Table I. Analysis of Knowns

Sample No.	Amount of Sample	0.001 *N*, Iodine Solution, Net	Carbon Disulfide		
			Present	Found	Difference
	Ml.	*Ml.*	*P.p.m.*	*P.p.m.*	*P.p.m.*
1	25	0.58	1.0	1.1	+0.1
2	25	1.16	2.0	2.2	+0.2
3	25	1.68	3.0	3.2	+0.2
4	25	2.78	5.0	5.3	+0.3
5	25	5.29	10.0	10.1	+0.1
6	25	12.89	25.0	24.6	−0.4
7	10	10.27	50.0	49.0	−1.0
8	10	20.63	100.0	98.4	−1.6
9	5	20.55	200.0	196.0	−4.0

Specific gravity of samples at 20°/4° C. = 1.5937

tion slightly acid by the addition of dilute acetic acid from a buret until 3 or 4 drops in excess are indicated. Immediately add 50 ml. of ethyl alcohol (3A specially denatured), connect the flask to the titration apparatus, and titrate to a dead-stop end point with 0.001 *N* iodine solution. Similarly treat a blank containing all the reagents and omitting the sample. At the start of the titration the galvanometer will show no reading. As the end point is approached the galvanometer will show a temporary deflection of about 3 scale divisions as each drop of iodine reagent is added. At the true end point one drop of reagent causes a permanent galvanometer deflection of 3 to 5 scale divisions. However, greater speed in the titration may be obtained without loss in accuracy by choosing a point at 10 or 15 on the galvanometer scale as the final end point and titrating to this same point with the blank and all the samples.

CALCULATION. 1 ml. of 0.001 *N* iodine = 76 micrograms of carbon disulfide.

EXPERIMENTAL RESULTS

The first series of experiments was made to find the time required to complete the reaction of the carbon disulfide with the alcoholic potassium hydroxide, and to determine the stability of the xanthate formed. Knowns of from 1 to 200 p.p.m. of carbon disulfide were used for this experiment. Figure 1 shows that any length of time from 30 minutes to 2 hours may be allowed for this reaction. However, the 30-minute point was chosen for a routine procedure to speed up the analysis.

A second series of experiments was carried out to determine the precision and accuracy of the method when applied to carbon tetrachloride containing various amounts of carbon disulfide (Table I).

The samples were prepared by carefully weighing known quantities of carbon disulfide in a weighed 100-ml. glass-stoppered volumetric flask containing about 25 ml. of carbon disulfide-free carbon tetrachloride. The mixture was then diluted to the mark at 20° C. Aliquots of this first 100-ml. mixture were measured from a jacketed buret at 20° C. and further diluted with carbon tetrachloride to obtain the desired knowns.

SUMMARY

The method described in this paper was found to be very practical and rapid, giving a relatively high degree of precision and accuracy. It was especially useful in routine work where a large number of samples, with approximately the same amount of carbon disulfide impurity, had to be analyzed in a short time.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Dept. Sci. Ind. Research (Brit.), *Leaflet* 6 (1939).
(2) Huff, *J. Am. Chem. Soc.*, 48, 81–7 (1926).
(3) Matuszak, M. P., IND. ENG. CHEM., ANAL. ED., 4, 98 (1932).
(4) Moskowitz, Siegel, and Burke, *N. Y. State Ind. Bull.*, 19, 33 (1940).
(5) Serfass, E. J., IND. ENG. CHEM., ANAL. ED., 12, 536–9 (1940).
(6) Viles, *J. Ind. Hyg. Toxicol.*, 22, 188 (1940).
(7) Wernimont, G., and Hopkinson, F. J., IND. ENG. CHEM., ANAL. ED., 12, 308–10 (1940).
(8) *Ibid.*, 15, 273 (1943).

Analysis of Cyclopropane-Propylene Mixtures by Selective Hydrogenation

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A new method, presented for the analysis of cyclopropane-propylene mixtures by selective hydrogenation, consists in passing the mixture with hydrogen over a nickel-kieselguhr catalyst partially poisoned with mercury to hydrogenate the olefin, then over a nonpoisoned catalyst to hydrogenate the cyclopropane. Accuracies of ±0.5 numerical % are obtained. The presence of inert components such as gaseous paraffins does not interfere with the analysis and hence a real advantage is realized over other methods described in the literature. Small samples (~1 cc. N.T.P.) may be analyzed with good accuracy.

A SEARCH of the literature reveals no method for the direct determination of cyclopropane. Several methods for the analysis of binary mixtures of propylene and cyclopropane have been proposed, the most widely used of which is based upon absorption of the propylene in a 3% aqueous potassium permanganate solution (*1*, *2*, *4*). Cyclopropane is found by difference after correcting for solubility effects. However, in the presence of saturated hydrocarbons or other inert gases, no analysis is possible. A new method, based upon selective hydrogenation, provides a direct analysis for cyclopropane. In addition, small gas volumes (~1 cc. at normal temperature and pressure) may be analyzed.

