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Walter B. James Laboratóry for Biophysics, The Biological Laboratory, Cold Spring Harbor, L. I., N. Y.

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Gas free solutions of carbon monoxide, alcohols, aldehydes, ketones and acids were irradiated in the concentration range 10 μM to 1 M, between pH = 1 to 13 and the reactions studied principally by gas analysis and potentiometric acid analysis. One organic component systems and, to a more limited extent, two organic component systems were investigated. To obtain significant results, foreign organic matter must be strictly excluded from the low concentration solutions and the methods used to accomplish this are described. Organic impurities in the water can be detected by irradiating the water with x-rays and measuring the evolved hydrogen and carbon dioxide. The reactions cannot be briefly abstracted, but oxidation and condensation reactions with the evolvement of gaseous hydrogen are important in the effect of the rays. Carbon dioxide was produced from certain acids, particularly strongly from those having an oxygen containing group in the α-position. No liberation of carbon monoxide, hydrocarbons or oxygen was found. The effect of the rays on all the compounds studied depends on the hydrogen ion concentration, this factor affecting reaction rates as well as the nature of the reactions. The relation of reaction rate to pH can in some cases be represented by

$$[P] = A(1 + 10^{-p\mathrm{H}+\alpha}/1 + 10^{-p\mathrm{H}+\alpha}).$$

The rates of the reactions are in many cases independent of concentration, at high concentrations, but generally the rates decrease at low concentrations. The reason for this decrease may be the deactivation of the activated water, although this interpretation would, because of the form of the reaction product concentration curves, lead to the conclusion that the deactivation is approximately monomolecular (rather than bimolecular) during its initial stage. The same conclusion is indicated since the reaction rates are independent of x-ray intensity down to the lowest concentrations used. The x-ray reactions show some similarity to, but they are generally more complex than, the reactions produced by water activated with light inside the absorption band at 1900A. The irradiation of formic acid in the presence of oxygen at pH = 3, results in a smaller decomposition of the formic acid than is produced in the absence of oxygen and a higher production of hydrogen peroxide than is obtained when oxygen is irradiated alone. This increased hydrogen peroxide production can be accounted for as resulting from the reaction of the oxygen with the nascent hydrogen liberated in the organic reaction.

T HE chemical effects produced by irradiating dilute solutions with x-rays have been the subject of considerable study.[1-6] To explain the

results it was found necessary to assume that the rays produce active derivatives of the water

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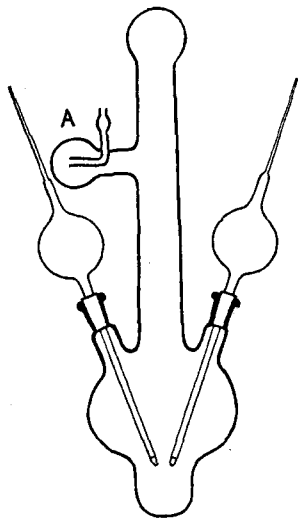
FIG. 1. Evacuation chamber with reaction cells.

molecule which react with the dissolved substances.[4] No decomposition was observed when water was irradiated under the same conditions.[1,2,7] The reactions show a certain similarity to, but they are more complex than, those produced when the water is activated with ultraviolet light inside the absorption band at 1900A.[8] This band is continuous and it is generally connected with the transition $H_2O \rightarrow H + OH$. Nevertheless, as in the case of x-rays, no decomposition was observed when water was irradiated with ultraviolet light in this region of wave-length.[7,8]

The present paper deals with the effect of x-rays on solutions of organic materials. These include carbon monoxide and alcohols, aldehydes, ketones and acids of the aliphatic series. The reactions were studied chiefly by a determination of the gases produced. Electrometric acid analysis was a useful method of inquiry in a number of the reactions.

The greater part of the work is concerned with reactions in solutions containing one organic component. The reactions in systems containing two organic components were studied to a more limited extent and finally, a short account is given of the reactions in the presence of oxygen. Practical interest in studies of the chemical activity of x-rays lies in the effects of the rays on life processes. Since the water content of the biological cell is about 75 percent, it is reasonable to assume that the reactions produced through the activation of the water play an important part in these effects.

EXPERIMENTAL PROCEDURE

The irradiations were carried out with a water-cooled tungsten tube capable of operation at 110 kv and 50 ma. The x-ray intensity produced under these conditions was about 2000 r per minute at a distance of 6 cm, and the effective wave-length as determined by the absorption in aluminum was $\lambda_{eff} = 0.35A$. The x-ray dosage was determined by the irradiation of 1 millimolar formic acid in sulfuric acid at pH of 3.0, using the earlier result $(3, f)$ that 3.2×10^{-6} M H_2 and 3.2×10^{-6} M CO_2 are produced per 1000 r and per 1000 cc.[9]

The solutions were irradiated in flat Pyrex cells 5 cm in diameter and 1 cm deep (see Fig. 1) designed to fit the Van Slyke apparatus into which the contents of the cells were transferred for the purpose of gas analysis. Four cells were usually irradiated at one time, placed at different distances from the x-ray tube so as to give a considerable variation in x-ray intensity.

