venient method for obtaining benzoins. This method should prove particularly useful in those instances when the aldehyde requisite for the usual benzoin condensation is not readily accessible.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 33]

THE RELATIVE RATES OF BROMINATION OF THE OLEFINS[1]

BY HAROLD S. DAVIS[2]

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This paper deals mainly with experimental work on the rates of reaction of the lower olefins with bromine, particularly in carbon tetrachloride solution.

1. **The Dark Reaction of Ethylene with Bromine in Dry Carbon Tetrachloride Solution Is Very Slow.**—Contrary to general belief,[3] it was found that ethylene brominates in carbon tetrachloride at a rate measurable with time and that if the solutions are dried and kept away from bright light, the reaction requires hours and even days for completion.

2. **The Rate of the Dark Reaction of Ethylene with Bromine in Carbon Tetrachloride Varies Greatly with the Quantity of Moisture in the Solution.**—Solutions of bromine in carbon tetrachloride were dried in the following ways: (*a*) by refluxing for four hours with phosphorus pentoxide and distilling into a dry receiver protected from moisture in the air by phosphorus pentoxide. In some cases the solution was first shaken for several days with phosphorus pentoxide before refluxing and distilling. (*b*) By shaking for different periods of time with phosphorus pentoxide and settling. Evaporation tests on the clear supernatant liquid showed that it contained less than one part of phosphorus pentoxide in one hundred thousand by weight.

When dry ethylene was added to these solutions the reaction went quite

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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 Mr. John D. Rockefeller. This fund is being administered by the Institute with the coöperation of The Central Petroleum Committee of the National Research Council.

[2] Director and Research Associate, Project No. 19.

[3] Thus Plotnikov, "Lehrbuch der Photochemie," **1920**, pp. 245–255, states that ethylene and bromine unite to form the dibromide at ordinary temperatures instantaneously and completely and the reaction only slackens to one measurable with time at −100°. Working at this temperature in petroleum ether solution, he found the reaction to be of the second order. On the other hand, Stewart and Edlund, THIS JOURNAL, **45**, 1014 (1923), found ethylene and bromine to be practically unreactive in the gaseous state.

slowly in the absence of light. Numerous experiments showed the reactions to be of the second order and in solutions 0.05 *M* for both bromine and ethylene, the lowest value obtained for the reaction coefficient,[4] *K*, at 25° was 0.006.

An indication of the quantitative relationships between the rate and the water content was obtained in the following experiment which showed the rate of reaction of ethylene with bromine in dry carbon tetrachloride to increase over five times on the addition of 5% by volume of carbon tetrachloride saturated with water.

TABLE I

EXPERIMENT SHOWING THE EFFECT OF WATER ON THE RATE OF DARK BROMINATION OF ETHYLENE IN DRY CARBON TETRACHLORIDE

Conditions: The bromine–carbon tetrachloride solution was distilled from phosphorus pentoxide, and ethylene dried by the pentoxide was added thereto. The course of the reaction was followed by the withdrawal of samples and titration for their bromine content. At the end of the fourth hour, 5% by volume of carbon tetrachloride saturated with water was added. (Water content of resulting solution 0.0005 *M*).[a] Temperature, 25°. a (ethylene) $= b$ (bromine) $= 0.057$ *M*.

t, hours	0	1	2	3	4	5
% reacted	0	5	8	10	12	20
K		0.0167	0.0095	0.0063	0.0065	0.035

[a] C. W. Clifford, *J. Ind. Eng. Chem.*, **13**, 632 (1921), gives the following values for the solubility of water in carbon tetrachloride expressed as grams per 100 g. of solution: at 24.0°, 0.010; at 28.5°, 0.013.

Preliminary experiments on the rates in solutions saturated with water at 25° gave much higher values for *K*(0.4 to 4.0).

