide preparation is superior to the other two. The olefin and aromatic weight percentages are 8 and 19 in the

liquid, the former significantly lower than that of 15% olefin normal to chromium oxide alone.

The silica incorporated served to render the chromium oxide more immediately available as shown by the high initial rate but the rate decreased more rapidly than normal. The oxide did not confer any increased catalytic stability on the gel as revealed by the marked deleterious effect of heat treatment at 650°.

The data for the zirconia catalyst, ZrI, indicate that the catalyst activity was maintained for a longer period of time. The improved activity at 475° over the standard gel is revealed in the considerably increased yield of toluene.

The tests on pure zirconia were of interest in that while the yields were much inferior to those with chromium oxide catalysts, the liquid products show that an appreciable amount of aromatization occurs. At 475° zirconia thus has definite dehydrogenation-cyclization characteristics.

Gel promoted with 10% stannic oxide, SnI, was superior in initial activity to standard gels but inferior to some promoted with zirconia. The rate of loss of activity was far less than that of any other catalysts tested at 475°. The hydrogen content of the gas was higher than normal and the increased gas yield shows up in both a high olefin and a high aromatic content of liquid product SnII, at 450° showed only a 10% decrease in activity over five hours of heptane through-put.

Summary

1. Various two-component gel catalysts containing chromium oxide have been studied for dehydrogenation-cyclization of heptane.

2. Incorporation of the hydrogenating oxide catalysts, zinc, manganese and molybdenum oxides produces catalysts which tend to favor low olefin content with a given production of aromatics.

3. Incorporation of silica does not materially increase gel stability but produces greater availability of chromium oxide surface.

4. Incorporation of zirconia and stannic oxide as promoters produces catalysts superior to standard gel due to slower rate of poisoning. The catalysts are somewhat sensitive to the revivification procedure and lose activity.

5. Zirconia has itself dehydrogenating-cyclizing activity toward paraffins at 475°.