For the purpose of removing the air from the solutions and introducing other gases, the "evacuation chamber" shown in Fig. 1 is used. It is made of Pyrex and carries six irradiation cells fitted through ground joints. Connection to a water pump and to the gas reservoirs is made at A. The water is transferred directly to this chamber from the purification system described below, the chemicals are added, connection made to the vacuum and the air is removed by simul-

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[7] In these experiments small amounts of hydrogen and carbon dioxide were obtained which were ascribed to organic impurities in the water. Recently we were able to produce water so pure that no carbon dioxide was obtained. However, we still obtained a trace of hydrogen (1 or 2 μM H_2 per 1000 cc). We could not be sure whether oxygen or hydrogen peroxide were also produced. The possibility remains that a slight decomposition of the water occurs during the initial period of irradiation. (These experiments were carried out in closed reaction vessels.) This is of great interest since there can hardly be any doubt that the water molecule dissociates under the influence of these radiations. The mechanism whereby the recombination of the dissociation products is accomplished is however, so far, a matter of conjecture.

[8] H. Fricke and E. J. Hart, J. Chem. Phys. 4, 418 (1936).

[9] The x-ray intensity in r/sec. is defined as the ionization current in electrostatic units produced in 1 cc of air at 76 cm Hg and at 0°C. The x-ray dosage is the average intensity in the irradiated solution, multiplied by the time of irradiation in seconds.

taneous heating and shaking of the solution. At the same time, the evacuation chamber is tilted from side to side to allow removal of the air from the irradiation cells. With gas free solutions the liquid is forced into the cells by slightly increasing the pressure (with air) on the surface of the liquid. Solutions prepared in this manner yield less than 1 micromole of dissolved gases per 1000 cc of solution. When a gas is present, the same method of filling the cells may be used if the pressure is low. At high pressure, the tips of the capillaries of the irradiation cells are broken, the solution forced through, and the tips sealed off.

The water used for preparing the solutions was purified as follows. Water from a Barnstead still was refluxed for extended periods successively in alkali permanganate and in acid dichromate mixtures. The vapor mixed with washed oxygen was then passed through a quartz tube heated to 900°C. This was condensed and redistilled into the evacuation chamber. With this method of purification, the organic impurities in the water are effectively decreased but they are not completely removed. The presence of organic impurities can be shown since they are decomposed by irradiation, with the production of hydrogen and carbon dioxide. In Fig. 2 are shown the results of such a test on (a) water from a Barnstead still and (b) water purified by the method described. The water can be further purified by irradiating it after it has been transferred to the evacuation chamber. Water thus purified gave on irradiation no carbon dioxide but it did give a small amount of hydrogen, of the order of 1 or 2 micromoles per liter (Fig. 2c).

Before irradiating very dilute solutions we usually heated the cells and the evacuation chamber to near the softening point of Pyrex, in order to remove all traces of organic materials. After using the cells for concentrated solutions this heating is especially necessary, since chemical methods apparently never completely remove the organic materials from the walls of the vessels. When the vessels are not heated in this manner an increased amount of hydrogen and carbon dioxide may be found on irradiating otherwise pure water. This may be due in part to traces of organic materials in the water, released from the walls of the evacuation chamber and the cells, and in part to a direct action of

the rays on organic materials adsorbed on the walls of the irradiation cells.

The gases produced by the irradiation were analyzed by means of a Van Slyke apparatus. The entire contents of the irradiation cell (usually about 20 cc) were transferred to the 50 cc extraction chamber and the analysis performed in the usual manner.[10] Potassium permanganate was used to liberate oxygen from hydrogen peroxide, sodium hyposulphite for the absorption of oxygen, sodium hydroxide for the absorption of carbon dioxide and ammoniacal cuprous chloride for the absorption of carbon monoxide. The composition of the residual gas could be determined by a combustion analysis.

The change in acid content resulting from irradiation was determined by potentiometric titration. A glass electrode was used for recording the pH values.

The hydrogen ion concentration is a factor in all the reactions. Different pH values were obtained as follows: $pH=1-4$, H_2SO_4 or H_3PO_4; $pH=5.5-8$, H_3PO_4+NaOH; $pH=8-10$, H_3BO_3+NaOH; $pH=10-13$, NaOH, KOH or Ca(OH)$_2$. The phosphate and borate buffers were usually used in 0.5 and 5.0 millimolar concentrations. The sulfate, sodium, potassium and calcium ions were not found to exert any influence on the reactions. The borate and phosphate ions were not always indifferent.
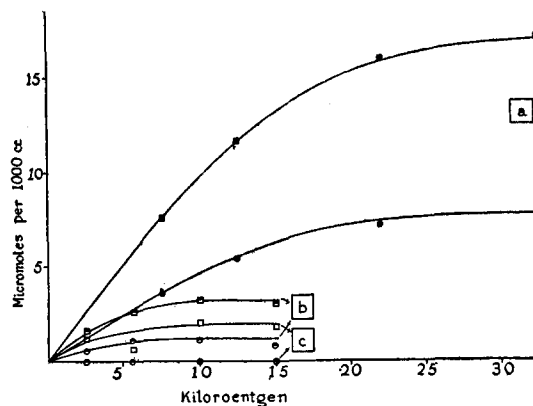

FIG. 2. Decomposition of organic impurities in water by irradiation with x-rays. Square, H$_2$; circle, CO$_2$. (a) Water from tin still. (b) Water purified chemically, as described in the text. (c) Water purified by irradiation with x-rays.