It might have been expected, from analogy with the effect of water on the photochemical reaction of hydrogen and chlorine,[5] that changes in the water content would affect the rate only when the merest traces were present. This does not, however, appear to be the case. Careful quantitative measurements on the problem will be of considerable value.

It seemed unlikely that water was the only substance which would change the rate of this reaction and tests were made on the effects of two others known to be present in the solutions, namely, oxygen and hydrogen bromide.

The effect of oxygen on the reaction did not appear to be great. That it had no accelerating influence was shown by the fact that the rate could be made very slow in solutions which had been in intimate contact with air. Nor was any increase in the rate noticed when in one experiment a volume of air equal to that of the dissolved ethylene was forced into the reaction tube. That oxygen does not hinder the reaction is indicated by the fact that the rate was still slow in dry solutions from which most of

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[4] $K = 1/[t(a - b)] \ln[(a - x)/(b - x)]\, b/a$, where t = time in minutes, a = initial molar concn. of ethylene, b = initial molar concn. of bromine, and x = molar quantity of each combined in time t.

[5] Coehn and Jung, *Z. physik. Chem.*, **110**, 719 (1924).

the air had been expelled by boiling for a few moments under reduced pressure. The following experiment shows that hydrogen bromide does not affect the rate.

Table II

Experiment Showing that Hydrogen Bromide Has Little or No Effect on the Rate of Bromination of Ethylene in Carbon Tetrachloride

a (ethylene), 0.071 *M*; *b* (bromine), 0.056 *M* Dry HBr forced into tube equiv. if dissolved to 0.0517 *M* soln.

Bromine reacted, %	*K*	Bromine reacted, %	*K*
28	0.43	64	0.55
42	0.33	74	0.44

The small increase in *K* can probably be attributed to traces of moisture added with the hydrogen bromide and not to the latter.[6]

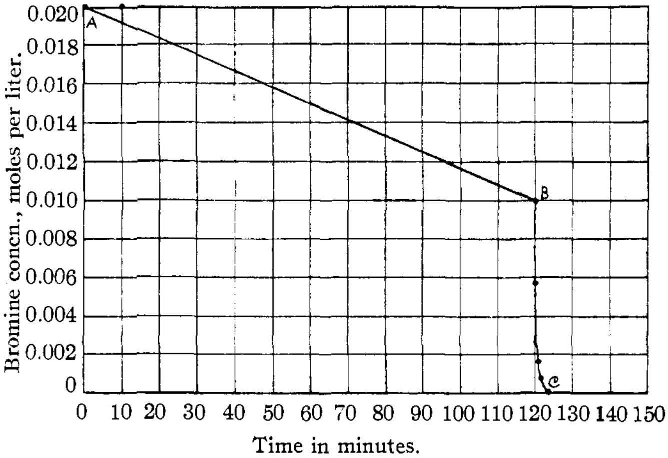

Fig. 1.—Curve showing the effect of sunlight on the rate of bromine addition to ethylene in carbon tetrachloride solution at room temperature. Ethylene concn., 0.06 *M*; bromine, 0.02 *M*. Curve A to B—rate of reaction in a 50cc. Nessler tube with light mainly excluded by a brass jacket, $K = 0.07$. Curve B to C—rate of reaction when the tube was removed from its jacket and exposed to bright sunlight, $K = 44$.

3. Bright Light Enormously Increases the Rate of Bromination of Ethylene in Carbon Tetrachloride.—This is illustrated by Fig. 1, which shows the effect of bright sunlight in speeding up the reaction. However, the rates were found to be little affected by illumination sufficient to permit color comparison measurements on the solutions in Nessler tubes, as described later.

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[6] However, Williams and James, *J. Chem. Soc.*, **1928**, 343, have shown that hydrogen bromide is a very effective catalyst in the addition reaction between ethylenic acids and bromine. Water and hydrogen chloride produce similar effects but not of the same degree.

