$(CH_2)_2$—CO— and bearing hydroxyl groups at its ends. Acidic ethylene succinates made up of similar chains of various lengths and bearing carboxyl groups at their ends have been prepared. Molecular weight determinations of these esters based on ebullioscopic measurements agree with those based on chemical evidence (estimation of hydroxyl or carboxyl).

A study of the ethylene succinate prepared by Tilitschejew verifies his claim that it is dimeric, and this ester is undoubtedly a 16-membered ring.

WILMINGTON, DELAWARE

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[CONTRIBUTION NO. 55 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

# THE RELATIVE RATES OF ABSORPTION OF THE GASEOUS OLEFINS INTO SULFURIC ACID AT 25°[1]

BY HAROLD S. DAVIS[2] AND REUBEN SCHULER[3]

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This paper deals with measurements of the rates at which the gaseous olefins and the vapors of some liquid olefins are absorbed by sulfuric acid of various concentrations at 25°.

The quantity of acid used was always much larger than the molecular equivalent of the amount of olefin taken so that the data apply only to sulfuric acid in the initial stages of saturation, where its character was not perceptibly changed by dissolved olefin reaction products. Thus the absorptions were of the type which take place in gas analysis pipets except that they were carried out at constant volume instead of at constant pressure.

**Apparatus.**—The apparatus employed to measure the rates of absorption (Fig. 1) consisted essentially of a cylindrical glass reaction chamber connected to a glass manometer tube dipping in mercury. A measured volume of the olefin gas was introduced into the evacuated chamber which contained sulfuric acid. The progress of the absorption was followed by recording the gaseous pressure shown by the height of mercury in the manometer tube at successive periods of time. When desired the chamber could be turned on its major axis at a definite number of rotations per minute (r.p.m.), the manometer tube turning with it. A flexible piece

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[1] This paper contains results obtained in an investigation on "The Relative Rates of Reaction of the Olefins" listed as Project No. 19 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

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of rubber tubing connected the two, and a stopcock isolated the chamber between readings.

Three absorption chambers were used during the course of the experiments. The inside dimensions of Nos. 2 and 3 used in the final experiments were: length 15.9 cm., diameter 5.1 cm., volumes 289 and 284 cc., respectively, including the connecting tubes. All three were made from standard 50 × 400-mm. pyrex test-tubes.

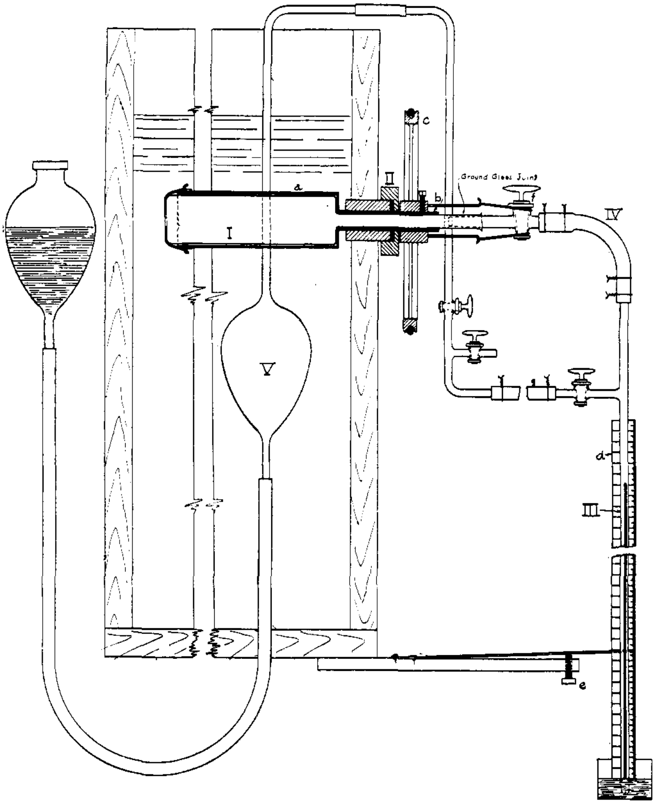

Fig. 1.—Apparatus for measuring the rate of absorption of an olefin gas into sulfuric acid. I.—Cylindrical glass reaction chamber, capacity 289 cc., in brass jacket "a," immersed in water-bath at 25°. II.—Water-tight stuffing box through which passes exit tube "b" of brass jacket to driving wheel "c." III.—Manometer tube dipping into mercury with a calibrated meter stick "d" adjusted to changing mercury level in cup by screw "e." IV.—Pressure tubing between chamber rotating horizontally and manometer rotating vertically. V.—Reservoir bulb for known volume of olefin gas to be introduced into reaction chamber "I" by mercury displacement.

**Experimental Procedure.**—Numerous preliminary experiments (1–12)

Table II, were necessary in order to develop our technique. These preliminary experiments contain, necessarily, many errors but they also contain material of such value that they have been included in the table of collected results.

The following discussion of the errors which were detected and of the methods used to overcome them throws light on the entire procedure. (1) In the preliminary experiments, the volume of the olefin gas was not measured before it was allowed to flow into the evacuated reaction chamber. Accordingly, it was not possible to gage the quantity absorbed by the liquid before the first pressure reading was taken. In the final experiments a definite volume of olefin gas, measured at atmospheric pressure and 25° in the reservoir bulb (V) was introduced into the evacuated chamber. From tests made with air and mercury in place of the olefin and the sulfuric acid, respectively, the pressure which the olefin gas would give in the reaction chamber if none dissolved in the acid was found. This calculated value represented the pressure reading at the beginning of an absorption, *i. e.*, $t = 0$. In no case was there any evidence of a rapid initial absorption which might have been attributed to physical solution of the gas in the acid.

(2) In the preliminary experiments care was not taken, during the addition of the acid, to prevent wetting the side walls and the ends of the chamber above the final level of the acid. However it soon became evident that a thin film of acid on the glass was, for a limited period of time, as effective for absorption as a similar area on the main body of the liquid. This error undoubtedly accounts for the wide variations in the preliminary results where the absorptions were measured with the chamber at rest [r.p.m. = 0]. In the final series the chamber was put in place as shown in the figure with the ground-glass joint open. The sulfuric acid was then poured into the center through a small funnel with a long bent stem. In this way wetting of the walls was largely avoided.

(3) Reaction chamber No. 1 was used in the preliminary experiments. It wobbled a little during rotation so that the sides were wetted unevenly and little waves were produced on the acid surface. Further, it had rounded ends, like an ordinary test-tube, from which at high speeds of rotation (100–200 r.p.m.) the acid drew away. Chambers 2 and 3 used in the final experiments were fitted inside a brass jacket which had been carefully centered to run true. Wobbling was thus cut down. Furthermore, their ends were flattened as much as possible which minimized, although it did not entirely eliminate, the errors caused by the round ends of No. 1.