Willstätter and Bruce (*5*) studied the hydrogenation of cyclopropane over a nickel catalyst and found that appreciable reaction occurred only at temperatures above 80° C. while propylene was easily hydrogenated at room temperatures. Accordingly, hydrogenation studies were undertaken in an attempt to apply this reported differential effect to a scheme of analysis.

Preliminary experiments were carried out using a nickel catalyst supported on kieselguhr. Results showed that this catalyst after reduction in hydrogen completely reduced cyclopropane to propane in a few passes over the catalyst at temperatures as low as 0° C. Consequently, a reduction of the activity by partial poisoning was attempted. It was found that the introduction of a few drops of mercury sufficiently deactivated the catalyst so that reduction of propylene was complete after a few passes while cyclopropane was unchanged at temperatures up to 200° C. The poisoning technique is described below. A nonpoisoned catalyst was used for the hydrogenation of cyclopropane.

Presumably the differences in activity of the Willstätter and Bruce catalyst and the one employed by the authors are attribut-

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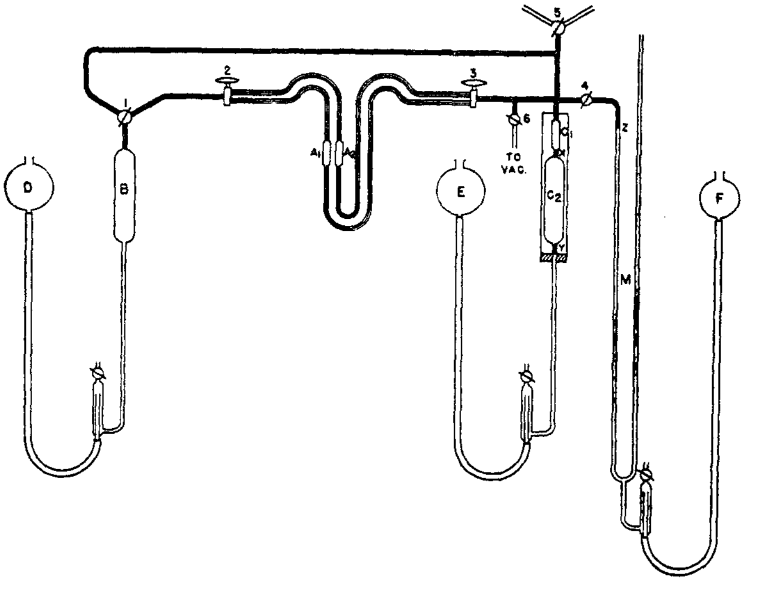

Figure 1. Diagram of Apparatus

able to differences in composition and method of preparation. The catalyst used in the authors' experiments is described by Trenner, Morikawa, and Taylor (*3*) as follows: "The nickel catalyst was a very active nickel-kieselguhr preparation, made by precipitation of the carbonate on kieselguhr, ignition, and reduction in hydrogen at progressively increasing temperature to 450°. It contained 15% nickel." Willstätter and Bruce (*5*) describe their catalyst as a mixture of equal parts of nickel oxide and pumice, reduced to the metal at 280° C.

A second difficulty encountered was adsorption on the catalyst surface. Saturation with hydrogen or with a hydrogen-hydrocarbon mixture before analysis proved unsatisfactory because of unequal adsorption of the constituents of the mixture. These effects were eliminated by evacuating the catalyst chambers with a Toepler pump after each hydrogenation and returning the recovered gases to the sample. As a further precaution, small volumes of catalyst were employed. The expected volumes were recovered within experimental error in all cases.

Since the usual stopcock greases absorb hydrocarbons readily, it was necessary to employ a lubricant made up of glycerol, dextrin, and mannitol, in which hydrocarbons are nearly insoluble.

APPARATUS AND PROCEDURE

A diagram of the apparatus is shown in Figure 1. Bulbs A_1 and A_2 each contained 2 or 3 cc. of catalyst (actually one bulb was placed behind the other). An electrically heated furnace with rheostat control was placed around these bulbs. C_1, used for the analysis of small samples, had a capacity of approximately 4 cc., while C_2 had a volume of 100 cc. These were enclosed in a water jacket. *B*, which served for passing the gaseous mixture over the catalysts, was also used as the Toepler pump for evacuating the catalyst bulbs. The manometer, *M*, completed the apparatus. Capillary tubing throughout minimized the dead space.

