The conclusion is drawn from these curves that the dissociation reaction in the absence of iodine has the same specific rate as the reaction in the presence of iodine, since in the limit, as the elapsed time becomes short, the rate of production of instantly titratable sulfite becomes the same in the presence and absence of iodine. The multiple ionizations of sulfurous acid and of the addition compound permit several paths for the reactions of addition and of dissociation but these ionizations are presumably maintained in equilibrium. Any extremely rapid isomerization could not be detected by these measurements. These factors will be discussed in a later paper.

## Summary and Conclusion

1. Sodium benzaldehyde bisulfite reacts with iodine at a rate independent of its own concentration and of that of the iodine.

2. The rate determining step is the dissociation into bisulfite or sulfite ion. There is no evidence of the presence of isomers of the bisulfite compound.

3. The rate changes with changing hydrogen-ion concentration, being very rapid at low hydrogen-ion concentration reaches a minimum at $P_H$ 1.8, and increases again with higher concentrations of acid.

4. The apparent heat of activation has been measured and found to vary with changing hydrogen-ion concentration.

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# THE ROLE OF LIQUID STATIONARY FILMS IN BATCH ABSORPTION OF GASES. III. RATES OF HYDROGEN ABSORPTION AND RELATIVE RATES OF CATALYTIC HYDROGENATION IN ALCOHOL[1]

BY HAROLD S. DAVIS,[2] GEORGE THOMSON[3] AND GEORGE S. CRANDALL[3]

During hydrogenations in solutions with metallic catalysts, the reaction proper must take place at or close to the surface of the solid. There is also good evidence that the course by which the hydrogen reaches this

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position is somewhat as follows. The very surface of the liquid is always practically saturated with dissolved hydrogen; thence the dissolved gas penetrates to the interior of the liquid mainly by diffusion through an unstirred layer beneath the liquid surface (liquid stationary film), it is distributed uniformly through the main body of the liquid by currents and finally passes thence to the surface of the catalyst by diffusion through another unstirred layer of liquid existing at the solid–liquid interface.

The stationary films are by no means monomolecular in thickness, nor must they be confused with adsorbed layers. Even in highly agitated liquids, they are much thicker. Strong evidence for their existence can be cited from the studies of numerous investigators on the rates of solution of solids and gases by liquids. Additional evidence is found in the phenomena attending the transfer of heat between phases. In the present and in the two former papers in this series[4] it has been assumed that the limits of the stationary films are sharply defined. It is noteworthy that by this same approximation, "The convection loss from bodies of simple geometric form, under widely different fluid conditions, can be computed by means of a few convenient equations," ["International Critical Tables," Vol. V, 1929, p. 234].

The first part of the present investigation deals with a study of the rates of hydrogen absorption during hydrogenations of olefins in alcohol with platinum platinum-oxide catalyst.

The catalytic reduction apparatus[5] used was that designed by Professor Roger Adams and his associates. The catalyst, solvent (alcohol) and unsaturated compound were shaken together in a stout bottle connected to a hydrogen pressure tank and the rate of hydrogen absorption was followed by the fall in the gage pressure (1 lb./sq. in. = 286 cc. of hydrogen at atmospheric pressure and 25°). The hydrogen was admitted to the reaction bottle, without first removing the air, so that the gage pressure measured the partial pressure of hydrogen above the alcohol. The absorptions were mostly so rapid that it seemed unlikely that much air or alcohol vapor could penetrate from the bottle to the tank against the inrushing hydrogen. Platinum-oxide platinum black was used, prepared according to the directions of Adams and Shriner[6] (fusion at about 500°); 150 cc. of reagent alcohol (No. 25 denatured, 95% ethanol and 5% methanol) was used in each experiment.

In any one experiment on the hydrogenation of an olefin, the rate of hydrogen absorption, after a short period from the beginning, remained fairly constant until hydrogen practically equivalent to the olefin had been absorbed.[7] This is shown by the linear form of the curves in Fig. 1.

The relationship between the magnitude of these uniform absorption rates and the quantity of catalyst can be seen from Table I, columns 2

[4] Davis and Crandall, THIS JOURNAL, **52**, 3757, 3769 (1930).