4. The Rate of the Dark Bromination of Ethylene in Dry Carbon Tetrachloride Increases Progressively as the Temperature is Lowered from 25 to 0°.—In the following experiments the rates at 25 and 0° were found on the same mixture at different stages of the reaction by simply changing the temperature. This procedure was necessary because as already pointed out the rates in separate experiments with dry solutions vary greatly even at the same temperature due to differences in the residual moisture content.

TABLE III

THE RELATIVE SPEEDS OF THE DARK BROMINATIONS OF ETHYLENE IN DRY CARBON TETRACHLORIDE AT 25 AND 0°

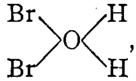
No.	Method of drying Br_2–CCl_4 soln.	Method of measurement	*K*		Ratios of *K*	
			25°	0°	25°	0°
1	Distn. from P_2O_5	Titration	0.008	0.4	1	50
2	Distn. from P_2O_5	Color comparison	.4	8	1	20
3	Shaking with P_2O_5	Color comparison	.013	1.4	1	110
4	Shaking with P_2O_5	Color comparison	.012	1.5	1	130

The reaction actually proceeds faster at 0° than at 25°. Measurements at intermediate temperatures have shown that there is no sudden change in the rate. It increases progressively as the temperature is lowered.

These are really very striking experiments. A solution of ethylene and bromine in dry carbon tetrachloride loses its color very slowly in the dark or even in ordinary daylight; but if placed in ice, or better in ice and salt, the color fades away rapidly even though the solution is kept absolutely in the dark. Reheating to 25° does not regenerate the color. On the other hand, if the solution is heated up to 25° before decolorization is complete, then the rate falls off to what it was originally at that temperature, but can be speeded up again by lowering the temperature, etc.

That the decreasing of the color really measures the course of the reaction is shown by the following facts. 1. Similar results were obtained when the course of reaction was followed by titration of the bromine (Expt. I, Table III). 2. The color of a bromine–carbon tetrachloride solution changes little, if any, on cooling from 25 to 0°. 3. The quantity of bromine used up was found to be equimolecular to the ethylene, the latter being determined by the volume of ethylene added and the former by the volume of the bromine-carbon tetrachloride solution and its fall in concentration as determined by titration.

The bromine unites to the double bond in the ethylene and there is little substitution as measured by the hydrogen bromide evolved. Thus the products from Expt. 1, Table III (including the gases) were washed with about an equal volume of water which was then filtered and the bromide ion precipitated by silver nitrate). Nephelometric comparisons with similar clouds produced in known solutions of potassium bromide showed that less than 1% of the bromine which had entered into the reaction was to be found as hydrogen bromide.

5. It Is Suggested that the Dark Bromination of Ethylene in Carbon Tetrachloride Proceeds Mainly through a Bromine Hydrate and that the Concentration of this Hydrate Increases as the Temperature Is Lowered from 25 to 0°.—The fact that the dark bromination of ethylene in dry carbon tetrachloride goes very slowly indicates the bromine molecule as such to be relatively inactive toward this olefin. Since traces of water speed up the reaction, it seems reasonable to assume that this is accomplished through a union between the bromine and the water, for ethylene shows little tendency to add the latter, while hydrates of bromine are known to exist. Further, the union of bromine with water, which we may picture thus , so weakens the bond between the bromine atoms that in dilute aqueous solution the complex separates largely into hydrobromic and hypobromous acids.

In support of the hypothesis that the concentration of the hydrate increases as the temperature is lowered, the following facts may be cited. (*a*) The critical temperature of decomposition for the hydrate of bromine in open vessels is 6.8°.[7] (*b*) I found that the color of an 0.057 N aqueous bromine solution decreased about 40% on cooling from 25 to 3°. On reheating to 25° the color returned to its original value. (*c*) The "Budde Effect" in bromine vapor is probably due to a photo-active bromine hydrate of composition Br_2H_2O[8] and this effect increases as the temperature is lowered, indicating that the equilibrium $Br_2 + H_2O \rightleftharpoons Br_2H_2O$ shifts to the right.[9]

This phenomenal increase in the rate of bromination of ethylene in dry carbon tetrachloride with decrease in temperature is of considerable interest.[10] It shows how minute traces of intermediate compounds may affect the temperature coefficient of a reaction. It is conceivable that in other cases they might cause an abnormal increase in the reaction rate with rise of temperature.