[10] J. P. Peters and D. D. Van Slyke, *Quantitative Clinical Chemistry*, II (1932).

Experimental Results

A. One organic component

Gas free solutions of the organic chemicals were irradiated at different concentrations and at different pH values. The rate of production of the reaction products is given in micromoles per 1000 cc per 1000 r, the values refer to the initial reactions when nothing else is said. The reactions were studied at x-ray intensities between 500 and 2000 r/min. and within this range the effects were found independent of the intensity when the intensity multiplied by the time of irradiation was kept constant. It should be noted, though, that the measurements are rather inaccurate at the very low concentrations at which the question of a dependence of rates on intensity is of particular interest.

If the absorbed x-ray energy is kept constant, the chemical effect of the rays is probably independent of wave-length, at least over a wide range.[3a, b] Since the ratio of the coefficients of absorption of water and air is slightly dependent on wave-length, the chemical effects would be expected to show a slight wave-length dependence when the rays are measured in terms of r. The wave-length dependence introduced by this factor should be negligible though for wavelengths longer than about 0.30A. The average wave-length used in the present work was 0.35A.

The solutions were irradiated at room temperature. The influence of temperature on the

Fig. 3. Irradiation of carbon monoxide in sulfuric acid at pH = 3.5. (a) 220 μM CO. (b) 22 μM CO. Triangle, CO; square, H$_2$; circle, CO$_2$; diamond, HCHO. The filled square and circle represent hydrogen and carbon dioxide produced by the irradiation of the sulfuric acid without carbon monoxide.

reactions has not yet been determined, but temperature fluctuations of several degrees were insufficient to affect the reproducibility of the results to any noticeable extent. (Compare also reference 3d.)

The change produced in the solutions by irradiation was usually so small that the reaction product-dosage curves remained linear over the whole range of dosages used. A few examples are given of highly dilute solutions irradiated to completion. The end point reached was a complete transformation of the organic compounds to hydrogen and carbon dioxide.

Carbon monoxide

The carbon monoxide was prepared from the reaction of warm sulfuric acid with formic acid. The reaction-dosage curves for solutions of 220 and 22 μM CO in sulfuric acid at pH = 3.5 are shown in Fig. 3. Both hydrogen and carbon dioxide were produced but there is less hydrogen than carbon dioxide and the difference between them equals the excess of carbon monoxide consumption over carbon dioxide production. It is concluded that non-gaseous reaction products of the over-all composition of CH$_2$O are present. The reaction mechanism can be represented by:

$$CO + H_2O(+h\nu) \rightarrow CO_2 + H_2^* \qquad (1)$$
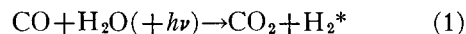
with part of the hydrogen reacting according to:

$$CO + H_2^* \rightarrow CH_2O. \qquad (2)$$
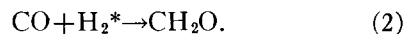
The irradiated solutions were tested for formaldehyde by Hehner's method.[11] The amounts could be estimated to an accuracy of 10 micromoles per liter. Formaldehyde was present according to this test (Fig. 3), but the amount was 10 to 20 percent only of the reaction products left unaccounted for by the gases.

