

receiving flask for the liquid product. The gases were analyzed by a combined low-temperature fractionation and absorption analysis. In the analysis of the butenes 63% sulfuric acid was used to absorb isobutene and 87% acid the *n*-butenes. The condensable portion of the gases was collected in a dry-ice-trichloroethylene trap, and the C₆ and higher-boiling hydrocarbons recovered by a low-temperature distillation with the column previously described.²¹ The dissolved gas was removed from the liquid product by the same column and separately analyzed, although in some cases a weighted composite sample of all the gaseous products was analyzed. Maleic anhydride absorption was used in butadiene determination.²³

Summary

A number of hydrocarbons cracked at atmospheric pressure in the presence of an activated silica-alumina catalyst showed the following behavior:

1. A mixture of *n*-butenes underwent extensive catalytic isomerization to isobutene in the temperature range 385 to 600°, accompanied by polymerization and cracking. Between 450 and 600° the isobutene content of the C₄-product was 24.1 ± 1.5%.

2. *n*-Pentenes showed reactions similar to those of the butenes, yielding 50% of isopentenes at 400°.

3. A mixture of *n*-octenes underwent both catalytic isomerization to iso-octenes and catalytic cracking to gaseous products consisting principally of equal amounts of normal and isobutene.

(23) Tropsch and Mattox, *Ind. Eng. Chem., Anal. Ed.*, **6**, 104 (1934).

The results are consistent with the theory that isomerization precedes cracking. In the temperature range 375 to 400° the conversion was over 80%.

4. The primary catalytic reaction of cetene in the range 300 to 450° was isomerization to iso-hexadecenes; the secondary reaction was cracking to lower-boiling olefins, accompanied by isomerization of normal olefinic products to iso-olefins. The iso-hexadecenes catalytically cracked approximately three times as rapidly as cetene itself.

5. *n*-Octane catalytically cracked seven to eight times as rapidly as in thermal decomposition, and the catalytic products contained more C₅-C₇ hydrocarbons and less methane, ethane, and ethylene than the pyrolytic products. The temperature required for the catalytic cracking of octane was 200° higher than that required for *n*-octenes.

6. Cetane was catalytically cracked largely to C₃, C₄ and C₅ hydrocarbons. The gasoline boiling-range products contained both branched-chain and straight-chain hydrocarbons, in contrast to the products of cetene cracking, which were essentially all branched-chain.

Although the behavior in thermal cracking of cetane and cetene is quite similar, cetane is far more stable toward catalytic cracking than cetene. In both cases, the products of catalytic cracking are quite different from those of pyrolytic cracking.

CHICAGO, ILLINOIS

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[CONTRIBUTION NO. 58 FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

The Adsorption of Hydrogen by Copper Dispersed in Calcium Oxide

By JOHN R. LEWIS, LAWRENCE J. E. HOFER AND HOWARD WHITEHEAD

Recently a paper¹ by Lewis and Taylor appeared in which the data for the adsorption of hydrogen by copper dispersed in magnesia were given. Papers by Joris, Verhulst and Taylor² and by Taylor and Joris³ showed (1) that copper, when prepared by the method¹ of Lewis and Taylor, is highly dispersed in magnesia, and (2) that this dispersed copper is an excellent catalyst for hydrogenation reactions.

Because of the chemical similarity of magnesia and calcium oxide, one would expect that calcium

oxide, like magnesia, would be an excellent dispersing medium for copper and therefore adsorption measurements and catalytic studies on copper dispersed in calcium oxide would prove to be of special interest.

This paper presents the data for the adsorption of hydrogen (1) on pure calcium oxide, and (2) on copper dispersed in calcium oxide.

Experimental

Apparatus.—The apparatus used for this work is a modified form of that used in Princeton for similar investigations.

Gases.—Hydrogen was prepared by the electrolysis of a 15% sodium hydroxide solution using nickel electrodes.

(1) Lewis and Taylor, *THIS JOURNAL*, **60**, 877 (1938).

(2) Joris, Verhulst and Taylor, *Bull. soc. chim. Belg.*, **46**, 393 (1937).

(3) Taylor and Joris, *ibid.*, **46**, 241 (1937).

The gas was purified and dried by first passing it through anhydrous calcium chloride and then through an electrically heated tube (350°) containing platinized pumice, and finally through a phosphorus pentoxide drying tube.

Nitrogen, used to determine the dead space of the adsorption tube, was prepared by the reaction of ammonium chloride on sodium nitrite. The gas was purified and dried by first passing it over anhydrous calcium chloride, then over finely divided copper maintained at 500°, and finally through a phosphorus pentoxide drying tube.