(4) In the preliminary experiments no stopcock existed between the chamber and the rubber tube so that part of the olefin might have been absorbed, not into the acid but into the rubber. However, an analysis of the data shows that this error was much smaller than might have been expected. In all fast experiments it was negligible. For Expts. 50–80 a stopcock (F) was placed between the chamber and the rubber connection (IV). It was kept closed except when a pressure reading was taken. Any olefin in the manometer tube itself was removed by evacuating shortly after the start and replaced by air. The resulting apparatus held the olefin in the chamber out of contact with the rubber and even those absorptions could be safely followed which were so slow that they required several days for completion.

**The Acid Surfaces and the Effects of Rotation.**—Numerous experiments were carried out with the chamber at rest (r.p.m. = 0). On rotation a fairly thick layer of acid was carried up one side. Part of this flowed back again but a thin film passed on to the other side. Here it met the surface layer of the liquid, which curved down several millimeters, and both were drawn under the liquid. Thus the surface of the film on the glass and that of the liquid itself were continuously renewed during rotation. A considerable mixing in the liquid also took place. If less than 10 cc. was used, the acid did not wet the surface uniformly on rotation but tended to form pools especially at high speeds. In the final experiments 20 cc. was used. Here the area of the film formed by rotation was nearly four times that of the liquid surface proper. Estimates were made of the average thickness of the acid films on the glass. This was done by measuring the change in the surface width of the acid, colored by purpurogallin, produced by rotation, and calculating its corresponding change in volume. For 70% sulfuric acid the thickness was 0.1 to 0.3 mm., increasing with the speed of rotation. For concentrated acid it was somewhat greater.

Thin as these films were, they were thicker than the layers containing acid molecularly equivalent to all the gaseous olefins in the chamber, which were calculated to be only 0.04 mm. thick for 70% acid and 0.023 mm. for concentrated.

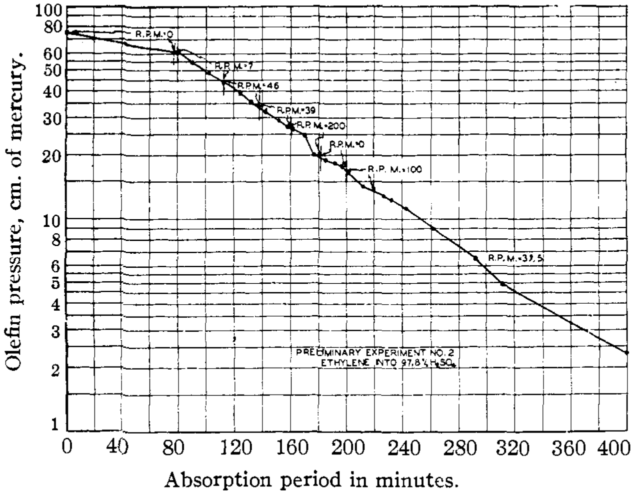

Fig. 2.

**Calculations.**—The actual variables measured in each experiment were (1) the length of the absorption period and (2) the gaseous pressure of the olefin. An examination of the absorption curves in Figs. 2 to 9, which are plotted on semi-logarithmic paper, shows that they tend to form straight lines over the greater part of the absorption. (The logarithm paper exaggerates the variations in the last period of absorption just as Mercator's projection makes Greenland seem larger than the United States on the map. Although the lower cycle is equal in width to the upper cycle, its range of values is only one-tenth.) That is, the logarithm of the olefin pressure decreased uniformly in proportion to the length of the absorption period and for each experiment the factor $1/t \ln 1/(1 - X)$ gave a fairly constant value of $K$ (where $X$ was the fraction of the olefin dissolved).

The magnitude of $K$ was independent of the partial pressure of the gas and of the time of contact. To this extent its values are characteristic for the absorptions of the separate olefins.

**Illustrative Calculations.**—Preliminary experiment No. 2 (Fig. 2).

The absorption was followed for the first seventy-seven minutes with the chamber at rest. A straight edge placed on the absorption curve shows that it is sloping quite uniformly. The pressure would reach half value (37 cm.) in 300 min. Accordingly, $K$ (for r.p.m. $= 0$) $= 1/300 \times 60 \ln (1)/(1 - 0.5) = 0.39 \times 10^{-4}$.

The chamber was then rotated steadily at the rate of seven turns per minute. The absorption rate at once increased, due, as will presently appear, to the absorbing power of the acid film now formed on the glass surfaces. Nor was the rate much affected by a change in the speed of rotation. The variations in the slope seem to have been caused by experimental errors. (See discussion above of preliminary results.) As a whole, this absorption curve, for the tube rotating, lies around a straight line of such a slope that the pressure at any time would reach half value in about 70 min. Accordingly, $K$ (chamber rotating) $= 1/(70 \times 60) \times 0.693 = 1.65 \times 10^{-4}$.

In order to compare the absorption rates in cases where different areas of acid surface were exposed, or where different volumes of gas were used, it was found convenient to calculate from $K$ in each case *a specific absorption coefficient* $C$ which may be defined as the proportional change in volume at constant pressure which would take place in an infinitesimally short time when 1 cc. of the gas was in contact with 1 sq. cm. of an acid surface having the average absorbing power of the total acid surfaces

$$C = \frac{V\mathrm{d}p}{Ap\mathrm{d}t} \text{ at constant volume, or}$$

$$= \frac{dv}{A\mathrm{d}t} \text{ at constant pressure}$$

where $A$ is the area of the absorbing surfaces.

At constant pressure, $C$ is evidently equal to the average number of cc. of gas absorbed by 1 sq. cm. of acid surface in 1 sec.

The gas volumes for each experiment were easily found by subtracting from the total volume of the chamber, that of the acid used. The measure-

TABLE I

CALCULATED VALUES OF THE FACTOR $m$ FOR THE VARIOUS EXPERIMENTAL CONDITIONS

| | Chamber No. 1 | | Chamber No. 2 | | Chamber No. 3 | |
|---|---|---|---|---|---|---|
| Vol. acid, cc. | At rest | Rotating | At rest | Rotating | At rest | Rotating |
| 10 | 8.06 | 1.30 | | | | |
| 20 | 6.11 | 1.25 | 5.50 | 1.12 | 5.40 | 1.09 |
| 25 | 5.69 | 1.23 | | | | |
| 30 | 4.99 | 1.21 | | | | |
| 90 | 2.73 | 0.887 | | | | |

Completing the calculations started above for preliminary experiment No. 2 (ethylene + concd. $H_2SO_4$)

Chamber at rest $C = 0.39 \times 10^{-4} \times 4.99 = 1.95 \times 10^{-4}$

Chamber rotating $C = 1.65 \times 10^{-4} \times 1.21 = 1.99 \times 10^{-4}$

ments of the surface areas were more difficult: (a) the acid surface proper, area = width × average length. This constituted the whole absorbing surface at r.p.m. = 0. On rotation the following additional areas of absorbing surface were formed: (b) the acid film on the cylinder walls, area = average length × perimeter above acid surface, (c) the acid film on the ends, area = total area of ends − (area under acid + area not wetted)

$$C = mK \qquad \text{where } m = \frac{\text{Total cc. of gas}}{\text{Total area of absorbing surface}}$$