The effect of the rays appears to be independent of the concentration of carbon monoxide, in the range of 10 to 800 μM CO. However, the accuracy is only fair at the low concentrations (Fig. 3). The initial reaction rates are 3.9 μM CO, 2.45 μM CO$_2$, 1.0 μM H$_2$, and 0.3 μM HCHO (pH = 3.5).[12]
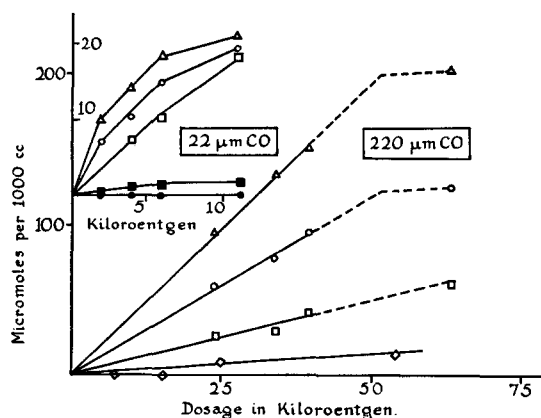
[11] C. C. Fulton, J. Ind. and Eng. Chem. (Anal. Ed.) **3**, 199 (1931).
[12] All reaction rates are given in micromoles per 1000 cc and per 1000 r, as noted above.
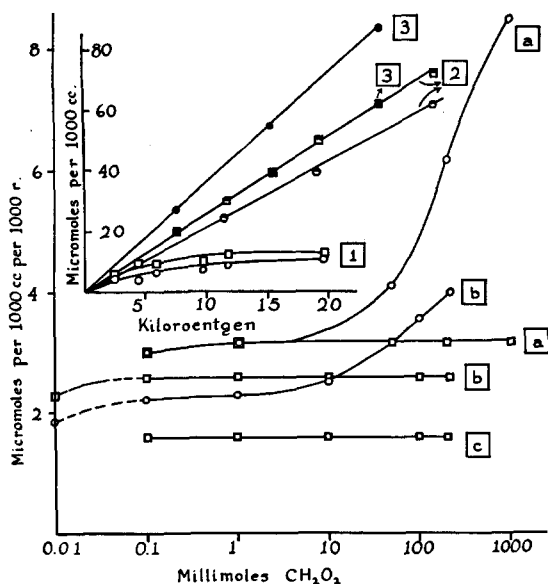
FIG. 4. Reaction concentration curves for formic acid. (a) $pH = 2.0$. (b) $pH = 3.8$. (c) $pH = 7.2$. Square, H_2; circle, CO_2. Inserted: Reaction dosage curves at $pH = 3.8$. (1) 10 μM CH_2O_2 (square, H_2; circle, CO_2). (2) 100 μM CH_2O_2 (upper half-filled square, H_2; upper half-filled circle, CO_2). (3) 100 mM CH_2O_2 (filled square, H_2; filled circle, CO_2).

A few experiments were carried out to determine the effect of the pH in the reaction. There is no great change in the range of $pH = 1$ to 7. Possibly the reaction rates increase with decreasing pH but the measurements were not accurate enough to make sure of the form of the relationship. In alkaline solution the character of the reaction changes. The hydrogen and carbon dioxide production decreases while the carbon monoxide consumption greatly increases. Apparently the principal reaction is the combination of the carbon monoxide with water to produce formic acid:

$$CO + H_2O \rightarrow HCOOH. \qquad (3)$$

Acids

Formic acid.—For pH values below $pH = 3$ and for concentrations of formic acid below 5 mM CH_2O_2, hydrogen and carbon dioxide are produced in equal amounts, indicating a decomposition of the formic acid according to

$$HCOOH \rightarrow H_2 + CO_2. \qquad (4)$$
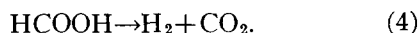
When the pH is increased above $pH = 3$, the reaction changes (Figs. 4b, c and Fig. 5a). The
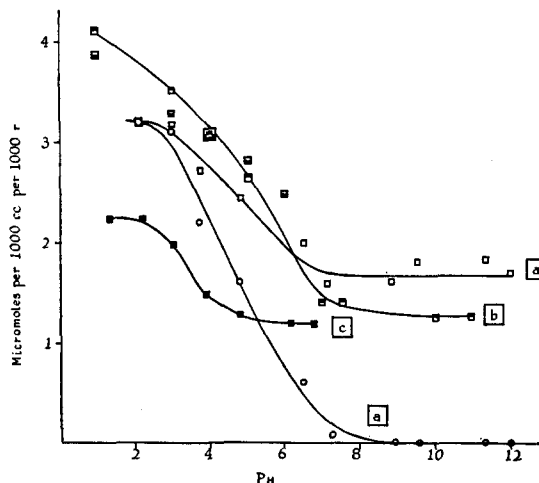

FIG. 5. Reaction pH curves for (a) 1.0 mM formic acid (square, H_2; circle CO_2); (b) 10 mM formaldehyde (upper half-filled square, H_2); (c) 10 mM butyric acid (filled square, H_2). A few observations on 100 mM methyl alcohol are also included (lower half-filled square, H_2).

production of both hydrogen and carbon dioxide decreases. The carbon dioxide decreases more rapidly than the hydrogen and for pH 7 only hydrogen is obtained. The simplest explanation would be that oxalic acid is produced, at these high pH values:

$$2\,HCOOH \rightarrow (COOH)_2 + H_2. \qquad (5)$$

The production of hydrogen is independent of the concentration of formic acid, between 1 mM and 1 M CH_2O_2, at all values of pH. The carbon dioxide remains constant over the lower portion of this range of concentrations, while a rapid rise is recorded at the highest concentrations, at small pH values.