[5] Purchased from the Burgess–Parr Co.

[6] Adams and Shriner, THIS JOURNAL, **45**, 2171 (1923).

[7] Numerous observers have pointed out this striking fact; see Lebedev, Kobliansky and Yakubschik. *J. Chem. Soc.*, 418 (1925).

and 6. The absorption rate increased from zero, at first in proportion to the quantity of catalyst, but evidently tended toward a maximum value which would have been unchanged by the addition of more catalyst.
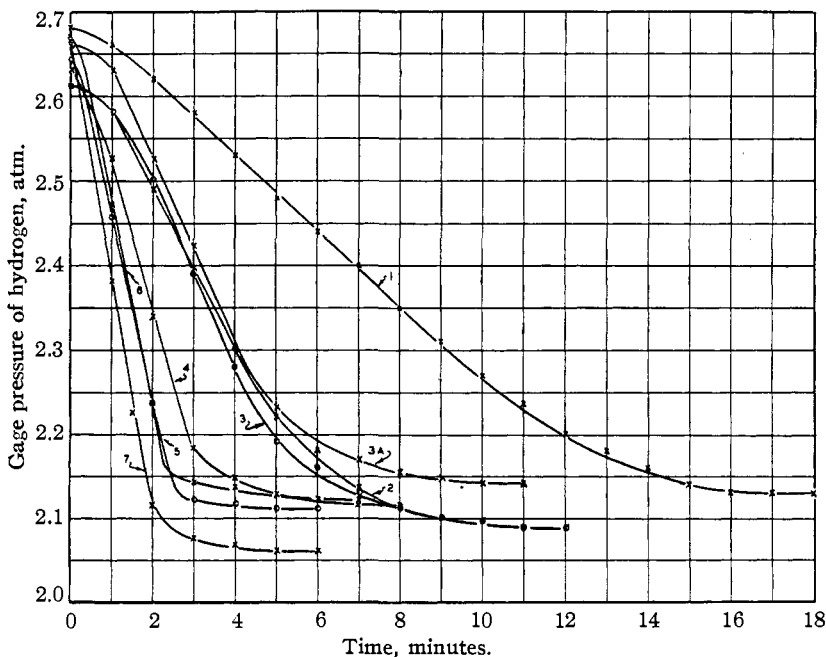


Fig. 1.—Hydrogenation of 10 cc. of 2-pentene in 150 cc. of alcohol, shaken 260 times per min. with various quantities of catalyst: (1) 0.03 g., (2) 0.07 g., (3) 0.10 g., (3A) 0.10 g., (4) 0.20 g., (5) 0.40 g., (6) 0.60 g., (7) 0.90 g.; average hydrogen pressure (gage), 2.4 atm.

In diffusing from the gas–liquid interface to the liquid–solid interface, the dissolved hydrogen must pass through two liquid stationary films by diffusion and the total drop in its concentration between the two interfaces is utilized in driving the dissolved gas through these films.

Let $C_i$ = concn. of dissolved hydrogen at gas–liquid interface

$\quad C_{cat.}$ = concn. of dissolved hydrogen at liquid–solid interface

$\quad R_1$ = total resistance, to diffusion, of the liquid stationary film at gas–liquid interface

$\quad r_2/W$ = total resistance, to diffusion, of liquid stationary film at liquid–solid interface ($W$ = g. of catalyst, $r_2$ = resistance per 1 g. of catalyst)

$\quad \rho$ = rate of hydrogen absorption (total)

$\quad K$ = a constant

Then $\rho = K \dfrac{C_1 - C_{cat.}}{R_1 + \dfrac{r_2}{W}}$ (1)

$$\frac{1}{\rho} = \frac{1}{K(C_i - C_{cat.})} \left( R_1 + \frac{r_2}{W} \right)$$

At a fixed rate of shaking $R_1$ remains unchanged and, for the same lot of catalyst, $r_2$ is constant.   If, finally, the variations in $C_{cat.}$ are negligible compared to $C_1 - C_{cat.}$ then

$$\frac{1}{\rho} = \text{Const.} + \text{Const.} \left(\frac{1}{W}\right) \tag{2}$$

