

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

## Dehydrogenation of Cyclooctene

BY SEYMORE GOLDWASSER AND HUGH S. TAYLOR

In view of the increased interest in the various properties of the hydrocarbons in the gasoline range, it was thought desirable to develop a method by which the behavior of vaporized hydrocarbons in various catalytic systems might be studied on a semi-micro scale. Such an apparatus has been devised and standardized by the use of *n*-heptane. This hydrocarbon is available in fair amounts and some of its reactions with chromium oxide gel catalysts are known, making it a very suitable material. Chromium oxide acts as a dehydrogenating catalyst at temperatures of 400° and higher so that an attempt to get cyclooctatetraene by dehydrogenating cyclooctene on this catalyst was therefore thought worthy of trial.

There have been attempts in the past to synthesize cyclooctatetraene, notably that of Willstätter.<sup>1</sup> He obtained a yellow liquid of specific gravity 0.940 which decolorized permanganate very readily, yielded a *di*-bromo derivative, added hydrogen bromide, and rearranged under certain conditions. These properties are distinctly not those to be expected if one argues from analogy with the benzene molecule. It has been suggested recently that what Willstätter obtained was styrene, a substance which has the same specific gravity and chemical properties identical with those he reported for his compound. The following investigation strongly indicates that this is so.

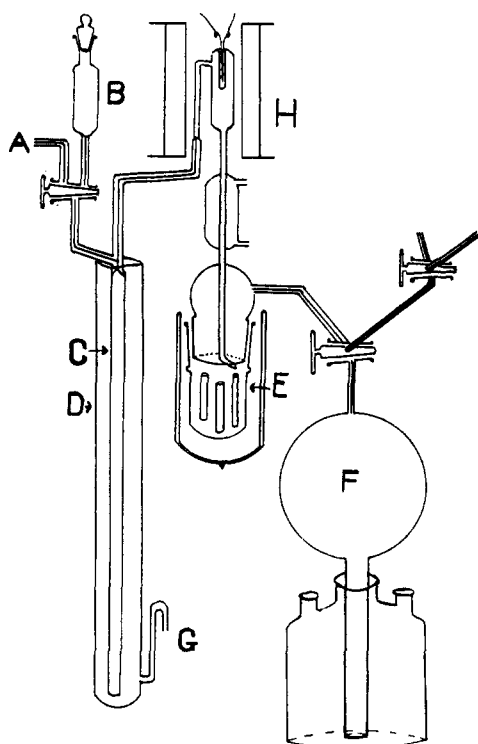


Fig. 1.

The compound cyclooctatetraene should, by analogy with benzene, display some very interesting properties. If it is resonance which causes the special properties of aromatic compounds, then cyclooctatetraene should display the stability and comparative chemical inertness peculiar to ben-

**Apparatus.**—The apparatus finally adopted is as diagrammed (Fig. 1). The calibrated inner tube, C, concentric with the larger tube, D, which served as a mercury well, may be of any convenient diameter depending on the amount of liquid available and the rates of passage to be studied. The tube actually used in the work of this paper was 4.5 mm. inside diameter. A suitable diameter for the outside tube is 35 mm. and a length of 70 cm. A Y-tube of 2 mm. capillary is used as shown with the capillary extending slightly below the rim of the mercury well into which it dips and branching as close to the rim as possible. If the total length of capillary used to lead the liquid to the furnace, H, is not over 15 cm., it is quite possible to use all but about 0.1 cc. of the liquid studied. The reservoir, B, is connected through a branch stopcock so that it is possible to sweep the entire apparatus quite free of any contaminating vapor and to reduce and otherwise treat the catalyst between runs without dismantling the apparatus.

The capillary tube, inclined to prevent trapping of air bubbles, enters the furnace for a distance of not over 4 cm. and is joined to the catalyst vessel with ordinary tubing. The actual rate of feed is controlled by the rate of dropping of mercury into the large tube around the central buret tube. Since a small displacement in the buret requires a considerable amount of mercury in the outer tube and since a small displacement in the buret causes a large displacement of liquid in the capillary, an accurate and uniform rate of flow of vapor over the catalyst may be obtained. The capillary tubing does not go all the way to the catalyst because, in the case of the most rapid rates of speed, heat transfer through the heavier glass can become insufficient and the cooling or flooding of the catalyst chamber follow. The exit gases, after passing through a small water-cooled condenser, are run through a pig, E, as shown, so that, if necessary, successive fractions of liquid may be taken without interrupting a run, or several runs may be made in succession. The gas

(1) Willstätter and Kametaka, *Ber.*, 40, 957 (1907).

which is not condensed by the use of the ice-bath in which the pig is immersed, is collected over a saturated salt solution in a calibrated vessel, F, from which samples may be taken for analysis.