These results suggest that reactions (4) and/or (5) are produced at a constant rate between 1 mM and 1 M HCOOH, while an additional reaction liberating carbon dioxide occurs in acid solution, at high concentrations. This reaction may be:

$$2\,HCOOH \rightarrow HCH : O + CO_2 + H_2O. \qquad (6)$$
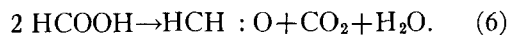
The rate of production of hydrogen varies with pH according to:

$$[H_2] = 1.6(1 + (10^{5.0-pH})/(1 + 10^{5.0-pH}))\mu M\ H_2.$$

The effect of the rays was studied in the range of concentrations 100 μM to 1 M HCOOH, at all the different pH values. In acid solution both
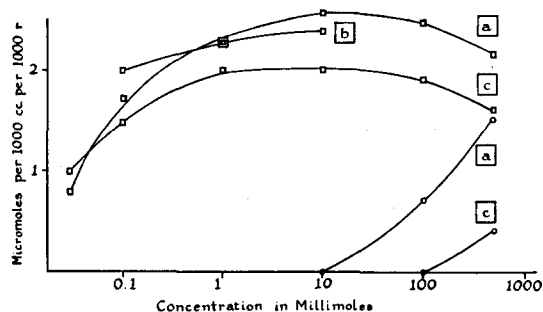
FIG. 6. Reaction concentration curves for (a) acetic acid; (b) propionic acid; (c) butyric acid. Square, H_2; circle, CO_2; $pH = 3$.

the hydrogen and the carbon dioxide production appeared to decrease slightly at the lowest concentration, but the change was not greater than the experimental error. Measurements were thereafter carried out on 10 μM HCOOH at $pH = 3$; the reaction-dosage curves are shown in Fig. 4. At the time these measurements were made the water was not as free from organic impurities as it was later possible to make it and it will be seen that all the hydrogen and carbon dioxide is not derived from the formic acid. The measurements do not make it completely certain that there is a decrease in reaction rate even at this low concentration of formic acid; the change, in any case, cannot be great.

Acetic acid.—The gas analytical data for the irradiation of solutions of acetic acid in sulphuric acid at $pH = 3$ are shown in Fig. 6a. At the lower concentrations, hydrogen is the only gas obtained, while at high concentrations carbon dioxide is also produced.

The production of either glycollic acid or succinic acid would be the simplest reactions at the lower concentrations:

$$CH_3COOH + H_2O \rightarrow CH_2OHCOOH + H_2, \quad (7)$$

$$2CH_3COOH \rightarrow (CH_2COOH)_2 + H_2. \quad (8)$$

To decide between these reactions, an unbuffered solution of 500 μM CH_3COOH was irradiated and the change in pH determined. The data are given in Table I. For comparison, pH measurements were made on mixtures of acetic acid with (a) glycollic acid and (b) succinic acid, as shown in the table. According to these measurements, the reaction could be the production of succinic acid.

Propionic acid.—Irradiations of propionic acid in concentrations between 0.1 and 10.0 mM CH_3CH_2COOH at $pH = 3$ gave hydrogen as the only gas. The quantities are given in Fig. 6b.

Butyric acid.—This acid was subjected to a more extensive study. The results at $pH = 3$ are similar to those for acetic acid. Hydrogen is the only gas produced at low concentrations, while at high concentrations carbon dioxide is also obtained. The rate of production of these gases as a function of concentration is represented in Fig. 6c. The relation of the hydrogen production to the hydrogen ion concentration for a solution of 10 mM C_3H_7COOH is shown in Fig. 5c. The reaction rate is represented by:

$$[H_2] = 1.2(1 + 10^{3.4-pH}/(1 + 10^{3.4-pH}))\mu M \ H_2.$$

The middle point of this curve is at $pH = 3.4$, which is 1.6 pH units to the acid side as compared with the corresponding curve for formic acid.

The irradiation of solutions of 1.0 and 10.0 mM isobutyric acid at $pH = 3$ gave no carbon dioxide. The total gas calculated as hydrogen was produced at the rates of 2.2 μM and 2.7 μM for the two concentrations, respectively.

Valeric and caproic acids.—A few preliminary irradiations of solutions of 1.0 mM concentrations at $pH = 3$ gave no carbon dioxide, while the total gas calculated as hydrogen was produced in about the same quantity as was obtained for butyric acid.

Oxalic acid.—Figure 7 shows the gas analytical data for the irradiation of different concentrations of oxalic acid at $pH = 3$. Both hydrogen

TABLE I.