Accordingly if $1/\rho$ is plotted against $1/W$, a straight line should result. In Fig. 2 the data from experiments with different quantities of catalyst are plotted in this way for three olefins, trimethylethene, 2-pentene and isopropylethene.   For the first two, the points lie quite well on straight lines.   In the case of isopropylethene, the second and fifth points are off from, but on opposite sides of, the straight line representative of the other five points.   Apparently this is due to experimental errors.
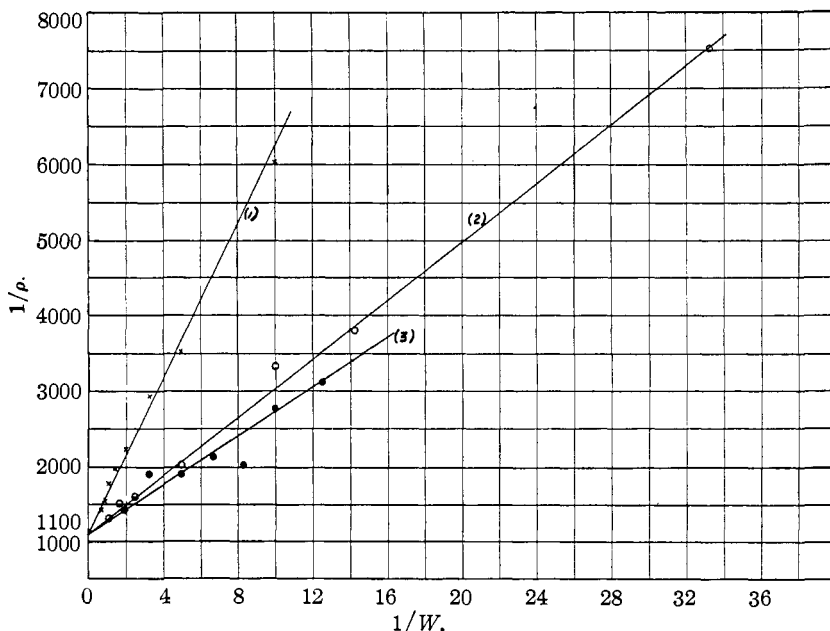


Fig. 2.—$\rho$ = rate of hydrogen absorption, over period of uniformity, in mole/sec.; $W$ = weight of catalyst in grams;   (1), trimethylethene;   (2), 2-pentene;   (3), isopropylethene;   average hydrogen pressure (gage) 2.4 atm.;   shaking rate 260 times per min.;   150 cc. of alcohol + 10 cc. of hydrocarbon.

Within the accuracy of the data, all three curves converge to the same point at $1/W = 0$ or $W = \infty$.   The corresponding value for $\rho$ is $9.1 \times 10^{-4}$ mole/sec.   Under these conditions the concentration of dissolved hydrogen in the main body of the liquid has become equal to $C_{cat.}$ and the full drop in concentration $C_i - C_{cat.}$ is utilized in driving dissolved hydrogen through the liquid stationary film at the gas–liquid interface.

The resistances of the two liquid stationary films will be equal ($R_1 = r_2/W$) when the absorption rate is just half the above maximum. The quantity of catalyst corresponding to this condition can be obtained, for each series, from the curves of Fig. 2. Having these values for $W$, it is now possible to calculate the ratios of the total resistances, $R_1 + r_2/W$, and finally the ratios of the hydrogen absorption rates, for different quantities of catalyst, Table I. The agreement between the calculated and the experimental ratios of the absorption rates is rather striking (last two columns).