TABLE II

MEASUREMENTS OF THE RATES OF ABSORPTION OF OLEFIN GASES INTO SULFURIC ACID AT 25° (PRELIMINARY EXPERIMENTS)

| | | Sulfuric acid | | | | | |
|---|---|---|---|---|---|---|---|
| Expt. no. | Olefin | Concn., % | Vol., cc. | Chamber | R.p.m. | $K \times 10^4$ | $C \times 10^4$ |
| (1) I | Ethylene | 97.8 | 30 | 1 | 0 | 0.53 | 2.7 |
| II | Ethylene | 97.8 | 30 | 1 | 34 | 1.89 | 2.3 |
| III | Ethylene | 97.8 | 30 | 1 | 0 | 0.29 | 1.5 |
| IV | Ethylene | 97.8 | 30 | 1 | 34 | 1.73 | 2.1 |
| (2) I (Fig. 2) | Ethylene | 97.8 | 30 | 1 | 0 | 0.39 | 1.95 |
| II to VII | Ethylene | 97.8 | 30 | | 7 to 200 | 1.65 | 1.99 |
| (3) I | Ethylene | 97.8 | 10 | 1 | 0 | 0.25 | 1.97 |
| II | Ethylene | 97.8 | 10 | 1 | 7 | 1.32 | 1.72 |
| III | Ethylene | 97.8 | 10 | 1 | 38 | 1.55 | 2.02 |
| IV | Ethylene | 97.8 | 10 | 1 | 100 | 1.91 | 2.48 |
| V | Ethylene | 97.8 | 10 | 1 | 208 | 1.65 | 2.15 |
| (4) I | Ethylene | 97.8 | 90 | 1 | 0 | 0.59 | 1.62 |
| II | Ethylene | 97.8 | 90 | 1 | 44 | 2.28 | 2.02 |
| III | Ethylene | 97.8 | 90 | 1 | 7.5 | 1.62 | 1.44 |
| IV | Ethylene | 97.8 | 90 | 1 | 64.5 | 2.01 | 1.78 |
| V | Ethylene | 97.8 | 90 | 1 | 180 | 2.00 | 1.77 |
| (5) I | Propene | 70 | 30 | 1 | 0 | 0.17 | 0.85 |
| II | Propene | 70 | 30 | 1 | 31 | 0.40 | 0.48 |
| (6) I | 1-Butene (A) | 70 | 30 | 1 | 0 | 0.13 | 0.62 |
| II | 1-Butene (A) | 70 | 30 | 1 | 31 | 0.39 | 0.47 |
| (7) I | Propene | 97.8 | 30 | 1 | 31 | 530 | 640 |
| II | Propene | 97.8 | 30 | 1 | 31 | | |
| III | Propene | 97.8 | 30 | 1 | 31 | | |
| IV | Propene | 97.8 | 30 | 1 | 31 | | |
| (8) I | 2-Butene (A) | 70 | 30 | 1 | 0 | [1.0] | [0.50] |
| II | 2-Butene (A) | 70 | 30 | 1 | 31 | [0.34] | [0.41] |
| (9) I | 1-Butene (B) | 70 | 30 | 1 | 0 | 0.12 | 0.61 |
| II | 1-Butene (B) | 70 | 30 | 1 | 31 | 0.32 | 0.38 |
| (10) I | *Iso*butene | 70 | 30 | 1 | 0 | 17.7 | 88.1 |
| II | *Iso*butene | 70 | 30 | 1 | 31 | 48.8 | 59.0 |
| (11) I | 2-Butene (B) | 70 | 30 | 1 | 0 | 0.35 | 1.98 |
| II | 2-Butene (B) | 70 | 30 | 1 | 31 | 0.61 | 0.74 |
| (12) I | 2-Butene (A) | 70 | 30 | 1 | 0 | 0.19 | 1.08 |
| II | 2-Butene (A) | 70 | 30 | 1 | 31 | 0.58 | 0.73 |

TABLE II (*Continued*)

FINAL EXPERIMENTS

| Expt. | Reference Fig. | Curve | Olefin | Sulfuric acid Concn., % | Vol., cc. | Chamber | R.p.m. | $K \times 10^4$ | $C \times 10^4$ |
|---|---|---|---|---|---|---|---|---|---|
| 65 | 9 | 65 | Ethylene | 95.8 | 20 | 3 | 0 | 0.25 | 1.4 |
| 66 | 9 | 66 | Ethylene | 95.8 | 20 | 3 | 28 | 1.6 | 1.8 |
| 39 | 4 | 39 | Ethylene | 87 | 20 | 2 | 28 | 0.124 | 0.14 |
| 77 | 4 | 77 | Ethylene | 87 | 20 | 3 | 28 | 0.120 | 0.13 |
| 34 | 9 | 34 | Ethylene | 80 | 20 | 2 | 0 | 0.0016 | 0.0096 |
| 32 | 9 | 32 | Ethylene | 80 | 20 | 2 | 28 | 0.0110 | 0.014 |
| 80 | 9 | 80 | Ethylene | 80 | 20 | 3 | 28 | 0.0085 | 0.0094 |
| [33 | | | Ethylene | 80 | 20 | 2 | 118 | 0.0115 | 0.013] |
| 78 | | | Ethylene | 60 | 20 | 3 | 28 | 0.00014 | 0.00015 |
| 62 | 3 | 62 | Propene | 95.8 | 20 | 3 | 0 | 74 | 400 |
| 63 | | | Propene | 95.8 | 20 | 3 | 28 | 565 | 630 |
| 56 | 3 | 56 | Propene | 87 | 20 | 2 | 0 | 9.6 | 52.8 |
| 35 | 4 | 35 | Propene | 87 | 20 | 2 | 28 | 32.5 | 36.4 |
| 38 | 4 | 38 | Propene | 87 | 20 | 2 | 28 | 35.4 | 39.7 |
| 57 | 4 | 57 | Propene | 87 | 20 | 2 | 28 | 34.5 | 38.6 |
| 59 | 4 | 59 | Propene | 87 | 20 | 2 | 28 | 34.1 | 38.1 |
| 30 | 5 | 30 | Propene | 80 | 20 | 2 | 0 | 1.05 | 5.77 |
| 58 | 5 | 58 | Propene | 80 | 20 | 2 | 0 | 0.98 | 5.40 |
| 31 | 6 | 31 | Propene | 80 | 20 | 2 | 28 | 3.62 | 4.06 |
| 60 | 6 | 60 | Propene | 80 | 20 | 2 | 28 | 3.50 | 3.92 |
| 29 | 6 | 29 | Propene | 80 | 20 | 2 | 119 | 3.50 | 3.92 |
| 61 | 9 | 61 | Propene | 70 | 20 | 2 | 0 | 0.0748 | 0.41 |
| 64 | 8 | 64 | Propene | 70 | 20 | 3 | 28 | 0.480 | 0.53 |
| 79 | 8 | 79 | Propene | 60 | 20 | 3 | 28 | 0.115 | 0.126 |
| 67 | 3 | 67 | 1-Butene A | 95.8 | 20 | 3 | 0 | 143 | 771 |
| 68 | | | 1-Butene A | 95.8 | 20 | 3 | 28 | 1880 | 2050 |
| 69 | 3 | 69 | 1-Butene A | 87 | 20 | 3 | 0 | 17.7 | 95.5 |
| 70 | 4 | 70 | 1-Butene A | 87 | 20 | 3 | 28 | 60.6 | 66.1 |
| 73 | 5 | 73 | 1-Butene A | 80 | 20 | 3 | 0 | 1.73 | 9.3 |
| 71 | 6 | 71 | 1-Butene A | 80 | 20 | 3 | 28 | 3.7 | 4.0 |
| 74 | 3 | 74 | 2-Butene B | 87 | 20 | 3 | 0 | 42.5 | 230 |
| 36 | 4 | 36 | 2-Butene B | 87 | 20 | 2 | 28 | 124 | 139 |
| 37[a] | 4 | 37 | 2-Butene B | 87 | 20 | 2 | 28 | 123 | 138 |
| 27 | 5 | 27 | 2-Butene A | 80 | 20 | 2 | 0 | 4.0 | 22.0 |
| [75 | 5 | 75 | 2-Butene B | 80 | 20 | 3 | 0 | 6.0 | 32.4] |
| 28 | 6 | 28 | 2-Butene A | 80 | 20 | 2 | 28 | 9.3 | 10.4 |
| 72 | 6 | 28 | 2-Butene B | 80 | 20 | 3 | 28 | 9.8 | 10.7 |
| [76 | 7 | 76 | 2-Butene B | 70 | 20 | 3 | 0 | 0.15 | 0.81] |
| 54 | 3 | 54 | *Iso*butene | 87 | 20 | 2 | 0 | 460 | 2530 |
| 55 | 4 | 55 | *Iso*butene | 87 | 20 | 2 | 28 | 2300 | 2500 |
| 18 | 5 | 18 | *Iso*butene | 80 | 20 | 2 | 0 | 36.5 | 201 |
| 19 | 5 | 19 | *Iso*butene | 80 | 20 | 2 | 0 | 36.5 | 201 |
| 20 | 6 | 20 | *Iso*butene | 80 | 20 | 2 | 28 | 575 | 642 |
| 21 | 6 | 21 | *Iso*butene | 80 | 20 | 2 | 28 | 560 | 624 |
| 22 | 7 | 22 | *Iso*butene | 70 | 20 | 2 | 0 | 11.0 | 60.5 |
| 23 | 7 | 23 | *Iso*butene | 70 | 20 | 2 | 0 | 10.9 | 59.9 |
| 50 | 7 | 50 | *Iso*butene | 70 | 20 | 2 | 0 | 10.25 | 56.4 |