The catalyst tube is 15 to 17 mm. in diameter and 11 cm. long. A thermocouple well extends to the center of the catalyst mass. The construction illustrated allows no channeling by the vapors and ensures complete preheating of all entering gases. The catalyst particles used were 2-4 mesh.

For convenience in following the rate of feed of liquid to the catalyst and in collecting off-gases, the actual runs were carried on slightly below atmospheric pressure, *i. e.*, 745-750 mm. This is sufficient to keep the mercury meniscus in the central buret visible throughout the run. The use of a liter flask as the receiver ensures that the pressure during a run will not change appreciably unless the gas evolution is excessive.

**Calibration.**—The balloon flask was calibrated by displacing the salt water with which it was filled by successive 10-cc. increments of air from a Hempel buret connected to the flask by a three-way stopcock. In this way the amount of evolved gas was known without troublesome pressure corrections. The buret was calibrated by weighing mercury into the apparatus from a weighing buret.

Temperatures were measured by the use of a L. and N. potentiometer and a calibrated chromel-alumel thermocouple inserted into the well of the catalyst tube. The furnace used was a heavily insulated cylinder with a 2-inch (5-cm.) brass center tube 12 inches (30 cm.) long, capable of being heated to 800°. The temperature of this furnace may be controlled to  $\pm 2^\circ$  over a period of hours with no difficulty.

**Analysis.**—Off-gases were analyzed in a modified Williams-Orsat type apparatus in which carbon dioxide, unsaturates, oxygen, carbon monoxide, hydrogen, and saturates are determined by means of potassium hydroxide, fuming sulfuric acid, alkaline pyrogallol, acid cuprous chloride, active cupric oxide at 250° and manganous oxide at 500°, respectively.

**Materials.**—The cycloöctene used in this work was kindly sent us from the Harvard Laboratories, through the courtesy of Professor G. B. Kistiakowsky.

The catalyst was chromium oxide gel slowly precipitated by 0.1 *N* ammonium hydroxide from 0.1 *N* chromium nitrate solution, washed and dried and then reduced *in situ* at 475°.

**Procedure.**—The catalyst was reduced with pure dry hydrogen at a temperature about 15° above the highest temperature to be used in a run, the temperature in this case being 475°. The hydrogen was introduced at A with the mercury well filled to the top and the ice-bath off. When there was no longer any trace of moisture in the exit tube, the catalyst was assumed to be entirely reduced. This is easily checked by trying such a catalyst with heptane, in which case there is carbon dioxide in the off-gas if reduction has been at all incomplete. The buret of the apparatus was filled by adjusting the reservoir stopcock to allow the liquid to flow in slowly and, at the same time, draining mercury from the bottom of the well at G so that the meniscus of the liquid coming in was held stationary below the first bend of the capillary tube. When the

buret was filled with the available liquid, the stopcock to the reservoir was shut and the meniscus of the liquid brought below the level of the rim of the well. The three-way stopcock was then turned so as to connect the buret to the liter flask previously filled with salt water from below by suction. After adjusting the pig so that liquid droplets would enter one of the tubes, the ice-bath was put in position around the pig.

Mercury was then run into the well at the desired rate. Zero time of the run was taken as the time of the first marked movement of the meniscus of the salt water in the calibrated receiving flask. Readings were taken at given intervals both on the buret and the flask. Two successive 50-cc. gas samples were discarded, and all subsequent gas samples analyzed. When the volume of gas evolved does not vary with time during a run, there is no poisoning of the catalyst, and there need be no interruption between runs. This is the case with cycloöctene. However, when there is poisoning or when the cleanness of the surface must be ensured, the procedure is as follows: when enough liquid for analysis has been collected in the pig, or the run was proceeded as far as is desired, the mercury flow is stopped and sufficient mercury drawn off from the well to bring the meniscus of the liquid being used back into the buret. Tank nitrogen is led directly to lead-in tube A and the stopcock opened. The three-way stopcock at the calibrated flask is then opened so that the nitrogen may pass into the open air.

After revivification, due to oxidation by the oxygen content of the nitrogen, the catalyst is again reduced for twelve hours or more in order to eliminate oxygen from the surface, and is then flushed with pure nitrogen. The catalyst is thus prepared for another experiment.

During the run, if desired, the liquid may be cut into fractions by rotating the pig so that the liquid drops into a different tube for each fraction. With the use of a micro-pipet of volume 0.2638 cc. samples of these liquids may be taken for specific gravity and Hanus number measurements.

**Experimental Results.**—Table I is a summary of results obtained. The runs were made in the order given. Before run 5 the catalyst was reduced at 500°.