Furthermore, it is calculated (by means of equation 3 below) that in the 2-pentene experiments, Table I, for 0.03 g. of catalyst, the main body

TABLE I

HYDROGENATIONS OF OLEFINS (10 CC. IN 150 CC. OF ALCOHOL) WITH DIFFERENT QUANTITIES OF CATALYST. RATE OF SHAKING, 260 TIMES PER MINUTE

| No. | $W$ | $R_1$ ratios | $r_2/W$ ratios | $R_1 + r_2/W$ ratios | $\rho$ mole $\times 10^4$/sec. | $\rho$ ratios Calcd. | Exptl. |
|---|---|---|---|---|---|---|---|
| | | | Trimethylethene | | | | |
| 1 | 0.1 g. | 1 | 4.8 | 5.8 | 1.62 | 1 | 1 |
| 2 | .2 | 1 | 2.4 | 3.4 | 2.83 | 1.7 | 1.8 |
| 3 | .3 | 1 | 1.6 | 2.6 | 3.40 | 2.2 | 2.1 |
| (3a) | ( .48)[a] | (1) | (1) | (2.0) | (4.55) | (2.9) | (2.8) |
| 4 | .5 | 1 | 0.96 | 1.96 | 4.50 | 3.0 | 2.8 |
| 5 | .7 | 1 | .69 | 1.69 | 5.28 | 3.4 | 3.3 |
| 6 | .9 | 1 | .53 | 1.53 | 5.73 | 3.8 | 3.5 |
| 7 | 1.1 | 1 | .44 | 1.44 | 6.38 | 4.0 | 3.9 |
| 8 | 1.4 | 1 | .34 | 1.34 | 6.52 | 4.3 | 4.0 |
| 9 | ∞ | 1 | 0.0 | 1.0 | (9.1) | 5.8 | (5.6) |
| | | | 2-Pentene | | | | |
| 1 | 0.03 g. | 1 | 5.8 | 6.8 | 1.27 | 1 | 1 |
| 2 | .07 | 1 | 2.5 | 3.5 | 2.54 | 2.0 | 2.0 |
| 3 | .10 | 1 | 1.8 | 2.8 | 2.90 | 2.4 | 2.3 |
| 3a | ( .175)[a] | (1) | (1) | (2) | (4.55) | (3.4) | (3.6) |
| 4 | .20 | 1 | 0.88 | 1.88 | 4.85 | 3.6 | 3.8 |
| 5 | .4 | 1 | .44 | 1.44 | 6.25 | 4.7 | 4.9 |
| 6 | .6 | 1 | .29 | 1.29 | 6.73 | 5.3 | 5.3 |
| 7 | .9 | 1 | .20 | 1.20 | 7.30 | 5.7 | 5.8 |
| 8 | ∞ | 1 | .0 | 1.00 | (9.1) | 6.8 | (7.2) |
| | | | Isopropylethene | | | | |
| 1 | 0.08 g. | 1 | 1.9 | 2.9 | 3.22 | 1 | 1 |
| 2 | .10 | 1 | 1.5 | 2.5 | 3.61 | 1.2 | 1.1 |
| 3 | .12 | 1 | 1.25 | 2.25 | 4.97 | 1.3 | 1.5 |
| 4 | ( .15)[a] | (1) | (1) | (2) | (4.68) | (1.5) | (1.5) |
| 5 | .20 | 1 | 0.75 | 1.75 | 5.27 | 1.7 | 1.6 |
| 6 | .3 | 1 | .50 | 1.50 | 5.27 | 1.9 | 1.6 |
| 7 | .5 | 1 | .30 | 1.30 | 7.02 | 2.2 | 2.2 |
| 8 | ∞ | 1 | .0 | 1.0 | (9.1) | 2.9 | (2.8) |

[a] From the curve of Fig. 2.

of the solution was 86% saturated with hydrogen, and for 0.9 g. only 20%. Since, as shown by Fig. 2 and Table I, $(C_1 - C_{\text{cat.}})$ remained substantially constant, then $C_{\text{cat.}}$ must have remained either constant, unaffected by large changes in the concentration of dissolved hydrogen in the main body of the liquid, or was negligible. If it was negligible, then the limiting rate of absorption reached with an infinite quantity of catalyst should be equal to the initial rate of hydrogen absorption by the solution. To test this conclusion, the rate of physical solution of hydrogen by alcohol in this apparatus was actually measured in the following way.