REDUCTION OF CATALYSTS AND POISONING TECHNIQUE. The catalysts were reduced in a slow stream of hydrogen, starting at 250° and slowly increasing to 400°. Tank hydrogen was purified by passing first over platinized asbestos and then through a liquid air trap to remove water.

After reduction was complete, the temperature was reduced to 150°, the hydrogenation temperature, and one of the catalysts was partially poisoned. A few drops of mercury from bulb *B* were introduced into the capillary between stopcocks 1 and 2 and then pushed over into the catalyst chamber with hydrogen by lifting bulb *D* after filling *B* with hydrogen. The catalyst then possessed the desired activity. Fifteen or twenty analyses could be made before regeneration of the catalysts became necessary. This was carried out by again passing hydrogen over the catalysts at approximately 300°. Mercury was driven off the poisoned catalyst, after which the activity returned to normal as measured by its ability to reduce cyclopropane readily. The catalyst was again poisoned by the technique described.

ANALYTICAL PROCEDURE. Before analysis the catalyst bulbs (maintained at 150°) were evacuated with the Toepler pump with stopcock 3 closed; three pumpings of each catalyst were sufficient. With the Toepler pump filled with mercury and stopcock 1 closed, the hydrogen pressure was adjusted at 400 to 500 mm. and the manometer read with the mercury levels at marks *b* and *c*. The hydrocarbon sample was then introduced and the manometer read with the mercury levels at marks *b* and *c* as before. To determine the olefin content, the mixture was passed several times over the poisoned catalyst and the pressure recorded after evacuating the catalyst. To check completeness of hydrogenation, the process was repeated. The cyclopropane was then determined over the active catalyst. Saturates, if present, were obtained by difference. The capillary tubing must be swept out during the analysis to ensure contact of all the sample with the catalysts.

For small samples, pressures were read with the mercury level adjusted to mark *a*. Before the mixture was passed over the catalysts, the volume was expanded by lowering *E* and reductions were carried out at low pressures. No noticeable difference was detected in the rates of hydrogenation at these reduced pressures. By this procedure very small samples (~1 cc. N.T.P.) could be analyzed.

A buret may be substituted for bulbs C_1 and C_2 for analyses at constant pressure. For small samples it would be necessary to attach a bulb below a microburet for expansion to facilitate hydrogenation.

The details of procedure outlined above apply to the highly active catalyst employed. Although the authors have no data on the behavior of less active catalysts, with appropriate modification in operating temperature and the like, such differential hydrogenation based on partial poisoning with mercury should be successful with any reasonably active supported catalyst.

Table I. Analysis of Cyclopropane-Propylene Mixtures

(*Approximate H_2–sample ratio 2 to 1*)

Volume of Sample + H_2	Composition of Synthetic		Found by Analysis	
	Cyclopropane	Propylene	Cyclopropane	Propylene
Cc.	*Vol. %*		*Vol. %*	
100	21.6	78.4	21.4	78.6
100	24.6	75.4	24.2	76.0
4	33.6	66.4	33.4	66.8
100	40.0	60.0	40.0	59.7
100	48.5	51.5	48.1	51.8
100	73.2	26.8	72.7	27.2
4	73.8	26.2	74.3	25.9
100	80.2	19.8	80.4	20.0
4	100.0	...	99.5	...
100	100.0	...	100.2	...
100[a]	27.3	26.1	27.0	26.2
100[a]	30.1	42.3	30.3	42.0

[a] Balance of sample *n*-butane.

RESULTS

Various mixtures of known composition have been analyzed and the results are tabulated in Table I. On a numerical percentage basis, accuracies of ±0.5% are obtained. An examination of the data reveals little or no difference in precision for the large or small samples—perhaps because of the few data presented. Errors arising from such factors as adjusting mercury levels would be magnified when analyzing small samples. However, it was found that reproducibility in adjusting these levels for one small sample was within 0.5%. The importance of using a stopcock lubricant in which hydrocarbons are nearly insoluble cannot be overemphasized.

Van der Waals corrections for perfect gas deviations were within experimental error and hence no corrections have been applied.

An apparatus similar to the one described, but using only one catalyst, may be employed for determining the olefin content in gaseous mixtures containing only olefins and paraffins. The method possesses definite advantages, since adsorption effects are minimized and very small samples may be handled.

CONCLUSIONS

A method developed for the analysis of cyclopropane-propylene mixtures by selective catalytic hydrogenation with accuracies of ±0.5% provides for the direct determination of cyclopropane, and hence the presence of saturated hydrocarbons does not interfere. No data are available as to possible interference by substituted acetylenes. Other methods described in the literature do not analyze for cyclopropane directly. Propylene is determined by absorption in a suitable reagent and cyclopropane obtained by difference. The time required for analysis probably represents a saving—for example, from 1 to 2 hours are required for the analysis of binary mixtures when using the dilute potassium permanganate procedure (*1*) while from 15 to 30 minutes are required with this method. An additional advantage is that small samples (~1 cc. N.T.P.) may be handled with good accuracy.