Preparation of Adsorbents.—**Adsorbent No. 1:** Copper dispersed in calcium oxide.—A solution of copper ion and calcium ion in the ratio of approximately one Cu^{++} to four Ca^{++} was precipitated by the dropwise addition of the hydroxide while the solution was stirred vigorously. The precipitate was washed by decantation and then treated as follows: first it was heated at 120° for forty-eight hours, then at 350° for forty-eight hours. Finally the dried precipitate was placed in a suitable tube and sealed to the adsorption apparatus. The temperature was raised to 434° and a stream of hydrogen, 25 to 30 bubbles per minute, was passed through the tube for forty hours. At this point the copper oxide was completely reduced to metallic copper. Chemical analysis showed this adsorbent to contain 22.5% copper.

Adsorbent No. 1a: Pure calcium oxide.—This adsorbent was prepared in a manner similar to that used for adsorbent No. 1 except no copper was present. The temperatures and the times of drying were the same as for Adsorbent No. 1.

Adsorbent No. 2: Copper dispersed in calcium oxide.—A solution containing copper ion and calcium ion in the ratio of approximately one Cu^{++} to four Ca^{++} was precipitated as before. It was dried at 60° for twenty-four hours, then at 90° for three hours, then at 120° for ten hours and finally at 360° for seventy-two hours. The dried precipitate was then placed in a reaction tube and sealed to the adsorption apparatus. The tube and contents were heated to 210° with the "Hyvac" oil pump in operation. This was continued for twenty-four hours, after which a stream of hydrogen was passed through the tube containing the mixed oxides, temperature remaining at 210°, for one hundred and sixty-eight hours. At this point reduction of the copper oxide was complete. Chemical analysis showed this adsorbent to contain 19.3% copper.

Adsorbent No. 2a: Pure calcium oxide.—This adsorbent was prepared in exactly the same way as Adsorbent No. 2 except that copper was not present. The temperatures and times of drying were the same.

Experimental Results

The quantities of hydrogen, in cubic centimeters, which were adsorbed at 650 mm. and at various temperatures have been calculated to standard temperature and pressure (S. T. P.) and placed in Table I, and also shown graphically in Fig. 1. Due to the very slow rate at which equilibrium is reached, the quantities reported are not necessarily the true equilibrium values. Some measurements extended over a period of seventy-two

hours before readings became sensibly constant. Duplicate runs checked within 10%.

TABLE I

THE VOLUME^a OF HYDROGEN ADSORBED ON PURE CALCIUM OXIDE AND ON COPPER DISPERSED IN CALCIUM OXIDE
CC. PER GRAM (S. T. P.)

Temp., °A.	Adsorb- ent 1	Adsorb- ent 1a	Adsorb- ent 2	Adsorb- ent 2a
273	0.101	0.006	0.076	0.016
298	.107	.002
348	.206	.008	.321	.014
369	.172	.006	.191	.014
399	.132	.007	.162	.014
451	.106	.008
483	.079	.027	.032	.004
570	.184	.155	.072	.024
707	.097	.160	.064	.095

^a The measurements were made on 25.94 g. of Adsorbent 1, 20.52 g. of Adsorbent 1a, 19.47 g. of Adsorbent 2, and 19.85 g. of Adsorbent 2a. From these were calculated the data which are given in this table.

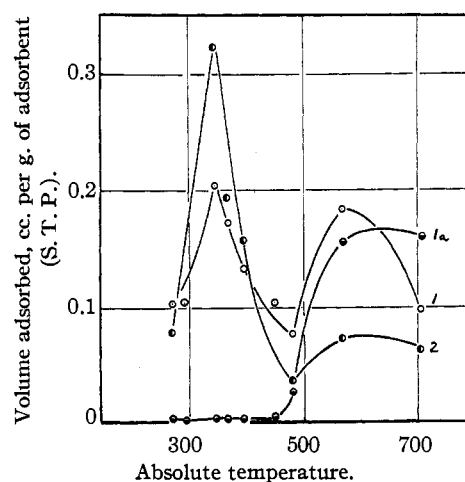


Fig. 1.—The adsorption of hydrogen on calcium oxide and on copper dispersed in calcium oxide at 650 mm. and at various temperatures: Curve 1a, cc. of gas on 1 g. of adsorbent 1a (pure calcium oxide); Curve 1, cc. of gas on 1 g. of adsorbent 1 (copper dispersed in calcium oxide); Curve 2, cc. of gas on 1 g. of adsorbent 2 (copper dispersed in calcium oxide).