The bottle containing 150 cc. of alcohol, without any catalyst or olefin, was evacuated to a pressure of 8–10 cm. of mercury and shaken for several minutes to remove dissolved gases. Then with the bottle at rest, hydrogen was admitted to a total pressure of about 1.9 atm. The pressure was registered by the height of the mercury level in a capillary tube dipping into mercury in a closed bottle, 3 cm. in diameter, which sustained the full hydrogen pressure.

With the liquid at rest, the rate of hydrogen absorption was fairly slow; but when shaking started it was rapid, although by no means immeasurable. A fraction of a second was required to start the shaking, so that measurements were taken after the motor was almost up to speed (260 ± 5 shakings per min.). Then the time was determined for the first 2 cm. drop in the mercury pressure out of the last 4 cm., that is, the time required for solution of half the hydrogen still undissolved. Two observers were required. One started the shaking, the other measured the time. To accomplish this, a moving paper was drawn against a pencil, rotating uniformly eleven times per second, when the mercury level reached a fixed mark and withdrawn when it had fallen 2 cm. more. The following were the numbers of the pencil marks in five successive tests: 10, 9, 9, 10, 10. Average, 9.6, corresponding to 0.87 sec.

Let $U$ = The unsaturation of the alcohol in regard to dissolved hydrogen at time $t$ (sec.) expressed as the moles of the gas (in addition to that already dissolved) necessary to saturate the alcohol

$$\text{Then} - \frac{dU}{dt} = \text{Const. } U \tag{3}$$

$$\text{and Const.} = \frac{1}{t} \ln \frac{U_0}{U}$$

If $t_{0.5}$ = time for a fall of 50% in $U$, then $- \dfrac{dU_0}{dt} = \dfrac{0.693\,U_0}{t_{0.5}}$

This relationship holds whatever the value of $U$, but if the readings could be started before any hydrogen was dissolved, then $U_0$ would be equal to the total quantity of hydrogen soluble, at this pressure, in the alcohol; 150 cc. of alcohol would dissolve about $1.27 \times 10^{-3}$ mole of hydrogen at 2.4 atmospheres. Accordingly the initial rate of solution of hydrogen in this quantity of alcohol in our hydrogenation experiments (Adams apparatus, hydrogen pressure 2.4 atm., and shaking rate (260 ± 5) times per min.) would be $(0.693/0.87) \times 1.27 \times 10^{-3} = 10 \times 10^{-4}$ mole/sec.

More than a year later the experiments (first series) were repeated, another observer replacing one of the first two (second series).

COLLECTED RESULTS ON THE INITIAL RATE OF HYDROGEN SOLUTION (AT 2.4 ATM. OF HYDROGEN) BY 150 CC. OF LIQUID SHAKEN 260 ± 5 TIMES PER MINUTE IN THE ADAMS APPARATUS

| | |
|---|---|
| 1st Series, alcohol only | $10 \times 10^{-4}$ mole/sec. |
| 2d Series, alcohol only | $11.5 \times 10^{-4}$ mole/sec. |
| 2d Series, alcohol 10 cc. 2-pentene | $9.6 \times 10^{-4}$ mole/sec. |
| 2d Series, alcohol 10 cc. trimethylethene | $9.0 \times 10^{-4}$ mole/sec. |

The absorption rate for an infinite quantity of catalyst, $9.1 \times 10^{-4}$ mole/sec. of hydrogen, was therefore approximately equal to the initial rate of physical solution of the hydrogen. The concentration of dissolved hydrogen in the liquid at the liquid–solid interface, $C_{cat.}$, must have been low in all our hydrogenation experiments.[8]

If these explanations are correct, then with a fixed rate of shaking the changes in the hydrogen absorption rate with the quantity of catalyst are caused by changes in the total resistance, $r_2/W$, of the liquid stationary film at the liquid–solid interface. On the other hand, one hydrogenation at a faster shaking rate (430 times per min. using 2-pentene and 0.6 g. of catalyst) gave an absorption rate $9.2 \times 10^{-4}$ mole/sec. of hydrogen, compared to only $6.7 \times 10^{-4}$ at 260. Undoubtedly this higher rate corresponds mainly to an increased ease of physical solution of hydrogen in the alcohol. ($R_1$ was less.)