			pH		
DOSAGE (kr)	HYDROGEN PRODUCED $\mu M/1000$ cc [x]	CONTROL (500 μM CH_3COOH)	IRRADIATED SOLUTION	$(500-x)$ μM CH_3COOH $+(x)$ μM $CH_2OHCOOH$	$(500-x)$ μM CH_3COOH $+(x/2)$ μM $(CH_2COOH)_2$
23.8	39.8	4.09	4.08	4.015	4.08
56.0	83.0	4.09	4.07	3.95	4.065

and carbon dioxide are obtained. At low concentrations these gases are produced in the ratio of 1 to 2, as they would be if the reaction was a decomposition of the oxalic acid, according to:

$$(COOH)_2 \rightarrow 2CO_2 + H_2. \qquad (9)$$
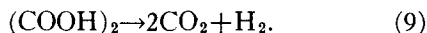
As the concentration is increased, the carbon dioxide increases and finally becomes constant. The hydrogen, however, shows a continued decrease.
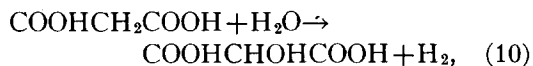
Figure 7 shows the productions of the gases as functions of pH for 100 mM $(COOH)_2$. The rate of production of carbon dioxide is represented by:

$$[CO_2] = 3.7(1 + 10^{5.6-pH}/(1 + 10^{5.6-pH}))\mu M \ CO_2.$$

At high concentration of oxalic acid and at high acidity, the rate of production of carbon dioxide becomes constant and equal to 7.4 μM CO_2.

Since the gas produced at high concentrations of oxalic acid is mainly carbon dioxide, it might be thought that the principal reaction at these concentrations is the formation of formic acid: $(COOH)_2 \rightarrow CO_2 + HCOOH$. Because of the high value found for the rate of production of the carbon dioxide, we are however inclined to believe that reaction (9) occurs at all concentrations but at higher concentrations the hydrogen is consumed with the reduction of the oxalic acid.

Malonic and succinic acids.—1.0 and 10.0 mM solutions of these acids were irradiated at pH = 3. Both acids yield hydrogen and a trace of carbon dioxide is also obtained for malonic acid. The rate of production of hydrogen, 2.5 μM H_2, is approximately the same for the two acids and for the two concentrations. The reactions may be:

$$COOHCH_2COOH + H_2O \rightarrow$$
$$COOHCHOHCOOH + H_2, \quad (10)$$

$$COOHCH_2CH_2COOH + H_2O \rightarrow$$
$$COOHCHOHCH_2COOH + H_2. \quad (11)$$

α-hydroxy isobutyric acid.—Irradiated at pH = 3 and at a concentration of 1.0 mM, carbon dioxide was produced at the rate of 0.8 μM CO_2. The residual gas calculated as hydrogen was produced at the rate of 1.1 μM. The high production of carbon dioxide is characteristic of an α-hydroxy acid.
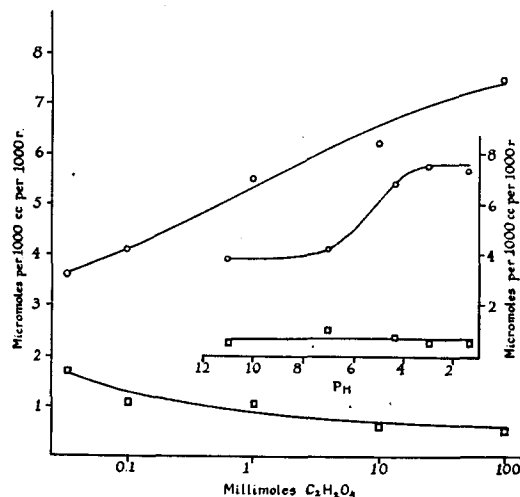
Tartaric acid.—Irradiated at pH = 3 and at a

FIG. 7. Reaction concentration curves for oxalic acid at pH = 3. Inserted: Reaction pH curves for 100 mM oxalic acid. Square, H_2; circle, CO_2.

concentration of 1.0 mM, carbon dioxide was produced at the rate of 1.2 μM CO_2. The residual gas calculated as hydrogen was produced at the rate of 2.5 μM. The carbon dioxide production is considerably greater than it is for α-hydroxy isobutyric acid.

Aldehydes

Formaldehyde.—The data obtained for solutions of formaldehyde at pH = 4 are shown in Fig. 8. The only gas produced was hydrogen. The solutions became acid as a result of the irradiation. The acid is assumed to be formic acid. In concentrated solutions the amount of acid formed is much greater than the hydrogen, but in dilute solutions the two quantities become more nearly alike and they agree at 1.0 mM HCHO. Below this concentration, the acid could not be determined with sufficient accuracy.

These results can be explained by assuming that the hydrogen is liberated in the reaction

$$HCHO + H_2O \rightarrow HCOOH + H_2. \qquad (12)$$

At the higher concentrations of formaldehyde an additional reaction liberating formic acid occurs, probably the reaction:

$$2HCHO + H_2O \rightarrow HCOOH + CH_3OH. \quad (13)$$

This reaction is exothermic to the extent of about 11 Cal. and occurs spontaneously in strong basic solution. The rapid increase in the formic

acid production with increasing concentration of formaldehyde, can, therefore, be understood since it may be assumed that reaction (13) has a tendency towards self-propagation outside the ranges of pH and concentration at which it occurs spontaneously. Accordingly we find that the excess acid is much greater when alkaline solutions are irradiated. This is shown by the reaction curves for solutions of formaldehyde in sodium hydroxide at $pH=10$, which are given in Fig. 8.