The data in Table II and curves 1 and 2 in Fig. 2 were obtained by applying a correction to the values given in Table I. These corrected values were obtained by means of the equation

$$A_t = A_{\text{Cu}}F_{\text{Cu}} + A_{\text{CaO}}F_{\text{CaO}} \quad (1)$$

where A_t is the total adsorption in cc. of hydrogen per g. of adsorbent. A_{Cu} is the adsorption due to copper; F_{Cu} is the fraction, by weight, of copper in the adsorbent; A_{CaO} is the adsorption of hydrogen in cc. per g. of pure calcium oxide; F_{CaO} is the

fraction by weight of calcium oxide in the adsorbent. The assumptions necessary to use Equation I are: (a) the adsorptive capacity of calcium oxide is the same in the pure state and when it is mixed with dispersed copper. (b) For each adsorbent, all the dispersed copper particles are in the same physical state, and their adsorptive capacity is not impaired until the sintering temperature is reached.

TABLE II

THE VOLUME OF HYDROGEN ADSORBED ON DISPERSED COPPER. CC. PER GRAM (S. T. P.) AS GIVEN BY EQUATION I

	Temperature, °A.								
	273	298	348	369	399	451	483	570	707
1	0.43	0.47	0.89	0.74	0.56	0.44	0.26	0.28	(-0.12)
2	0.32	..	1.56	0.91	0.76	..	0.15	0.27	(-0.06)

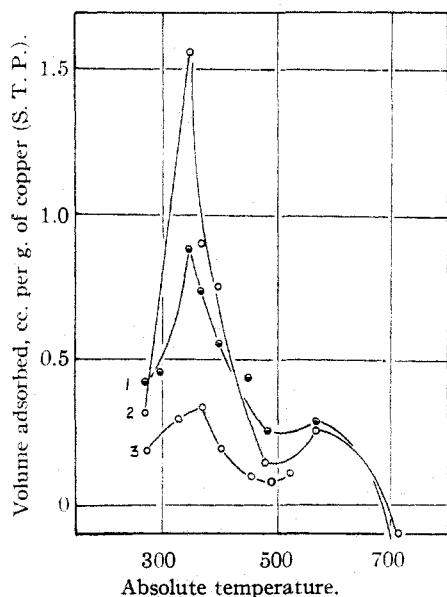


Fig. 2.—The adsorption of hydrogen on pure copper and on copper dispersed in calcium oxide at 650 mm. pressure and at various temperatures and corrected for the hydrogen adsorbed on the calcium oxide by the use of Equation (1). Curve 1 shows the cc. of gas per gram of copper dispersed in adsorbent 1; Curve 2 shows cc. of gas per g. of copper dispersed in adsorbent 2; Curve 3 is for pure copper and was taken from the paper by Lewis and Taylor⁶ for purposes of comparison.

Discussion of Results

An examination of the data in Table I and the curves in Fig. 1 show: (1) calcium oxide, curve 1a, is a poor adsorbent over the temperature range 300 to 475° A., but at 475° A. the adsorption increases rapidly with temperature rise until 570° A. is reached. From there on up to 707° A. the

slope of the curve decreases. In general we can say that calcium oxide resembles magnesia in its ability to adsorb hydrogen.

Curve 1, Fig. 1, shows the adsorption on adsorbent 1, while curve 2 shows the adsorption on adsorbent 2. The difference in the amounts adsorbed by the two adsorbents, at the various temperatures, is attributed to the different methods used in their preparation. It is interesting to observe, however, that maximum and minimum adsorptions for each adsorbent come at practically the same temperatures. This indicates that the same type of activated adsorption is taking place on each adsorbent. It is also interesting to observe that adsorbent 2 is more effective at 348° A., whereas adsorbent 1 is more effective at 570° A. The higher adsorptive capacity of adsorbent 2 at 348° A. is attributed to the higher activity of the copper.^{4,5} It is more active because (1) it was prepared by the reduction of the oxide at 210°, whereas the copper in adsorbent 1 was obtained by reducing the oxide at 434°, and (2) adsorbent 2 was always degassed at 210°, rather than at 434° the temperature used in degassing adsorbent 1. The higher adsorptive capacity of adsorbent 1 at 570° A. is due to the fact that it was completely dehydrated, whereas adsorbent 2 was not.