The *absorption rate per unit area of surface* could be calculated if the area of the gas–liquid interface of the shaken liquid were known. An estimate of this surface was made by measuring the rate of absorption of pure ethylene by 150 cc. of 95.8% sulfuric acid, when shaken in the apparatus, and dividing by the rate per unit area into the acid at rest ($6 \times 10^{-9}$ mole/sec.). This method is based on the postulate, which is supported by experimental evidence, that the absorption rate of ethylene per unit area of surface of this acid is unaffected by the rate of shaking.[9]

| | | |
|---|---|---|
| Rate of shaking per min.................. | 260 | 420 |
| Over-all ethylene absorption rate, moles per sec.................................... | $24000 \times 10^{-9}$ | $28000 \times 10^{-9}$ |
| Calculated area of liquid surface, sq. cm.... | 4000 | 4700 |

[8] Carothers and Adams, THIS JOURNAL, **45**, 1071 (1923), using a similar method of hydrogenation, studied the rates of the absorption during the reduction of aldehydes. Ferrous chloride was found to "promote" the reaction and, with a fixed quantity of catalyst, 0.23 g., the absorption rate increased with the quantity but approached a maximum asymptotically which was practically attained with 0.001 mole of the iron salt. On the other hand, using 0.001 mole of ferrous chloride, but changing the quantity of catalyst, the absorption rates increased in the same manner as those in Table I, and the rate with 0.23 g. of catalyst ($4 \times 10^{-4}$ mole/sec. of hydrogen) was evidently approaching the maximum that could be obtained with the quantity of alcohol, 50 cc., and the shaking rate (260 ± 5 times per min.) employed. Further, the fact that this rate is about half the maximum in our experiments where three times as much alcohol was used, indicates that $C_{cat.}$ was low in their experiments also.

[9] Davis and Crandall, THIS JOURNAL, **52**, 3781–3782 (1930).

The maximum rate of absorption during the hydrogenation experiments (Table I) would, therefore, be $2.3 \times 10^{-7}$ mole/sec. per sq. cm.[10]

In a former communication,[11] some evidence has been given that the resistances to solute diffusion (per unit area of interface) through the liquid stationary films at the gas–liquid interface and liquid–solid interface are of the same order. If they are assumed to be *equal*, then it would follow that when their total resistances are the same ($R_1 = r_2/W$), the areas of the two interfaces are also equal. Taking 4000 sq. cm. for the area of the gas–liquid interface in the experiments summarized in Table I, it can now be calculated from the weights of catalyst having an equal film resistance that the average diameters of the platinum particles (if spherical) in the three series of experiments were as follows, trimethylethene series $0.34 \times 10^{-4}$ cm., 2-pentene series $0.12 \times 10^{-4}$ cm. and isopropylethene series $0.11 \times 10^{-4}$ cm. This is in qualitative agreement with the values 0.3 to $1 \times 10^{-4}$ cm. obtained by Taylor, Kistiakowsky and Perry[12] from direct measurements of the average sizes of the particles in platinum black catalyst prepared by three different methods.

A new lot of catalyst was used in each series shown in Fig. 2 but possibly the differences in the slopes of these curves are not caused entirely by variations in the particle size of the catalyst. The bases for these calculations of surface areas and particle sizes are only approximate. However, the qualitative agreement of the calculations with the above-mentioned direct measurements substantiates the theory of the part played by the liquid stationary films in these hydrogenations. More accurate methods of experimentation will be necessary for determining whether all curves extrapolate to exactly the same point at $1/W = 0$, and whether the differences in the slopes are entirely due to variation in the particle size.

The Adams apparatus is not suitable for testing these questions, mainly because the rate of hydrogen solution is very high (the exact purpose of its design). One needs a large body of liquid, moderately stirred, and having only a small liquid–gas interface. Under the latter conditions the time necessary to half saturate the alcohol with hydrogen might become a matter of minutes, instead of less than one second as was the case in our experiments. Absorption rates under various conditions could then be followed accurately.