TABLE I

Run	<i>T</i> , °C.	Mols H <sub>2</sub> per mol cyclo- octene	Gas compn.	Unsat. %	Sp. gr. 20°
1	400	1.0	100% H <sub>2</sub>	50	0.874
2	425	2.7	100% H <sub>2</sub>	92	.902
3	455	2.7	100% H <sub>2</sub>	93	.904
4	425	2.7	100% H <sub>2</sub>	92	.902
5	500	2.7	100% H <sub>2</sub>	..	..

The check run at 425° was made to ascertain whether the catalyst had changed its activity. Although there was no revivification between the runs, there was (a) no diminution of gas evolved with time, (b) no change in catalyst activity, as shown by runs (2) and (4). The gas proved to be entirely hydrogen even at the highest tempera-

ture, so that there was no decomposition of the cyclooctene. The condensed liquid may be assumed to have the formula  $C_8H_x$  or  $C_{8n}H_y$  if there is polymerization. The fact that the full three molecules of  $H_2$  per molecule of cyclooctene were not found is due to the fact that disproportionation occurs on the surface of the catalyst. The Hanus numbers, from which the percentage of unsaturation is calculated, show that unsaturation of the liquid increases with increase of specific gravity. Instead of decreasing, as would be expected if production of the benzene analog accompanies increased hydrogen yield, there is a two-fold increase, the assumption being made, for purpose of calculation, that there is one double bond per  $C_8H_x$  molecule. This assumption is borne out by further investigation.

The condensates of runs (2), (3), (4), were placed in turn in a 40-mm. quartz absorption vessel and the absorption spectra photographed using a hydrogen discharge tube as light source. Pure styrene likewise was photographed. The absorption spectra of all four were found comparable in every respect, including the fine line structure. Since there was no fine structure present other than that of pure styrene, it may be concluded that there is no ultraviolet absorbing system present other than styrene—this excludes cyclooctatetraene, cyclooctene, benzene, and other unsaturated systems.

The liquid condensates were therefore mixtures of cyclooctane and styrene. Table II gives the composition of the liquid products.

TABLE II

Run	From $H_2$ evolved		From specific gravity		From unsaturation	
	Cyclo-octane	Styrene	Cyclo-octane	Styrene	Cyclo-octane	Styrene
1	50%	50%	50%	50%	50%	50%
2	7	93	8	92	8	92
3	6	94	7	93	7	93
4	7	93	7	93	7	93

Specific gravities: styrene, 0.9074; cyclooctane, 0.8349.

From the excellent agreement of the compositions calculated in Table II by three independent methods, it is quite evident that there can be little else than cyclooctane and styrene present in the condensate. On standing, the liquid takes on the yellow color characteristic of styrene.

**Discussion.**—Tables I and II are fully accounted for if it is assumed that the reactions occurring are: (1) dehydrogenation with formation of styrene, (2) hydrogenation of cyclooctene

to cyclooctane. The first reaction is the straight rearrangement under dehydrogenating conditions of an eight-membered ring to a six with liberation of hydrogen. The second reaction is the hydrogenation on the surface of cyclooctene, with hydrogen from the dehydrogenation of cyclooctene, to styrene. This self-hydrogenation is the reaction known as disproportionation. That this type of reaction may occur as much as  $100^\circ$  below the lowest temperature at which there is actual dehydrogenation, has been shown by others and by the present writers in work on the cyclohexenes.

At  $400^\circ$  there are two molecules of cyclooctene losing hydrogen and going directly to styrene for every molecule which yields hydrogen to cyclooctene neighbors on the catalyst surface. The rapid change of the ratio of the two reactions in a  $25^\circ$  interval has a two-fold reason: (a) the concentration of cyclooctene on the surface becomes too small for rapid occurrence of the second process, and (b) rising temperature of the chromium oxide facilitates reaction (1) as hydrogen evaporates more rapidly from the surface and the stability of cyclooctene decreases.

The fact that there is no apparent change in the ratio of the two reactions in the interval from  $425$  to  $455^\circ$  shows that in this temperature range the ratio of cyclooctene to hydrogen is sensibly constant. The maximum yield of styrene is about 93%.

Of other cases reported in the literature where a poly-membered ring rearranges to the more stable six-membered ring, we may cite the following. Willstätter and Kametaka<sup>1</sup> found that cyclooctane on nickel at  $210^\circ$  gave 1,1-dimethylcyclohexane while Ruzicka<sup>2</sup> found that cycloheptane on nickel at  $230^\circ$  gave methylcyclohexane. Ruzicka and Seidel<sup>3</sup> found that cycloheptane heated in a bomb to  $440^\circ$  gave toluene, and under the same conditions cyclooctane gave *p*-xylene.

In all cases the six-membered ring has been formed from the seven- and eight-membered ring. The aromatic ring is not obtained in the above reactions on nickel because they were carried out in an atmosphere of hydrogen and at a temperature favorable to hydrogenation of benzene. This indicates that even the saturated six-membered ring tends to be formed from the seven-

(2) L. Ruzicka, *Helv. Chim. Acta*, **9**, 499 (1926).