As evidenced by the hydrogen production, reaction (12) is produced at a constant rate at high concentrations of formaldehyde. The production of hydrogen as a function of the pH is shown in Fig. 5b for 10.0 mM HCHO. The relationship does not have the same simple form found for the acids. The hydrogen production becomes constant in alkaline solution but continues to rise with increasing acidity.

When we irradiate a mixture containing equal amounts of formic acid and formaldehyde, the formic acid is acted upon to a much greater extent than the formaldehyde, as shown later in this paper. This explains the rather short range of linearity of the formic acid dosage curves obtained in the irradiation of formaldehyde. At higher dosages, carbon dioxide appears, owing to the decomposition of the formic acid. (Fig. 8). For this reason, the determination of the formic acid production is rather difficult in dilute solutions of formaldehyde. This determination could not be carried through at concentrations below 1 mM HCHO.

Acetaldehyde.—Irradiations were carried out on solutions of acetaldehyde in sulphuric acid at $pH=4$ and in sodium hydroxide at $pH=10$ (Fig. 9) The reaction products observed were hydrogen and an acid which is assumed to be acetic acid

We consider, first, the reactions in alkaline solution. The results are similar to those obtained with formaldehyde. The hydrogen is constant. The acetic acid is higher than the hydrogen and increases as the concentration of acetaldehyde increases. The increase is, however, less rapid than it is for formaldehyde. We may assume the presence of the two reactions:
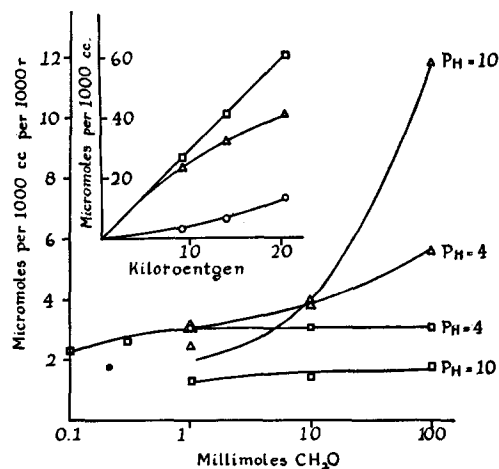
$$CH_3CHO + H_2O \rightarrow CH_3COOH + H_2 \quad (14)$$

Fig. 8. Reaction concentration curves for formaldehyde at $pH=4$ and 10. Inserted: Reaction dosage curves for 1 mM formaldehyde at $pH=4$. Square, H_2; triangle, CH_2O_2; circle, CO_2.

and

$$2CH_3CHO + H_2O \rightarrow \\ CH_3COOH + CH_3CH_2OH, \quad (15)$$

of which reaction (14) is produced at a constant rate, over the whole range of concentrations studied, while the rate of reaction (15) increases as the concentration of acetaldehyde increases. Reaction (15) is exothermic and occurs spontaneously in strong basic solution.

At $pH=4$ the acetic acid production is constant over a wide range of concentrations of acetaldehyde. At the highest concentration there is a just perceivable rise in the acetic acid probably because of the occurrence of reaction (15).

The constant part of the acetic acid production is probably to be explained by the occurrence of reaction (14). Since the production of hydrogen is greater than that of acetic acid, other reactions yielding hydrogen must occur. The simplest possibilities are:

$$CH_3CHO + H_2O \rightarrow CH_2OHCHO + H_2, \quad (16)$$

$$2CH_3CHO \rightarrow (CH_2CHO)_2 + H_2. \quad (17)$$

The hydrogen does not show the usual constancy at high concentrations, but it reaches a maximum and thereafter it decreases, as the concentration increases. This need not mean that the rates of the reactions in which hydrogen is produced
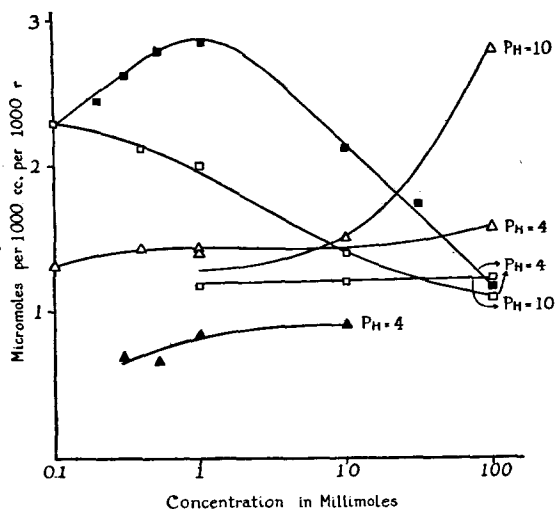
FIG. 9. Reaction concentration curves for (a) acetaldehyde at $pH = 4$ and 10 (square, H_2; triangle, CH_3COOH); (b) propionic aldehyde at $pH = 4$ (filled square, H_2; filled triangle, C_2H_5COOH).

primarily decrease at high concentrations. The constancy of the acetic acid shows that at least the rate of reaction (14) is independent of concentration. Possibly the decrease in the hydrogen results from the occurrence of a secondary reaction between the hydrogen in its nascent state and the acetaldehyde at the higher concentrations of acetaldehyde.