[10] Conant and Scherp, THIS JOURNAL, **52**, 3764 (1930), measured the rate of hydrogen solution by tetrachloroethane shaken 250 times per minute. The initial rate at 2.4 atm. has been calculated from their data to be $2.1 \times 10^{-7}$ mole per sec. per sq. cm. (The solubility of hydrogen in tetrachloroethane is about 15% lower than in alcohol.)

[11] Davis and Crandall, *ibid.*, **52**, 3761 (1930).

[12] Taylor, Kistiakowsky and Perry, *J. Phys. Chem.*, **34**, 749 (1930). The experiments of Bredig and Allolio, *Z. physik. Chem.*, **126**, 41–47 (1927), showed that the particles in the Adams catalyst are also minute.

The Relative Rates of Hydrogenation of the Components in Mixtures of Olefins.—Lebedev and his co-workers[13] have concluded that olefinic compounds of different types of substitution are hydrogenated consecutively and selectively, in the presence of colloidal platinum, that is to say, in general, one compound is almost completely hydrogenated before the next is attacked.

However, in no case in their experiments were the products from a partial hydrogenation of a mixture of two compounds analyzed by methods entirely independent of their hydrogenation hypotheses. And mostly the products were not analyzed at all, the conclusions being drawn from breaks which appeared in the curves of the rates of hydrogen absorption, which, as pointed out by Lebedev, are not sharp. Furthermore, in many cases there is no rigorous proof of the order of hydrogenation.

They also measured the hydrogen absorption rates for single ethylenic compounds at atmospheric temperature and pressure employing approximately 0.01 mole of the compound, in 10–15 cc. of alcohol with 0.05 to 0.3 g. of catalyst or in a few cases even greater amounts. The averages of the values for the different types of compounds do not appear to be particularly significant. As calculated from their curves they are (expressed in moles of hydrogen per sec. $\times$ $10^3$) monosubstituted 11, *sym.*-disubstituted 7, *unsym.*-disubstituted 10 and tri- and tetrasubstituted 6.

They state that "in general the effect of doubling the concentration of catalyst in a given case was to increase the rate of absorption of hydrogen by about 50%." On our hypotheses this would indicate relative values for $R$ and $r_2/W$ in their experiments 1 and 2.

Adkins, Diwoky and Broderick,[14] concluded that "the relative ease of reduction of two substances in a mixture may not be certainly determined even qualitatively by determining the rates of reduction of the two substances separately." They measured rates of reduction by the periods required for complete reduction of the compounds under similar conditions. However, these periods are perhaps not so significant as the rates of hydrogen absorption, while still fairly uniform. The rate nearly always falls off near the end of the reduction. Further, Thomson (unpublished data) has shown that the period required to completely reduce olefins depends greatly on their peroxide content.

The writers have, therefore, half hydrogenated four different mixtures of two olefins of different types of substitution and have analyzed the products by methods entirely independent of hydrogenation. The limited experimental data (Table II) indicate that in hydrogenation of mixtures of olefins, as pointed out by Vavon[15] and Lebedev,[13] the order of reduc-

[13] Lebedev and others, *J. Chem. Soc.*, 417–440 (1925); 823–837, 2190–2204 (1928); 220–225 (1929); 321–336 (1930).

[14] Adkins, Diwoky and Broderick, This Journal, **51**, 3423 (1929).

[15] Vavon and Kleiner, *Compt. rend.*, **177**, 401 (1922).

tion is as follows: monosubstituted, disubstituted, trisubstituted. However, the more rapidly reacting constituent was not hydrogenated to the exclusion of the other component, since in all cases there was an appreciable quantity of the latter reduced.

Synthetic mixtures of two pure olefins in approximately equal molecular proportions were hydrogenated until 50% or somewhat more of the total had been converted to paraffins. The proportion of each olefin left unchanged in the mixture was then determined by analysis.

In the case of the first mixture, propene and 2-butene, a 5-liter flask was used the neck of which had been drawn down and a stopcock sealed thereto. The alcohol and catalyst were placed inside, the flask was evacuated and the gas mixture, 0.12 mole of hydrogen and 0.078 mole of each olefin, drawn in. The other experiments, 2, 3 and 4, were carried out in the Adams apparatus already described. The olefins were here measured out in the liquid state, the quantities being checked both by weight and by volume and were poured directly into the chilled reagent alcohol (150 cc.).