Using the equation as given above, the data in Table II and the curves in Fig. 2 were obtained. Curve 3, Fig. 2, was taken from the data obtained by Lewis and Taylor⁶ for purposes of comparison. It will be observed that, when the adsorption on calcium oxide is corrected for, by use of the equation, the dispersed copper is a much more effective adsorbing agent than is the pure copper. The apparent negative adsorption for adsorbents 1 and 2 at 707° A. may be due to the fact that the calcium oxide is not adsorbing as much hydrogen at that temperature when it is mixed with the copper, as when it is pure. Also, at 707° A. copper may have lost part of its capacity for adsorbing hydrogen, due perhaps to the adsorption curve passing through a temperature minimum. The third possibility is that part of the calcium oxide is covered with copper, which makes that part of the oxide unavailable to the hydrogen.

Summary

1. The adsorption of hydrogen on pure calcium oxide and on copper dispersed in calcium

(4) Gauger and Taylor, *THIS JOURNAL*, **45**, 920 (1923).

(5) Pease, *ibid.*, **45**, 2296 (1923).

(6) Lewis and Taylor, *ibid.*, **60**, 877 (1938).

oxide has been measured at 650 mm. and at various temperatures.

2. Copper, when dispersed in calcium oxide, is a better adsorbent for hydrogen than is the pure copper.

3. In general the activated adsorption of hydrogen on calcium oxide and on copper dispersed

in calcium oxide resembles the adsorption of hydrogen on magnesia and on copper dispersed in magnesia.

4. An equation has been suggested, the use of which permits the more uniform treatment of the data for copper dispersed in oxides.

SALT LAKE CITY, UTAH

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NOTES

Note on the Dipole Moment of 1-Chloroanthraquinone

BY ERNST BERGMANN AND ANNA WEIZMANN

In connection with a stereochemical investigation in the series of anthracene dichlorides, we

to calculate the electric moment, instead of extrapolating to infinite dilution, which would have given even a slightly higher figure.

The *significance* of figures in the tables is as in previous communications.

τ	ρ	ϵ	n^2	$P^{1/2}$	$P_E^{1/2}$	P	P_E	P_{A+O}
Dioxane solution; $t = 24.2^\circ$								
0	1.0276	2.2553	2.0135	25.2628	21.6250
0.00906	1.0350	2.3200	2.0278	26.3919	22.0405	149.91	67.51	82.40
.01566	1.0404	2.3562	2.0392	27.0544	22.3584	139.62	68.43	71.19
.01739	1.0418	2.3645	2.0415	27.2100	22.4300	137.23	67.90	69.31
$P_{A+O}^\infty = 74.30; \mu = 1.9 D$								
Benzene solution: $t = 24.6^\circ$								
0	0.8732	2.2747	2.2404	26.6302	26.1288
0.00914	.8832	2.3220	2.2506	27.5327	26.4831	124.69	64.88	59.81
.01282	.8872	2.3468	2.2570	27.9744	26.6447	131.06	66.39	64.67
.01817	.8930	2.3923	2.2627	28.7420	26.8606	142.53	66.40	76.13
$P_{A+O}^\infty = 66.87; \mu = 1.8 D$								

reported, a short time ago,¹ some figures on the dipole moment of chloroanthraquinone, which we calculated to 1.9 *D*. Fischer and Rogowski² arrived recently at lower figures of 1.53 (in benzene) and 1.55 (in dioxane), respectively. Although without influence on the general results put forward in our paper, we have reinvestigated 1-chloroanthraquinone both in benzene and again in dioxane solution and have found 1.8 and 1.9 *D*, respectively. Following the procedure of the German authors, we have taken the average of the (atomic and) orientation polarization in order

(1) E. Bergmann and A. Weizmann, *THIS JOURNAL*, **60**, 1801 (1938).

(2) Fischer and Rogowski, *Physik. Z.*, **40**, 331 (1939).

THE DANIEL SIEFF RESEARCH INSTITUTE
REHOVOTH, PALESTINE

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The Optical Activity of α -Bromopropionitrile

BY KENNETH L. BERRY AND JULIAN M. STURTEVANT

In connection with recent physical theories of optical rotatory power,^{1,2} it would be of interest to know the optical properties of one or more compounds of simple, fixed structure, *i. e.*, compounds containing one asymmetric carbon atom substituted by four groups having optical axes of symmetry parallel with the valence bonds to the asymmetric carbon atom.

(1) Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937).

(2) Condon, Altar and Eyring, *ibid.*, **5**, 753 (1937).