TABLE II (*Concluded*)

| Expt. | Reference Fig. | Reference Curve | Olefin | Sulfuric acid Concn., % | Sulfuric acid Vol., cc. | Chamber | R.p.m. | $K \times 10^4$ | $C \times 10^4$ |
|---|---|---|---|---|---|---|---|---|---|
| 24 | 8 | 24 | *Iso*butene | 70 | 20 | 2 | 28 | 53.5 | 59.9 |
| 25 | 8 | 25 | *Iso*butene | 70 | 20 | 2 | 28 | 52.3 | 58.6 |
| 51 | 8 | 51 | *Iso*butene | 70 | 20 | 2 | 28 | 49.0 | 55.0 |
| 26 | 8 | 26 | *Iso*butene | 70 | 20 | 2 | 119 | 46 | 51.6 |
| 52 | 7 | 52 | *Iso*butene | 60 | 20 | 2 | 0 | 2.67 | 14.7 |
| 53 | 8 | 53 | *Iso*butene | 60 | 20 | 2 | 28 | 8.66 | 9.7 |
| 40 | | | Propene 77% + oxygen 23% | 87 | 20 | 2 | 28 | 35.7 | 39.8 |
| 41 | | | Ethene 50.4% + propene 49.6% | 87 | 20 | 2 | 28 | 35.7 | 39.9 |
| 42 | . | .. | *Iso*propyl-ethene | 70 | 20 | 2 | 28 | 0.248 | 0.278 |
| 47 | 7 | 47 | | 70 | 20 | 2 | 0 | 0.132 | 0.730 |
| 43 | 8 | 43 | Trimethylethene | 70 | 20 | 2 | 28 | 68.5 | 76.4 |
| 44 | | | Trimethylethene 3.8% + air 96.2% | 70 | 20 | 2 | 28 | 72.4 | 80.7 |
| 45 | | | Trimethylethene | 80 | 20 | 2 | 28 | 2111 | 2353 |
| 46 | | | Trimethylethene | 80 | 20 | 2 | 0 | 120 | 660 |

[a] The olefin was first exposed to ultraviolet light for 9 hrs.

TABLE III

COLLECTED SPECIFIC ABSORPTION COEFFICIENTS PER UNIT AREA ($C \times 10^4$) FOR THE GASEOUS OLEFINS INTO SULFURIC ACID IN A ROTATING CHAMBER AT 25°

The data in Table III represent the average values from the final experiments 18–80 in Table II with the following exceptions: (a) 1-butene and 2-butene into 70% $H_2SO_4$ were calculated from the preliminary experiments 1–18; (b) *iso*butene into 70% acid at 28 r.p.m. was derived from two preliminary experiments and three final; (c) the results from Expts. 33, 75 and 76 have been excluded

| Concn. of acid | 95.8% | | 87% | | 80% | | | 70% | | | 60% | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| R.p.m. | 0 | 28 | 0 | 28 | 0 | 28 | 119 | 0 | 28–31 | 119 | 0 | 28 |
| Ethylene | 1.4 | 1.8 | .. | 0.135 | 0.01 | 0.012 | 0.013 | ... | ... | .. | .. | 0.00015 |
| Propene | 400 | 630 | 52.8 | 38.2 | 5.58 | 3.99 | 3.92 | 0.412 | 0.526 | .. | .. | 0.126 |
| 1-Butene | 771 | 2050 | 95.5 | 66.1 | 9.3 | 4.0 | ... | 0.619 | 0.429 | .. | .. | ..... |
| 2-Butene | ... | .. | 230 | 138 | 22.0 | 10.5 | ... | 1.53 | 0.742 | .. | .. | ..... |
| *Iso*butene | ... | .. | 2530 | 2500 | 201 | 633 | ... | 58.9 | 57.8 | 51.6 | 14.7 | 9.7 |