As will be seen from Table II, there was a considerable difference between the boiling points of the two olefins chosen for each mixture so that fractional distillation could be utilized in the analyses of the products. By means of a vacuum-jacketed column containing a glass spiral with forty turns,[16] the

TABLE II

COMPETITIVE HYDROGENATIONS OF MIXTURES OF TWO OLEFINS

The corresponding paraffin formed by hydrogenation is given under each olefin in parentheses.

| No. | Olefins, paraffin product | B. p., °C. | Formula and type of olefin | Mole in original mixture | % of olefin hydrogenated |
|---|---|---|---|---|---|
| I | Propene | −47.5 | $CH_3CH = CH_2$ Monosubstituted | 0.078 | 90 |
|   | (Propane) | (−44.5) | | | |
|   | 2-Butene | 1.5–1.7 | $CH_3CH = CHCH_3$ Sym.-disubstituted | .078 | 20 |
|   | (n-butane) | (0.6) | | | |
| II | 1 Butene | −6.3—5.1 | $CH_3CH_2CH = CH_3$ Monosubstituted | .040 | 79 |
|   | (n-butane) | (0.6) | | | |
|   | 2-Pentene | 36.3–36.5 | $CH_3CH_2CH = CHCH_3$ Sym.-disubstituted | .051 | 21 |
|   | (n-pentane) | (36.2) | | | |
| III | Isobutene | −7.0—6.9 | $(CH_3)_2C = CH_2$ Unsym.-disubstituted | .0485 | 96 |
|   | (Isobutane) | (−10.2) | | | |
|   | Trimethylethene | 38.2–38.4 | $(CH_3)_2C = CHCH_3$ Trisubstituted | .0530 | 44 |
|   | (Isopentane) | (28) | | | |
| IV | Isopropylethene | 20.1–20.4 | $(CH_3)_2CH_2CH = CH_2$ Monosubstituted | .044 | 93 |
|   | (Isopentane) | (28.0) | | | |
|   | Trimethylethene | 38.2–38.4 | $(CH_3)_2C = CHCH_3$ Trisubstituted | .044 | 20 |
|   | (Isopentane) | (28.0) | | | |

[16] Davis, *Ind. Eng. Chem.. Anal. Ed.*, 1, 61 (1929).

mixtures of unchanged olefins and their hydrogenation products were easily separated from the alcohol and were refractionated several times from metallic sodium. Although the quantity of liquid hydrocarbon was in no case greater than 12 cc., it readily separated, in the first three experiments, into two sharply differentiated fractions each of which boiled over the range of one olefin and its corresponding paraffin. The product from No. 4 was more difficult to fractionate because both olefins yield the same paraffin, isopentane, which boils about half-way between them.

The composition of the separate fractions was then determined by chemi- cal tests.[17]

## Summary

1. A study of the rates of catalytic hydrogenation of three olefins has been made. The results have been examined in the light of the theory that the rate of hydrogen absorption is controlled by the rate of diffusion of hydrogen through liquid stationary films at the gas–liquid and liquid– solid interfaces.

2. The ratios of the hydrogen absorption rates for different quantities of catalyst, in three series of experiments with different olefins, have been calculated from this theory and agreed very well with those determined experimentally.

3. The value of the absorption rate with an infinite quantity of cata- lyst (obtained by extrapolation) agreed with an approximate value found, by direct measurements, for the initial rate of absorption of hydrogen in alcohol, and in alcohol solutions of olefins, under similar conditions.

4. The average area of gas–liquid interface during these hydrogena- tions has been determined and, with the aid of this value, the particle size of the catalysts calculated.

5. The relative proportions of two olefins reacting during partial hy- drogenation of an equimolecular mixture of the two have been measured for four different mixtures. The products were analyzed by methods inde- pendent of hydrogenation.

CAMBRIDGE, MASSACHUSETTS

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[17] Davis and Daugherty, *Ind. Eng. Chem., Anal. Ed.*, **4**, 193 (1932).