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[7] Mellor, "Treatise on Inorganic and Theoretical Chemistry," Longmans and Co., New York, **1922**, Vol. II, p. 71.

[8] Lewis and Rideal, *J. Chem. Soc.*, **1926**, 583.

[9] Lewis and Rideal, *ibid.*, **1926**, 596.

[10] Bodenstein, "Photochemical Reactions in Liquids and Gases," The Faraday Society, **1925**, p. 533, with great perspicacity has thus expressed himself regarding the "purely chemical dark reactions" which very often follow primary photochemical changes—"It need not appear strange that the velocity should decrease with a rise of temperature for the velocity of a reaction which 'uselessly' consumes the intermediate products may easily increase far more rapidly with the temperature than that of the reaction leading to the desired ultimate product."

The reactions I have described are, however, not initiated by visible light, since they take place in complete darkness.

6. The Olefins Brominate (Dark Reaction) at Very Different Rates in Dry Carbon Tetrachloride.—It has been shown that rates of dark bromination of ethylene in carbon tetrachloride can vary (one hundredfold, at least) with changes in the minute moisture content of the solution. It was further found that the rates of bromination of propene and several higher olefins are also greatly dependent upon the dryness of the solutions. Quantitative data on the relation between the rates and the moisture content for the separate olefines have not yet been obtained.[11]

Qualitatively it was found that, just as for ethylene, the bromination of propene goes considerably faster at 0° than at 25°. On the other hand, temperature changes seem to have little effect on the rates of bromination of trimethylethene or di-*iso*butene in dry carbon tetrachloride. Note the following values for *di-iso*butene: at 25°, $K = 23$; at 3°, $K = 21$.

To be consistent with the hypothesis given above for ethylene, it must be considered that the main reaction here is not through a hydrate of bromine but either with the bromine itself or with an intermediate compound between the bromine and the solvent, or between the bromine and some impurity. The di-*iso*butene was only moderately pure and air was always present. Further, in the bromination of both trimethylethene and di-*iso*butene, large quantities of hydrogen bromide are given off. Although such foreign substances do not appreciably affect the rate of bromination of ethylene, they may influence that of a higher olefin.

Accordingly, it is not possible to give figures which will represent the relative rates of bromination of the olefins in carbon tetrachloride because the ratios change with the temperature and probably, as my results indicate, with the moisture content. Nevertheless, the data show tremendous differences in the rates at which the olefins are brominated. Thus on intensive drying the bromination of ethylene required days, that of propene, hours, but that of trimethylethene could not be extended beyond a few minutes. The lowest values obtained so far for the different olefins are as follows.

7. Light Increases the Rates of Bromination of the Olefins but Decreases the Relative Differences between Them.—In the following experiments the rates of dark bromination of the olefins in dry carbon

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[11] Reliable data on this subject may help to clear up the discordances found by other investigators of the rates of bromination of unsaturated compounds in carbon tetrachloride and other solvents. Thus Sudborough and Thomas, *J. Chem. Soc.*, **97**, 715, 2450 (1910), found great variations (even 12-fold) in the reaction coefficient for the bromination of olefinic acids in this solvent, although their materials were purified with great care. They state that, "The only reason for this that we can offer is that a trace of some impurity has a considerable effect on the velocity of the reaction," and they also showed that the rate of bromination of crotonic acid is dependent on the dryness of the carbon tetrachloride. See also Herz and Mylius, *Ber.*, **39**, 3817 (1906); Hofmann and Kirmreuther, *Ber.*, **42**, 4481 (1909).

tetrachloride were first found by the color comparison method and then before the reaction was complete the vessel A, Fig. 2, was exposed to radiation from a 200-watt, 120-volt, clear "Higrade" tungsten lamp suspended end on with the filament 20 cm. from the reaction tube. The reaction rate was again followed by color comparison.