TABLE IV

RATIOS OF THE ABSORPTION RATES OF THE GASEOUS OLEFINS INTO SULFURIC ACID AT 25°

| Sulfuric acid | 95.8% | | 87% | | 80% | | | 70% | | 60% |
|---|---|---|---|---|---|---|---|---|---|---|
| R.p.m. | 0 | 28 | 0 | 28 | 0 | 28 | 119 | 0 | 28 to 31 | 28 |
| Propene/ethylene | 288 | 350 | ... | 283 | 550 | 362 | 305 | | | 840 |
| 1-Butene/propene | 1.9 | 3.2 | 1.8 | 1.7 | 1.7 | 1.0 | | 1.5 | 0.82 | |
| 2-Butene/propene | | | 4.3 | 3.6 | 3.9 | 2.6 | | 3.7 | 1.4 | |
| *Iso*butene/propene | | | 48 | 65 | 36 | 160 | | 135 | 112 | 77 |
| 2-Butene/1-butene | | | 2.4 | 2.1 | 2.3 | 2.6 | | 2.5 | 1.7 | |
| *Iso*butene/2-butene | | | 20.9 | 18.1 | 9.2 | 61.6 | | 36.5 | 80 | |

## Discussion of Data

**Reliability of the Measurements.**—An examination of the figures shows that the absorption curves for check experiments usually lie very close to each other. The average deviation of $K$ from the mean in 22 experiments in nine different types of absorptions was 1.6% (excluding Nos. 27 and 75 for 2-butene, where the deviation was 19%).

**The Effects of Changes in the Rate of Rotation and in the Quantity of Acid Used.**—For ethylene these effects are shown by Table VI.

TABLE V

EXPERIMENTAL RESULTS

The solutions of sulfuric acid were prepared from C. P. material and their concentrations were checked by titration

| Olefin | Method of preparation[a] | B. p., °C. | F. p.,[b] °C. |
|---|---|---|---|
| Ethylene | "Refined" ethylene purchased from a well-known firm | ...... | ..... |
| Propene | *Iso*propanol and phosphorus pentoxide | −47.3 at 770 mm. | ..... |
| 1-Butene (A) | *n*-Butyl iodide and alcoholic potash | −6.0−−5.8 | ..... |
| 1-Butene (B) | Dehydration of *n*-butanol over alumina | −6.3−−5.1 | ..... |
| 2-Butene (A) | *Sec.*-butyl iodide and alcoholic potash | 1.8–2.2 | −113 |
| 2-Butene (B) | 2-Butanol and phosphoric acid | 1.5–1.7 | −122 |
| *Iso*butene | *Tert.*-butanol and oxalic acid | −7.0–6.9 | −140.3 |
| Trimethylethene | *Tert.*-amyl alcohol and oxalic acid | 38.4–38.45 | −134 |
| *Iso*propylethene | Dehydration of *iso*-amyl alcohol over alumina and treatment of product with dilute sulfuric acid | 20.1–20.4 | ..... |

[a] All the samples were finally purified by fractionation in a vacuum-jacketed spiral column. For details of the preparations see Davis, THIS JOURNAL, **50**, 2769 (1928); *Ind. Eng. Chem., Anal. Ed.*, 1, 61 (1929). For *iso*propylethene the method of Norris and Reuter was used, THIS JOURNAL, **49**, 2526 (1927). The sample of trimethylethene was supplied by Mr. George Thomson.

[b] The freezing-point curves were kindly made by Professor E. L. Skau of Trinity College, Connecticut, who also supplied the following information drawn from the freezing-point curves. The *iso*butene is really quite pure. The 2-butene from 2-butanol and phosphoric acid seems to be a mixture. That from *sec.*-butyl iodide and alcoholic potash is better but is still far from pure. However, it may be noted that all the freezing points are higher than those found by Coffin and Maass for these substances: *iso*butene, 146.8°; 2-butene, −127° [THIS JOURNAL, **50**, 1433 (1928)]. The samples of 1-butene and *iso*propylethene did not freeze in liquid air (Coffin and Maass, *supra*, Norris and Reuter, *ibid.*).

TABLE VI

ABSORPTION RATES PER UNIT AREA ($C \times 10^4$) FOR ETHYLENE INTO CONCENTRATED SULFURIC ACID AT DIFFERENT RATES OF ROTATION AND FOR DIFFERENT VOLUMES OF ACID

| Expt. | $H_2SO_4$, cc. | R.p.m., 0 | R.p.m., 7 | R.p.m., 38–44 | R.p.m., 100 | R.p.m., 200 |
|---|---|---|---|---|---|---|
| 3 | 10 | 1.97 | 1.72 | 2.02 | 2.48 | 2.00 |
| 2 | 30 | 1.90 | 1.78 | 2.33 | 3.12 | .. |
| 4 | 90 | 1.62 | 1.44 | 2.02 | .. | 3.93 |

These results show that for the absorption of ethylene into concentrated sulfuric acid: (a) the film of acid on the glass absorbed as well per unit area as the surface of the acid itself, (b) the absorption rate was not greatly changed by the renewal of the surfaces or by the agitation in the liquid caused by rotation.[4] (c) The rate was hardly affected by a nine-fold change in the volume of the acid. Accordingly it must be concluded that the reaction between the ethylene and sulfuric acid took place entirely in a very thin film at the surface. The ethylene never reached the main body of the acid at all.

Similar conclusions hold for the absorption of ethylene into 80% acid and of *iso*butene into 70% acid (see Table III). In other cases the values for $C$ at r.p.m. = 0 are quite different from those obtained with the chamber rotating. These divergencies might in part be attributed to errors in the former measurements, *e. g.*, part of the glass surface is wetted by acid drawn up through surface tension. They are worthy of further study because of their bearing on the selection of methods for separating olefins in gas analysis by selective absorption in sulfuric acid.[5]

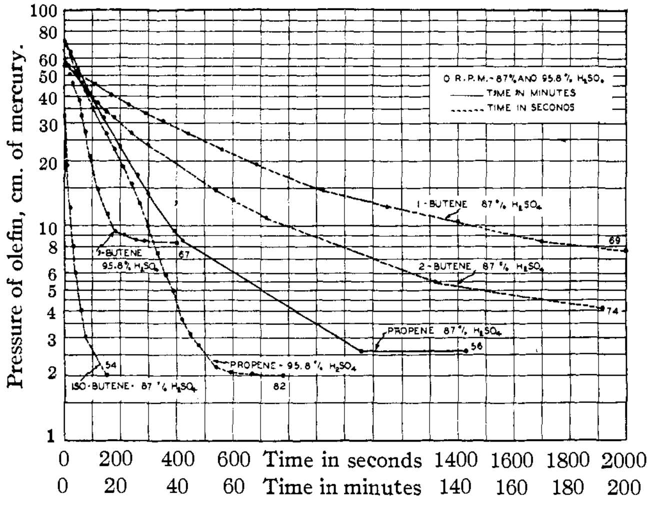

Fig. 3.

**The Effect of Foreign Gases (Table II).**—Propene was absorbed into 87% sulfuric acid from a 77% mixture with oxygen (No. 40) at the same rate, $C = 39.8$, as pure propene, $C = 38.2$. Nor was its absorption affected by the presence of an equal volume of ethylene (No. 41) $C = 39.9$. Tri-

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[4] This very important conclusion has since been confirmed by absorption measurements in another apparatus where the liquid can be stirred without changing the area of its surface. Identical rates of absorption for ethylene into concentrated sulfuric acid were found when the rates of stirring were, respectively, 0, 90 and 480 r.p.m. Full details will be published later. On the other hand, Becker, *Ind. Eng. Chem.*, **16**, 1236 (1924), showed that slow stirring (60 r.p.m.) increased the rate of absorption of oxygen into water 25 times.

