for any of the organic acid decompositions studied to date.

7. A new means for measuring the acidity function of oleum up to 28.3% free sulfur trioxide concentration, by kinetic measurements with *o*-benzoylbenzoic acid, is shown to have experimental basis and proof.

SUMMIT, NEW JERSEY RECEIVED SEPTEMBER 19, 1944

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

The Poisoning of Nickel Hydrogenation Catalysts by Water Vapor[1,2]

BY W. B. BURFORD, III, AND J. C. W. FRAZER[3]

During some experiments on the hydrogenation of ethylene over nickel catalysts anomalous results were observed which indicated that traces of water vapor might be acting as a catalyst poison. The following experiments, which were performed to detect the limit of such action, showed that the effect could be observed at a pressure of water vapor as low as 10^{-4} mm.

A similar poisoning effect by oxygen or water vapor was observed by Normann[4] for palladium hydrogenation catalysts, and Woodman and Taylor[5] have shown that water vapor causes a decrease in rate of hydrogenation over zinc chromite catalysts, although in this case the amount of water vapor was much larger.

Experimental Part

Catalyst.—To make the catalyst as sensitive to poisoning as possible it was prepared with a small, highly active surface area. This was done by etching C. P. nickel pellets of 1 to 3 mm. diameter with aqua regia to produce a mat, after which they were oxidized in a stream of oxygen at 550 to 700° for sensitization. Batches of about 70 g., occupying about 25 ml., were then placed in the catalyst chamber and reduced *in situ*. These catalysts had an activity sufficient to convert 150 ml. per minute of ethylene–hydrogen mixture practically completely at temperatures above 75°, but only about 30% at room temperature.

Reagents.—The ethylene was "anesthetic" grade, with listed impurities of 0.35%. It was purified by passage first through a pre-catalyst tube containing finely divided nickel reduced from carbonate which was maintained at a slightly higher temperature than the main catalyst tube. The gas next passed through a trap cooled with Dry Ice in acetone and then through a large tube of phosphorus pentoxide free from phosphorus trioxide.

The hydrogen was a commercial grade prepared electrolytically and contained about 1.8% oxygen. It was purified by passage over platinized asbestos at 350° with subsequent drying in the same manner as for the ethylene.

Apparatus and Procedure.—Known mixtures of the purified gases were prepared and measured by flow meters patterned after a design by Bruun,[6] and were then led to the catalyst bulb, part of the hydrogen being by-passed through the humidifying train and returned to the main stream. In the experiments cited the gas was generally mixed in the ratio 3 hydrogen to 1 ethylene at a total flow of 200 ml. per minute.

In the by-pass humidifying line the hydrogen first picked up water vapor from a trap at room temperature, after which the excess moisture was frozen out in a condenser cooled with Dry Ice in acetone. Temperatures as low as −106° were obtained by evacuating the vessel containing the Dry Ice.

The gases coming from the catalyst chamber were analyzed in a standard gas analysis apparatus. Ordinarily analyses were made only for ethylene by absorption in fuming sulfuric acid, though a few check determinations of the other constituents were also carried out. Sample analyses agreed with flowmeter readings within one half per cent.

The operating technique was to cool the catalyst chamber in boiling water immediately after reduction of the catalyst until the thermocouple within the catalyst bed showed 108°. At this point the gas mixture, which had been flowing to waste under operating conditions for some time to sweep out the system, was admitted to the catalyst tube. The heat of reaction was great enough to maintain the reaction vessel at 106 to 108° when the vessel was immersed in boiling water. Samples were taken at numerous time intervals beginning at two minutes and continuing for several hours.

Results

Using the catalyst which gave complete hydrogenation with pure gases above 75°, it was found that at 107° the presence of 3×10^{-4} mm. of water vapor was sufficient to cause a decrease of 5% in the amount of hydrogenation after a reaction period of forty minutes. With higher amounts of water vapor—about 10^{-3} mm.—the drop in activity was more pronounced and it required less time for a noticeable effect to occur. With pressures of 0.1 mm. of water vapor the activity dropped ultimately to about 30% of its normal value.

One attempt to find an effect of water vapor at a pressure of 5×10^{-5} mm. gave negative results after an hour at 107°, so that 10^{-4} mm. is presumably the lowest pressure at which poisoning can be detected under these conditions. However, since the catalyst is not as sensitive to poisoning at 107 as at 74°, the lowest temperature at which it attains complete conversion, it is possible that some retardation might be observed for smaller water vapor pressures at the lower temperature.

Effects with such small amounts of water vapor were probably made possible by the extremely sensitive form of catalyst used. The surface

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(2) Abstract of part of a dissertation submitted to the Board of University Studies of the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Original manuscript received January 27, 1943.

(3) This manuscript is published after the death of Professor J. C. W. Frazer on July 28, 1944. His part in the work and the preparation of the original manuscript of this article was too considerable to permit its publication without acknowledgment.

(4) W. Normann, *Ber.*, **55**, 2193 (1922).

(5) J. O. Woodman and H. S. Taylor, THIS JOURNAL, **62**, 1393 (1940).