(3) Ruzicka and Seidel, *ibid.*, **19**, 424 (1936).

and eight-membered rings with rearrangement taking place to a considerable extent. The other experiments are at higher temperatures and in the presence of iron, conditions favoring dehydrogenation and giving toluene and *p*-xylene. In all of these cases the original compounds are saturated. Cyclooctene is dehydrogenated more easily than any of the saturated compounds mentioned probably because of a higher degree of adsorption on the catalyst.

### Summary

1. An apparatus has been described for the catalytic study of the vapors of hydrocarbons in the gasoline range.

2. Catalytic dehydrogenation of cyclooctene with chromium oxide gives styrene, not cyclooctatetraene.

3. The eight-membered ring tends to form the six-membered ring at temperatures of 300° and over.

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## The Magnetic Study of the Equilibrium between Ferrohemoglobin, Cyanide Ion, and Cyanide Ferrohemoglobin

BY FRED STITT<sup>1</sup> AND CHARLES D. CORVELL<sup>2</sup>

Cyanide ion combines readily with ferrihemoglobin to form the very stable compound ferrihemoglobin cyanide, containing one cyanide group per iron atom. This is characterized by an absorption spectrum showing a broad band with a maximum at about 5400 Å. The properties of a new stable compound of ferrohemoglobin with cyanide are reported in this paper.

In the course of an extensive investigation of the effects of various substances on the spectroscopic and magnetic properties of ferrihemoglobin and ferrohemoglobin, we noticed that on addition of sodium hydrosulfite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) to ferrihemoglobin cyanide solution at either pH 6 or 10 the spectrum changes immediately to one showing a double band, and then fades in about a minute into the ferrohemoglobin spectrum. This observation has been made also by Balthazard and Philippe<sup>3</sup> and by Anson and Mirsky.<sup>4</sup> If sufficient cyanide is added to the alkaline solution after the double-banded spectrum has faded, this spectrum reappears and then remains indefinitely. The same spectrum is obtained also by adding a large amount of cyanide to ferrohemoglobin solution alkaline enough to prevent the formation of hydrocyanic acid.

The spectrum of the cyanide compound has a fairly narrow band maximum at about 5610 Å., approximately 120 Å. wide, a minimum at about

5500 Å., and a second maximum (somewhat broader and slightly higher than the first) at about 5335 Å. This spectrum is closely similar to those of the previously recognized compounds of ferrohemoglobin with oxygen, carbon monoxide, nitric oxide,<sup>5</sup> and the alkyl isocyanides.<sup>6</sup> Each of these compounds contains one added molecule per iron atom; it is accordingly probable that the compound with cyanide ion whose existence is indicated by the spectrum is similar in composition, and contains one cyanide ion per iron atom. It is also probable that the cyanide ion is attached by a covalent bond directly to the iron atom, occupying the sixth coordination position about it, since similar covalent structures have been verified by magnetic measurements for the ferrohemoglobin compounds mentioned above<sup>7</sup> and for dicyanide hemochromogen<sup>8</sup> and ferrihemoglobin cyanide.<sup>9</sup> Evidence supporting this assumption is given in this paper.

Magnetic measurements of the equilibrium involved in the formation of cyanide ferrohemoglobin were made with the technique described in detail below. The first measurements were made

(5) F. Haurowitz, *Z. physiol. Chem.*, **138**, 68 (1924); D. L. Drabkin and J. H. Austin, *J. Biol. Chem.*, **112**, 51 (1935).

(6) O. Warburg, E. Negelein and W. Christian, *Biochem. Z.*, **214**, 26 (1929).

(7) (a) Oxyhemoglobin and carbonmonoxyhemoglobin, L. Pauling and C. D. Coryell, *Proc. Natl. Acad. Sci.*, **22**, 159 (1936); (b) nitric oxide hemoglobin, C. D. Coryell, L. Pauling and R. W. Dodson, to appear in *J. Phys. Chem.* (1939); (c) ethyl isocyanide ferrohemoglobin, L. Pauling and C. D. Russell, unpublished experiments.

(8) L. Pauling and C. D. Coryell, *Proc. Natl. Acad. Sci.*, **22**, 159 (1936).

(9) C. D. Coryell, F. Stitt and L. Pauling, *THIS JOURNAL*, **69**, 632 (1937).

(1) At present National Research Fellow in Chemistry at Harvard University.

(2) Present address: Dept. of Chemistry, Univ. of California at Los Angeles.

(3) V. Balthazard and M. Philippe, *Ann. méd. légale*, **6**, 137 (1926).

(4) M. L. Anson and A. E. Mirsky, personal communication.