The following explanation is suggested for the striking fact that light greatly decreases the relative differences in the bromination rates of the olefins. Assume that an olefin molecule and a molecule of the brominating agent must together have a minimum of activity before interaction can take place. A highly active molecule of either can react with a relatively inactive one of the other. When now a large number of brominating molecules are highly activated by the absorption of light quanta, interaction is extended to olefin molecules which escaped in the dark because of the lowness of their activity. Further, since degrees of activity must be distributed among molecules somewhat like speeds according to the kinetic theory of matter, it is evident that the proportional number of additional molecules thus caught over unit time in the reaction net will be greatest for the olefin having the smallest number reacting in the dark. Thus in Table V, ethylene gave the least increase but the greatest proportional increase (200) for K under the influence of light.

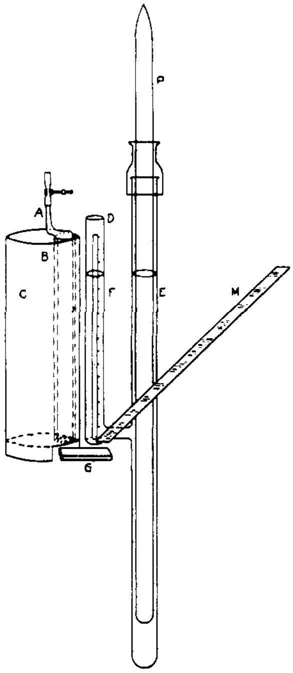

Fig. 2.—Diagram of apparatus used in the color comparison method. A—Reaction chamber, a 50-cc. tube with clear glass ends. B—Brass tube open at both ends and soldered through bottom of bath C. D—Nessler tube containing color standard. F—Scale lettered backwards. M—Mirror for reading scale from above. E—Auxiliary tube with plunger P for rapidly raising or lowering the liquid level in D. G—White surface to reflect light through reaction tube.

From similar reasoning, water or other catalysts which increase the activity of the brominating agent should decrease the relative differences in the rates of reaction; and if an agent is found which increases the rates and also the relative differences in the rates of reaction of the olefins, we may feel sure that it is operating in some way through the olefin molecules and not through the other reactants.

8. Studies on the Reactions of Olefins with Halogens May Clear Up Many of the Questions Unanswered by Researches on the Photochemical Reactions of Halogens with Hydrogen.—There are many analogies between the reactions of halogens with hydrogen and with olefins. The following peculiarities of the latter type offer addi-

TABLE IV

LOWEST VALUES OBTAINED AT 25° FOR THE DARK BROMINATION RATES OF VARIOUS OLEFINS IN CARBON TETRACHLORIDE DRIED BY PHOSPHORUS PENTOXIDE. THE RELATIVE VALUES ARE ONLY QUALITATIVE

Olefin	*K*	Olefin	*K*
Ethylene	0.006[a]	2 Butene *Iso*butene	60.0
Propene	0.2	Trimethylethene	250.0
1-Butene	2.0	Di-*iso*butene	20.0

[a] The fact that the ethylene brominates at the slowest rate does not agree with the statement of Plotnikov, "Lehrbuch der Photochemie," **1920**, 245, that ethylene reacts with bromine, the fastest of all the olefinic compounds. Suida and Wesley, *Z. anal. Chem.*, **64**, 147 (1924), state that ethylene reacts the slowest of the olefins to bromine water but do not give the basis for this conclusion.