LITERATURE CITED

(1) Chambers and Kistiakowsky, *J. Am. Chem. Soc.*, 56, 399 (1934).
(2) Roginski and Rathmann, *Ibid.*, 55, 2800 (1933).
(3) Trenner, Morikawa, and Taylor, *Ibid.*, 59, 1103 (1937).
(4) Wagner, *Ber.*, 21, 1236 (1888).
(5) Willstätter and Bruce, *Ibid.*, 40, 4456 (1907).

Ternary Mixtures of Three Isomeric Hexanes

Quantitative Method of Analysis

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Solution temperature measurements were made using all the isomeric hexanes with both nitrobenzene and diethyl phthalate. Data are given which make it possible for a hexane ternary mixture composed of 2,2-dimethylbutane, 2,3-dimethylbutane, and 2-methylpentane to be analyzed with an accuracy of 0.5% in approximately one hour.

IN CONNECTION with research at the General Motors Research Laboratory it was necessary to analyze hexane mixtures that contained much smaller quantities of the doubly-branched than of the singly-branched hexanes.

The automatic stills available at this laboratory are able to separate the isomeric hexanes (*6*) and, when the distillation curve is supplemented with a refractive index curve, a good analysis of a hexane mixture can be obtained as long as there is a sufficient quantity of each isomer in the mixture to obtain a flat portion in both the refractive index and boiling point curves. Table I shows that as the boiling point of the hexanes increases the refractive index alternates up and down.

In the distillation of the mixtures under investigation there was not enough 2,3-dimethylbutane present to give a flat on the refractive index curve. In the distillation break between 2,2- and 2,3-dimethylbutane the refractive index would rise but before it reached the value for pure 2,3-dimethylbutane it would turn downward again, showing that some 2-methylpentane was in the distillate. This particular part of the distillate was a ternary mixture composed of 2,2- and 2,3-dimethylbutane with 2-methylpentane, the composition of which could not be determined accurately.

A previous paper (*5*) described a method for quantitative analysis of ternary mixtures of three isomeric heptanes based on their solution temperature in nitrobenzene and diethyl phthalate. This paper covers the extension of this method of analysis to the above-mentioned hexane ternary mixture. This work makes it possible to analyze a ternary mixture composed of 2,2-dimethylbutane, 2,3-dimethylbutane, and 2-methylpentane with an accuracy of 0.5% in approximately one hour.

In the previous paper (*5*), the author stated that no mention had been found in the literature of any attempt to use critical solution temperature measurements for the quantitative deter-

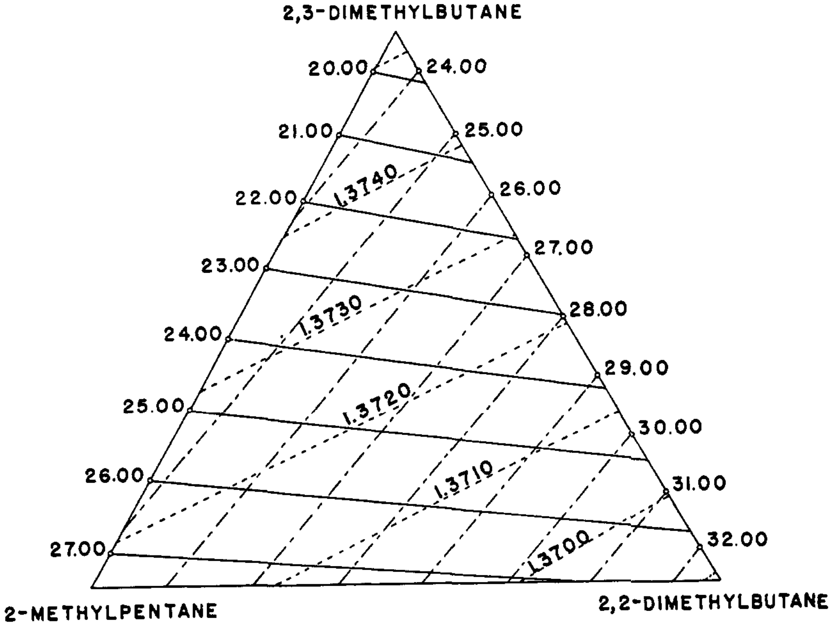

Figure 1. Bath Temperature from Refractive Index

——————— Diethyl phthalate point data
— — — — — Nitrobenzene point data
- - - - - - - - - Refractive index data