[5] Unpublished data by Davis and Quiggle show that propene is absorbed about 1000 times faster than ethylene by 87% sulfuric acid in an Orsat pipet. Compare the corresponding ratios in Table IV, 550 at r.p.m. = 0 and 362 at r.p.m. = 28.

methylethene vapor was absorbed at the same rate when pure and when mixed with 96% of air (Nos. 43 and 44).

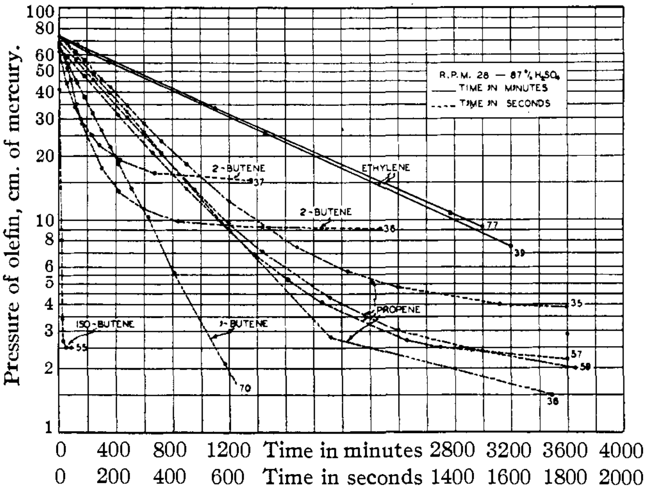

Fig. 4.

**The Relation between the Acid Concentration and the Relative Rates of Absorption of Ethene and Propene (Table IV).**—Considering only the measurements made on these two gases with the chamber rotating, those for 80 and 87% acid are the most reliable both because of the number of check experiments and because of the magnitudes of the pressure changes and of the periods of time involved. The values for propene in 95.8%

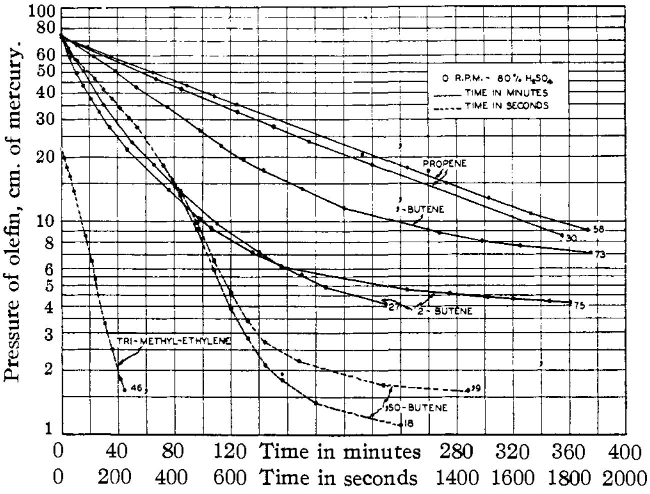

Fig. 5.

acid and for ethene in 60% acid are approximate only, because the former was a very rapid and the latter a very slow absorption.

It appears then that, within the accuracy of the measurements, the absorption rate of propene remained always about 300 times that of ethylene for concentrations of acid from 80% to concentrated, this in spite of the fact that the absolute values for the rates of both changed almost 200 times. This result is of importance in relation to the selection of the concentration of sulfuric acid most suitable for selectively absorbing propene from gases containing ethylene in the manufacture of *iso*propanol. It also raises doubt as to whether the superior merits claimed by Tropsch and Philippovich[6] for 87% acid in gas analysis absorptions for separating propene and its higher homologs from ethylene will hold for all types of pipets.

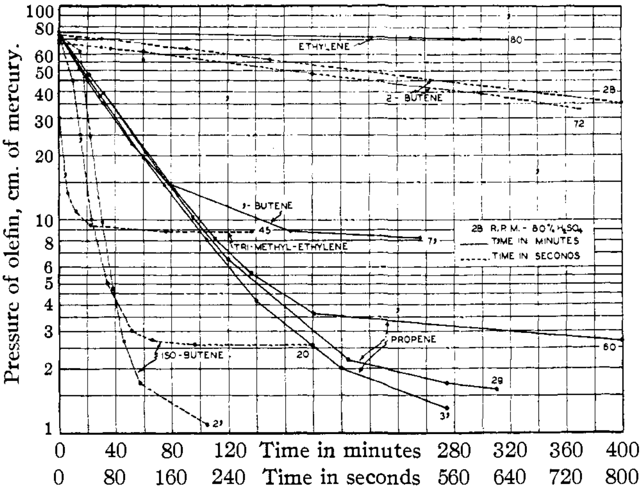

Fig. 6.

**The Relative Rates of Absorption of Propene and the Three Butenes (Table IV).**—The results show conclusively that propene and 1-butene

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[6] Tropsch and Philippovich, *Brennstoff-Chem.*, 4, 147 (1923). It may be noted that the following table prepared from the excellent data of these observers on absorptions from synthetic mixtures of ethylene and propene hardly supports their conclusion.

| | | | | |
|---|---|---|---|---|
| $H_2SO_4$ used, % | 99 | 90 | 88 | 87 |
| Contact in Hempel pipet with pearls, minutes | 5 | 2 | 5 | 5 |
| Relation of absorption to propene taken, % | 100 | 104, 99.7, 99.5 | 102, 92 | 96.1, 100 |

Manning, King and Sinnatt, *Dept. Sci., Ind. Research* (Brit.), Technical Paper No. 19, p. 8, who used 87% acid for this purpose in a standing pipet, found it necessary to correct for the ethylene absorbed. They state "It is interesting to note that the diminution in volume after ten minutes' absorption does often coincide with the true volume of the higher olefins as found by the above method (T. and P.), the small ethylene absorption compensating at that moment for the residual unabsorbed higher olefins."

dissolve at about the same rate in sulfuric acid of any concentration. Indeed for dilute acids it is uncertain which dissolves the faster. This question has considerable theoretical importance and is being investigated further. The somewhat higher rate of 1-butene, relative to propene, in concentrated acid may be due to its greater ease of polymerization.