TABLE V

A COMPARISON OF THE LIGHT AND DARK BROMINATIONS OF OLEFINS IN DRY CARBON TETRACHLORIDE

	K, Dark reaction		*K*, Total light reaction	
Olefin	Values	Ratios	Values	Ratios
Ethylene	0.01	1	2	1
Propene	0.2	20	2.5	1.3
Di-*iso*butene	20.0	2000	40.0	20.0

tional opportunities for learning about the mechanisms involved.[12] (*a*) The reactions are not only photosensitive but proceed in the dark. (*b*) The nature of the unsaturated hydrocarbons can be modified by the radicals attached thereto and it is therefore much easier with olefins than with hydrogen to find what influence the substance being halogenated has on the reaction. (*c*) The effect of the solvent can be studied. Preliminary experiments showed that the rate of bromination of ethylene is much higher in acetic acid than in carbon tetrachloride, the lowest value obtained for K in the former solvent being 15 compared to 0.006 in the latter when both had been distilled from phosphorus pentoxide.

9. The Methods Used for Following the Course of the Brominations Were (A) Color Comparison with a Standard Bromine Solution, (B) Titration of the Bromine. Care Must Be Taken in the Preservation of the Dried Bromine–Carbon Tetrachloride Solutions.—A. In the color comparison method, the bromine concentration was measured by the height of a standard bromine solution necessary to give the same color intensity. The following measurements will show the degree of accuracy in these measurements.

Actual height of solution..................	100	67.4	60.6	29.6	26.2
Height estimated from color comparison....	100	66.8	54.8	29.9	23.7

The method has the disadvantage that some light must always be sent through the solution during the measurements but the low illumination

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[12] Plotnikov, ref. 3, has stressed the importance of research in this field.

required seems to have little effect on the reaction. It has the great advantages that no samples need be withdrawn from the sealed up reaction vessel and that as many measurements as desired can be made quickly.

Except for preliminary experiments, the reactions were carried out in closed tubes of the type shown in A, Fig. 2, which permitted clear vision through the glass surfaces at the top and bottom. Fifty cc. of the solution of bromine in carbon tetrachloride was placed in the tube through the side neck and then the olefin was added. If a liquid, it was measured from a pipet. If a gas, it was drawn into the partially evacuated chamber from a mercury buret.

There was a vapor space of about 15 cc. in the reaction tubes, but from solubility experiments[13] it was calculated that 93% of the ethylene and 99% of the propene were dissolved by the carbon tetrachloride. Accordingly, no correction was made for the undissolved part.

B. Titration.—In order to follow by titration the course of the bromination of an olefin in carbon tetrachloride, measured samples were removed at definite intervals and shaken with a little water saturated with potassium iodide. The precipitated iodine was then titrated. The bromine reacts with the iodide before the water can appreciably speed up the bromination of the olefin. The titration should be carried out at once as the brominated olefin products can slowly liberate iodine from potassium iodide.[14]

Some of the difficulties encountered in making these measurements account for the discrepancies shown in the results. At 25° carbon tetrachloride dissolves about 0.012% of water by weight, corresponding to a 0.01 *M* solution. Yet, apparently, it is the variations in this minute content which cause the differences in the dark bromination of ethylene in this solvent at 25°.

It is hard to dry carbon tetrachloride thoroughly but when once dry it does not readily take up moisture again. If a drop of water is added without shaking to a solution of equimolecular quantities of bromine and ethylene in dry carbon tetrachloride, the color may persist for a long time, although in solutions saturated with water it will disappear in a few minutes.

Naturally, moisture diffuses but slowly into dry carbon tetrachloride and when its solutions of bromine and ethylene are shaken with water, the greater part of the reaction takes place in the water phase. If potassium iodide is present in the latter, then apparently the bromine as it diffuses from the carbon tetrachloride into the water reacts much faster with the

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[13] Carbon tetrachloride was saturated with the gaseous olefin by bubbling and the concentration of the solution determined by bromine titration. The following values were found for the solubility, X, expressed as the concn. of the dissolved olefin divided by the concentration of the gaseous olefin at equilibrium: ethylene at 25°, $X = 4.3$; ethylene at 0°, $X = 5.1$; propene at 25°, $X = 32$ (approx.).