(6) Bruun, *Ind. Eng. Chem., Anal. Ed.*, **11**, 655 (1939).

area was undoubtedly relatively small and hence easily affected by small amounts of material. However, it does suggest that even with the very large area of ordinary nickel catalysts, hydrogenations of a difficult character may well be made more efficient by rigorous drying of all materials in contact with the catalyst during the course of the reaction.

The poisoning was found to be reversible since the catalysts could be reactivated completely by reheating in hydrogen at 375° after having been poisoned to 30% of their original activity. Thus the effect of the water vapor appears to be due to a preferential adsorption which can be removed by treatment with excess hydrogen.

Summary

Water vapor has been shown to be a poison for nickel hydrogenation catalysts, the effect being noticeable as low as 3×10^{-4} mm. pressure of water vapor in the present experiments.

The poisoning is reversible, the catalyst being reactivated by heating in hydrogen.

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The Structure of Spiropentane

BY JERRY DONOHUE, GEORGE L. HUMPHREY AND VERNER SCHOMAKER

Murray and Stevenson[1] have prepared a C_5H_8 hydrocarbon by the debromination of pentaerythrityl bromide with zinc dust. They assigned to this substance the spiropentane structure (I) on the basis of its Raman spectrum, chemical properties, and method of preparation. We have confirmed this assignment of structure by an electron diffraction investigation carried out on a sample of the new hydrocarbon supplied us by Dr. Murray.

Experimental.—The electron diffraction apparatus used in this investigation has been described by Brockway.[2] The camera distance was 10.86 cm., and the wave length of the electrons, determined against zinc oxide smoke,[3] was 0.0609 Å. Photographs taken with the sample at 0° showed features extending to q values of about ninety-five ($q = 40/\lambda \sin \vartheta/2$).

Interpretation.—Both the radial distribution method[4] and the correlation method[5] were used in interpreting the photographs. The radial distribution curve was calculated with the equation

$$rD(r) = \sum_{q=1}^{q_{\max}} I(q) e^{-aq^2} \sin\left(\frac{\pi}{10} rq\right)$$

where a was so determined that e^{-aq^2} equals 1/10 at $q = 100$. The values of $I(q)$ were taken from curve V (Fig. 1), which was drawn to represent the appearance of the photographs. The unobservable first feature (dotted) was drawn to agree approximately with the theoretical curves.

Theoretical intensity curves for the correlation treatment were calculated using the simplified theoretical scattering formula

$$I(q) = \sum_{i,j} \frac{Z_i Z_j}{r_{ij}} e^{-b_{ij}q^2} \sin\left(\frac{\pi}{10} r_{ij} q\right)$$

The temperature factor b was given the value 0.00016 for bonded C–H terms, 0.0003 for non-bonded C–H terms, and zero for C–C terms. These calculations were made with punched cards on International Business Machines.

The radial distribution curve, R of Fig. 1, shows maxima at 1.09, 1.49, 2.19 and 2.77 Å., and a shelf at 3.0 Å. This curve is in complete agreement with the spiropentane structure, as shown by the heavy vertical lines representing the various distances and their amplitudes in the finally accepted model. Direct estimates of the angle parameters of the spiropentane structure (I) can easily be made with the information provided by the radial distribution function. The average C–C bond distance 1.49 Å. and the non-bonded C···C distance 2.77 Å. correspond to a $C_2C_3C_1$ bond angle of 61°. Taken with these data, the C–H distance 1.09 Å. and the shortest non-bonded C···H distance 2.19 Å. then imply an HCH bond angle of 121°.

Theoretical intensity curves were drawn (Fig. 1) for various models of the spiropentane structure (I) with a molecular symmetry of $D_{2d} - \bar{4}2m$, with the reasonable assumption that the plane of ∠ HCH bisects ∠ CCC. There are then three parameters which determine the configuration of the molecule. These were taken as $\angle C_2C_3C_1$, ∠HCH, and the ratio $C\text{–}H/C_2\text{–}C_3$. These parameters were varied in a systematic fashion. Since the curves are relatively insensitive to changes involving the hydrogen atoms only, the second and third parameters cannot be determined with great accuracy. Thus if $\angle C_2C_3C_1 = 61.5°$ and $C\text{–}H/C_2\text{–}C_3 = 1.08/1.48$, then comparison with the appearance of the photographs show that $\angle HCH = 120 \pm 8°$, whereas if $C\text{–}H/C_2\text{–}C_3 = 1.08/1.48$ and $\angle HCH = 120°$, $\angle C_2C_3C_1 = 61.5°$ with an uncertainty of only about one degree. With a longer or shorter C–H distance and/or an HCH angle differing considerably from 120°, however, the range of

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(1) M. J. Murray and E. H. Stevenson, THIS JOURNAL, **66**, 812 (1944).

(2) L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

(3) C. S. Lu and E. W. Malmberg, *Rev. Sci. Instr.*, **14**, 271 (1943).

(4) L. Pauling and L. O. Brockway, THIS JOURNAL, **59**, 2181 (1937); R. Spurr and V. Schomaker, *ibid.*, **64**, 2693 (1942).

(5) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).