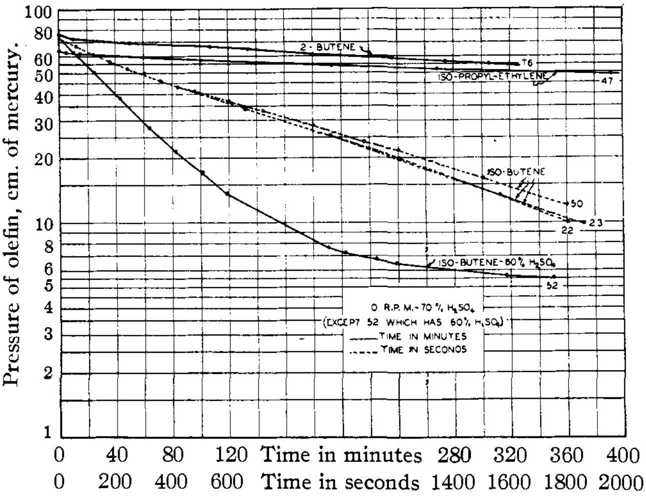

Fig. 7.

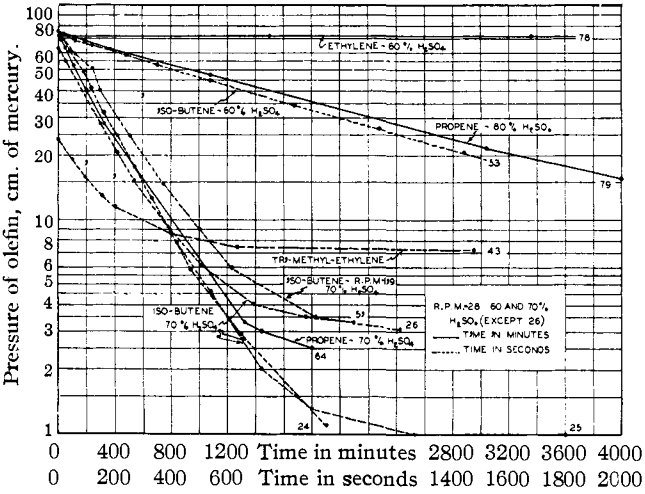

Fig. 8.

The ratio of the absorption rate of 2-butene to 1-butene is remarkably constant, 1.7 to 2.6 for 70 to 87% acid.

These facts show the unreliability of certain gas analysis methods which have been proposed involving the separation of the normal butenes from propene by selective absorption in sulfuric acid. This subject will be dealt with in another paper.

The values for *iso*butene vary in a puzzling manner However, it dissolved about 10 to 80 times as fast as 2-butene, which shows that it can be separated from propene and the normal butenes by selective absorption in sulfuric acid, although not as sharply as can propene from ethylene.

**Isobutene and Trimethylethene (Table II).**—According to our measurements, trimethylethene vapor was absorbed three to four times faster than gaseous *iso*butene into 80% sulfuric acid and 1.3 times faster into 70% acid. However Michael and Brunel[7] showed that when liquid *iso*butene and trimethylene were shaken with 65% sulfuric acid or with more dilute acids in sealed tubes under similar conditions, *iso*butene dissolved at least three times as fast as trimethylethene.

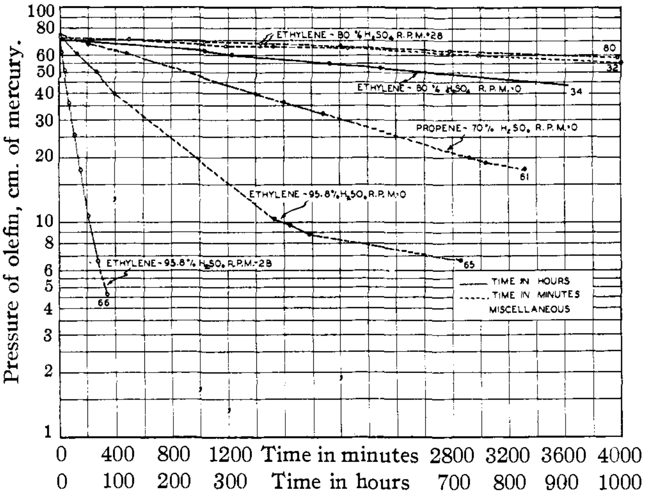

Fig. 9.

Consideration must, however, be given to the differences in the conditions existing in the two methods of experimentation. In that of the writers the ratio of the absorption coefficients ($C$) of two olefins shows the ratio of the quantities which are dissolved *when their gaseous partial pressures are equal.* On the other hand, in the reaction tubes of Michael and Brunel the partial pressure of the *iso*butene (b. p. −6.8°) must have been much larger than that of the trimethylethene (b. p. 38.4°).

From data obtained by the same experimental procedure, these investigators have compared relative rate of reaction with sulfuric acid for the two liquids cited above and also tetramethylethene (b. p. 71–72°) and

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[7] Michael and Brunel, *Am. Chem. J.*, 41, 118 (1909).

di-*iso*butene (b. p. 102–102.5°). When two liquids dissolve in and react with a solvent, to what extent are their relative rates of solution, on shaking, characteristic of their rates of reaction in the solution?

**Isopropylethene.**—The two measurements Nos. 42 and 47 indicate that this olefin is absorbed only slowly by 70% sulfuric acid at a rate comparable with that of propene.

**The Researches of Michael and Brunel.**[7]—These investigators measured the rates at which the individual butenes were absorbed when shaken with sulfuric acid of various concentrations in Hempel pipets. It has been pointed out by one[8] of us from their data that approximately the same fraction of the olefin was dissolved in unit time over the whole range of each experiment. This is also clearly shown by the fact that the absorption curves when plotted on semi-logarithmic paper are nearly straight lines (Fig. 10).

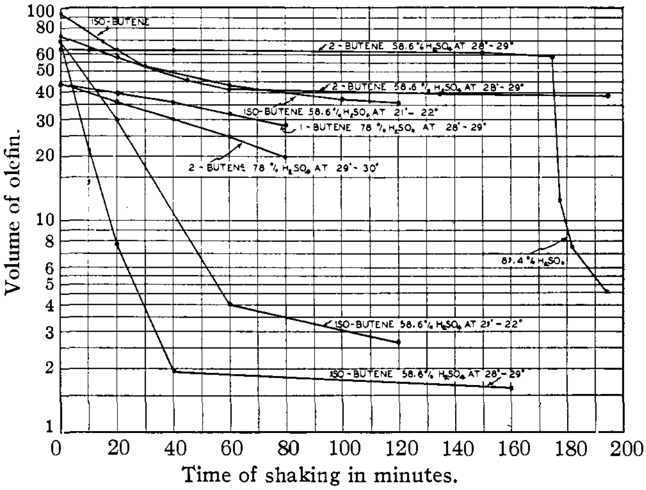

Fig. 10.—Michael and Brunel's absorptions in Hempel pipets.

This experimental fact could be explained if the amount of the absorption was always proportional to the area of the absorbing surface and if this area decreased proportionally with the gas volume. The actual relationships between the volumes of gas and the surfaces exposed in an ordinary Hempel pipet are shown in Table VII.

Michael and Brunel assumed that the rate of absorption of the olefin was proportional to the area of the liquid surface and corrected for variations in the sizes of their pipets on that basis. However, as has been shown above, a fresh acid film on the glass is as effective for absorption per unit area as the liquid surface itself, and moderate shaking wets the whole

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[8] Davis, This Journal, 50, 2780 (1928).

surface of a Hempel pipet if the gas volume is not excessive. As a first approximation the area of the absorbing surface may be taken as the sum of the liquid surface and of the glass above it with the pipet at rest. Table VII shows that this total area holds a more constant ratio to the gas volume than that of the liquid surface only.