[14] See Sudborough and Thomas, *J. Chem. Soc.*, **97**, 717 (1910).

iodide than with the olefin. These facts are illustrated by the following measurements.

Method of treatment of the bromine-carbon tetrachloride solution (10 cc. samples)	Concn. of bromine as shown by titration of the iodine
1. Original solution shaken with potassium iodide solution	0.0558 *M*
Solutions containing ethylene	
2. After two minutes the sample was poured into potassium iodide solution and shaken	.0538 *M*
3. Sample was poured into water, shaken and allowed to stand for ten minutes. Then potassium iodide solution was added	.0165 *M*
4. One drop of water was added and the sample allowed to stand for ten minutes. Then it was poured into potassium iodide solution and shaken.	.0433 *M*

It is now evident that concordant results for the bromination of olefins in carbon tetrachloride cannot be expected unless the solutions have very accurately the same moisture content, and a large number of my results have had to be rejected on this account. Great care must be taken to preserve the dried solutions from atmospheric moisture. All samples removed must be replaced by dried air since there may be enough water vapor in air at 25° to form a solution over 10% saturated in an equal volume of carbon tetrachloride. As already shown, this may increase the bromination rate many times. Finally, bromine-carbon tetrachloride solutions decompose cork and rubber connections and must be preserved in all glass containers.

Materials.—Commercial refined ethylene was used. It dissolved at a slow, steady rate in 86% sulfuric acid (about 0.13% per pass into an Orsat pipet). This showed the absence of propene and higher olefins which are readily absorbed by this acid. Before use it was passed through two bubblers of concentrated sulfuric acid.

Propene was prepared by dehydrating C. P. *iso*propanol. The alcohol was kept well cooled and well stirred while an equal weight of phosphorus pentoxide was slowly added. On heating the product, propene was smoothly evolved. It was washed with dilute alkali and with water.

*Iso*butene was made by heating tertiary butanol (m. p. 15° and miscible without any cloud in water) with about one-third its weight of hydrated oxalic acid. The reaction proceeded smoothly at 87–100°, giving an almost quantitative yield of olefin.

1-Butene was prepared by warming normal butyl iodide (Eastman Kodak Co.) with saturated alcoholic potash containing about three times the quantity of hydroxide theoretically necessary. The product was washed well with water, liquefied and distilled. Coffin and Maass[15] have shown that this method yields a very pure product. It is, however, rather expensive.

Impure 1-butene was made by dehydrating normal butanol, b. p. 117.4–117.9°, at 340–360° over an active alumina catalyst which had never been heated above 400°; 80% of the alcohol passed was dehydrated and over 90% of this appeared as olefins. It has been reported that this method yields a mixture of 1-butene and 2-butene in

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[15] Coffin and Maass, THIS JOURNAL, **50**, 1429 (1928).

the approximate proportions of 70 to 30.[16] I found that about 5% of the alcohol appeared as normal butyl ether.

When this olefin mixture was dried by rapid passage through phosphorus pentoxide and brominated in dry carbon tetrachloride, its bromination curve showed a very sharp break. About 35% (presumably 2-butene) reacted very rapidly and the remaining 65% slowly. This would indicate that the mixture contained about 35% of 2-butene and 65% of 1-butene.

The mixture was washed with 50% sulfuric acid and with 10% caustic potash, liquefied and distilled from sodium. A column was used provided with an evacuated and silvered jacket and with a still-head cooled by chilled air to −12°. The fraction boiling at −5.5 to −4.8°, which was 70% of the total, was collected and stored in a steel cylinder. Its dry bromination curve indicated that it contained 13% of 2-butene and 87% of 1-butene.