TABLE VII

RELATIONS BETWEEN GAS VOLUMES AND ACID SURFACES FOR A SPHERICAL HEMPEL PIPET OF 175-CC. CAPACITY AT REST

$r$ = radius. $h$ = distance from center to liquid level

| $h$ cm., | Volume of gas, cc. $\frac{2}{3}\pi r^3 - \pi\left(r^2h - \frac{h^3}{3}\right)$ | Liquid surface sq. cm. $\pi(r^2 - h^2)$ | Glass surface above liquid, sq. cm. $2\pi r(r - h)$ | Total liquid and glass surface exposed, sq. cm. | Ratio of liquid surface/ vol. of gas | Ratio of total surface/ vol. of gas |
|---|---|---|---|---|---|---|
| −1 | 124 | 35 | 97 | 132 | 0.28 | 1.16 |
| 0 | 88 | 38 | 76 | 114 | .43 | 1.30 |
| +0.5 | 69 | 37 | 65 | 102 | .54 | 1.48 |
| 1 | 51 | 35 | 54 | 89 | .68 | 1.74 |
| 1.5 | 34 | 31 | 43 | 74 | .89 | 2.14 |
| 2 | 20 | 25 | 32 | 57 | 1.23 | 2.8 |
| 3 | 2.4 | 10 | 10 | 20 | 4.0 | 8.2 |

Nevertheless, for gas volumes from 70 to 20 cc. the ratio of the total surface to the volume changes about 100%, while some of the curves for the absorptions of Michael and Brunel remain fairly straight for even larger changes of gas volume. It appears that the course of their absorptions in Hempel pipets, moderately shaken, was much more uniform than would be predicted from the postulate that the quantity absorbed in unit time was always proportional to the total area of the liquid surface and the film on the glass measured at rest. This is not an academic problem. It is fundamental for the standardization of selective absorptions in gas analyses that the laws governing the absorption rates should be known for the various types of pipets.

To calculate the specific absorption coefficients $C$ from the data of Michael and Brunel the constants $K = 1/t \ln (V_0/(V_0 - V_t))$ as calculated from the absorption curves, must be multiplied by the ratio of the volume of the gas to the area of the absorbing surface. Taking the ratio of total acid surface to volume existing for 50 cc. of gas, the following values were calculated in two cases where comparisons could be made with ours for the rotating absorber.

| Absorption conditions | $C$ |
|---|---|
| 2-Butene into 81.4% $H_2SO_4$ in Hempel pipet at 28–29° | $55 \times 10^{-4}$ |
| 2-Butene into 80% $H_2SO_4$ in rotating absorber at 25° | $10.5 \times 10^{-4}$ |
| *Iso*butene into 58.6% $H_2SO_4$ in Hempel pipet at 28–29° | $12 \times 10^{-4}$ |
| *Iso*butene into 60% $H_2SO_4$ in rotating absorber at 25° | $9.7 \times 10^{-4}$ |

The agreement is rather remarkable. In the case of 2-butene they used a stronger acid at a higher temperature than we and a greater value for $C$ would be expected. In the case of *iso*butene the effects of the differences in acid concentration and in temperature tended to counterbalance.

**The Research of A. Dobrjanski.**[9]—Instead of a Hempel pipet, this investigator used a glass cylinder of constant cross section for absorption into sulfuric acid. The olefin gas was introduced from a mercury buret, and in taking the separate volume readings as the absorption proceeded only part of the gas was withdrawn into the buret, apparently up to a fixed mark in the chamber. After a somewhat higher initial rate had subsided, each olefin gas dissolved at uniform speed for a long time. In each experiment an excess of acid 800 to 1000 times the theoretical was used.

Dobrjanski criticizes the use of Hempel pipets by Michael and Brunel for measuring absorption rates because, as pointed out above, the ratio of the area of the liqud surface to the volume of the gas changes as the absorption proceeds. For this reason he used a vessel of constant cross section 19.5 sq. cm. and tried to avoid wetting the upper surfaces during the volume readings. Unfortunately he does not seem to have recognized the high absorbing capacity of the acid films left on the glass and the errors from this source appear to have vitiated much of his otherwise valuable data.

He attributes the high initial rates of absorption to physcal solution of the gases in the acid. It seems more probable, however, that the observed effect was due to absorption into the film of acid left on the whole glass surface when the acid was forced down to admit the gas at the beginning.

For ethylene and propene the absorptions were carried out in three ways: first with the pipet at rest, second with the acid in the pipet tossed back and forth every five minutes, which about doubled the rate, and third with the pipet shaken continuously 120 times per minute, which increased the rate 5 to 28 times, depending on the concentration of the acid. The volume readings were taken every ten minutes. Evidently such procedures will give great variations in the total area of the absorbing surface and in the freshness of the acid film. It is not possible to calculate from Dobrjanski's data specific absorption coefficients comparable to ours and even his values for the relative rates of absorption of the different olefins appear to be only qualitative.

The present paper deals only with experimental investigations of the rates at which olefins are absorbed by sulfuric acid. The expression "rate of reaction" has been purposely avoided. The relationships between the rates of absorption of gases and the rates and types of the reactions which take place in solution need further consideration. The magnitudes of the physical solubilities of the gases and their rates of diffusion in the

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[9] Dobrjanski, *Neftyanoe Khozyaistvo*, 565–737 (1925). For a critical translation of this article we are indebted to Professor Paul N. Kogerman.

solution are important factors. Nor should the possibility be overlooked that reactions may take place between the gaseous olefin molecules and the surface molecules of the acid.

## Summary

1. Measurements have been carried out on the rates of absorption of olefin gases and vapors into sulfuric acid at constant volume by following the change in the gaseous pressure with time.

2. The logarithms of the olefin pressures plotted against periods of absorption form fairly straight lines. That is, the quantity absorbed in unit time was proportional to the partial pressure of the olefin.

3. When the reaction tube was rotated, the increase in the total absorption was largely proportional to additional area of acid surface formed on the glass.

4. Specific absorption factors (*C*) have been calculated on all the gaseous olefins into a large excess of sulfuric acid of various concentrations at 25° (Table III). They represent the cc. of gas absorbed, at constant pressure, by 1 sq. cm. of acid surface in one second and appear to be definite entities. They were often unaffected by the rate of renewal of the acid surface, by variations in the volume of the acid or in the degree of its agitation.

5. The reactions appeared to take place in a very thin film at the surface of the sulfuric acid. The gases never reached the main body of the liquid. Accordingly it seems advisable to use caution in drawing conclusions regarding the rates of reaction of gases with liquids in which they are sparingly soluble, from their rates of absorption.

6. Objections are raised to the practice of drawing conclusions regarding the relative rates of reaction of two liquids with another liquid from measurements of their relative rates of solution in it on shaking.

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