The main interest of these experiments lies in the possibilities they show of making pure 1-butene by acid treatment and fractionation of the butene mixture obtained by dehydrating normal butanol over alumina.

2-Butene was prepared by dehydrating 2-butanol manufactured from petroleum gases. Harries[17] states that dehydration with phosphorus pentoxide gives a very pure product but obtained a yield of only 64%. It was found that excellent yields, over 90%, of olefin could be reached by heating the alcohol with about 1.5 times its volume of 86% phosphoric acid at 95 to 120°. The product was liquefied and distilled from calcium chloride in the column already described. The fraction boiling from 1.5–1.7° was collected. Its bromination curve showed that 84% brominated rapidly (2-butene) and the remaining 16% slowly.

A mixture of the product with 50% by volume of propene gave a bromination curve in dry carbon tetrachloride which indicated that approximately 50% of the material, evidently propene, had brominated at a much slower rate than the residue.

These preliminary results with mixtures of the butenes and propene show clearly the possibility of measuring the relative rates of bromination for two olefins under identical conditions by tests on known mixtures of the pure substances.

The trimethylethene obtained through the kindness of Dr. R. Reuter had been made by dehydrating tertiary amyl alcohol with 46% sulfuric acid; b. p. 38.4–38.5°.

The di-*iso*butene was prepared by distilling tertiary butanol with 50% sulfuric acid and fractionating the product; b. p. 101–103°.

The bromine before use was distilled from potassium bromide.

Carbon tetrachloride guaranteed to be free from sulfur compounds was used to make up the bromine solutions, which were then dried as already described.

Summary

1. The dark reaction of ethylene with bromine in dry carbon tetrachloride solution is very slow.

2. The rate of the dark reaction of ethylene with bromine in carbon tetrachloride varies greatly with the quantity of moisture in the solution.

3. Bright light enormously increases the rate of bromination of ethylene in carbon tetrachloride.

4. The rate of the dark bromination of ethylene in dry carbon tetrachloride increases progressively as the temperature is lowered from 25 to 0°.

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[16] Lépingle, *Bull. soc. chim.*, [4] **39**, 741, 864 (1926); *Bull. Amer. Petroleum Institute*, **8**, No. 54, 8 (1927).

[17] Harries, *Ann.*, **383**, 181 (1911).

5. It is suggested that the dark bromination of ethylene in carbon tetrachloride proceeds mainly through a bromine hydrate and that the concentration of this hydrate increases as the temperature is lowered from 25 to 0°.

6. The olefins brominate at very different rates in carbon tetrachloride.

7. Light increases the rates of bromination of the olefins but decreases the relative differences between them.

8. Studies in the reactions of olefins with halogens may clear up many of the questions unanswered by researches on the photochemical reactions of halogens with hydrogen.

9. The methods used for following the courses of the bromination were (A) color comparison with a standard bromine solution, (B) titration of the bromine.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 35]

THE RELATIVE RATES OF ABSORPTION OF THE GASEOUS BUTENES INTO SULFURIC ACID[1]

BY HAROLD S. DAVIS[2]

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In 1909 Michael and Brunel[3] published data on the proportions of the butenes which were absorbed by sulfuric acid in Hempel pipets after definite periods of shaking. From inspection of the results they gave certain approximate figures for the relative rates of absorption of the three isomers.

Calculations from the data of Michael and Brunel show that in each experiment the rate of solution of the butene was approximately proportional to the quantity undissolved. The following table gives the values of K calculated for the separate experiments where $K = 1/t \ln 1/(1-x)$, t = minutes the pipet was shaken, and x = fraction of olefin dissolved at time t.

The following conclusions can be drawn regarding the rates of solution of olefin gases when shaken with sulfuric acid in Hempel pipets.

1. A pure butene was absorbed at a rate approximately proportioned to the gas undissolved (see Experiments 1, 2, 5, 6 and 7. The high initial rate of solution in 5 may perhaps be attributed to traces of *iso*butene).

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