Propyl aldehyde.—Irradiations were carried out at $pH = 4$. (Fig. 9.) The reaction products observed were hydrogen and an acid, which was assumed to be propionic acid. The reaction concentration curves are similar to those found for acetaldehyde and they may be similarly interpreted. The results indicate that the oxidation of the aldehyde group is a still smaller part of the total reaction than it is in the case of acetaldehyde.

Ketones

Acetone.—The irradiation of unbuffered solutions of acetone produced no acid. The data obtained in the irradiation of solutions of acetone in sulfuric acid at $pH = 3$ are given in Fig. 10. An unusual result was the production of a small amount of hydrogen peroxide. The only gas produced was hydrogen. The hydrogen shows a decrease at high concentrations similar to that observed for acetaldehyde and propyl aldehyde.

Alcohols

Methyl alcohol.—Hydrogen was the only gas produced. Hydrogen reaction curves showing the influence of the methyl alcohol concentration, at $pH = 1$, and for unbuffered solutions, are given in Fig. 11. The irradiated solutions were tested for formaldehyde by Hehner's method.[11] Formaldehyde was found to be present but only to the extent of about 10 percent of the hydrogen. Representative reaction dosage curves are shown in Fig. 11. Measurements of the production of hydrogen in solutions of different pH are shown in Fig. 5. The values agree approximately with those obtained for formaldehyde.

Higher alcohols.—Solutions of ethyl alcohol, propyl alcohol and diethyl carbinol were irradiated at $pH = 3$, in concentrations between 0.1 and 10.0 mM. Carbon dioxide was not produced. The total gas calculated as hydrogen was approximately the same as for methyl alcohol.

The rates of the reactions produced by irradiating the organic chemicals decrease generally, at low concentrations. In Fig. 12 we have replotted some of the reaction product concentration curves obtained above. For each particular curve, the reaction rates are given as percentages of the constant reaction rate obtained at high concentrations. The curves can be represented approximately by:

$$[P] = (C/Co)/(1 + C/Co) \qquad (18)$$

when C is the concentration and Co is constant for each particular curve. [These curves were obtained at $pH = 3$, but it is interesting to note that the position of the curves (the Co values if the curves are represented by (18)) does not appear to depend on pH.]

This decrease in reaction rates may be accounted for by a deactivation of the activated water. However, if this interpretation is correct, then it would appear that the deactivation does not consist in a recombination of the active particles. This conclusion is indicated (1) since the reaction rates show no dependence of x-ray intensity down to the lowest concentrations used (2) because of the form of the reaction concentration curves. On the other hand, it is difficult to believe that active states other than dissociation products of the water molecule could be of suffi-
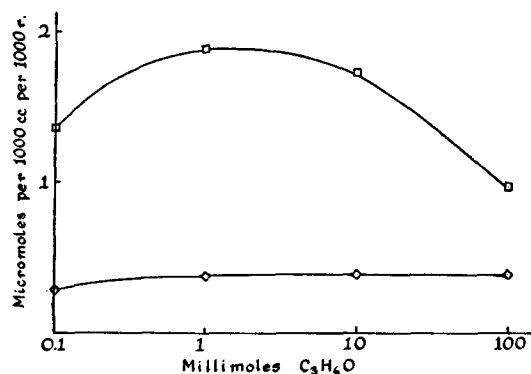
FIG. 10. Reaction concentration curves for acetone at $pH = 3$. Square, H_2. Diamond, H_2O_2.

cient stability to play a role in the reactions at the low concentrations used.

B. Two organic components

We have irradiated systems containing formic acid or oxalic acid as one of the components. In these systems the effect of the rays can be studied by recording the carbon dioxide production. Usually the hydrogen changes so little with the composition that its measurement is without significance.

The relation of the gas production to the composition of the systems is shown in Figs. 13, 14, and 15. They include mixtures of formic acid with methyl alcohol, formaldehyde, acetone, acetic acid, caproic acid, oxalic acid and benzene, and of oxalic acid with methyl alcohol. These irradiations were all carried out at $pH = 3$. In most of the curves the transitional region extends over 3 or 4 units in the log concentration ratio. Many of the curves can be represented rather closely by the expression:

$$[P] = \frac{C_1}{C_1 + \alpha C_2}[P]_1 + \frac{C_2}{C_1 + \alpha C_2}[P]_2, \quad (19)$$

where $[P]$ is the rate of production of the reaction product, C_1 and C_2 are the concentrations of the components, and $[P]_1$ and $[P]_2$ are the rates at which the reaction product is produced when the components are irradiated separately at the concentrations C_1 and C_2, respectively; α is a constant.

The position of the transitional region in the reaction curves shows the relative susceptibilities to irradiation of the substances in the mixture.
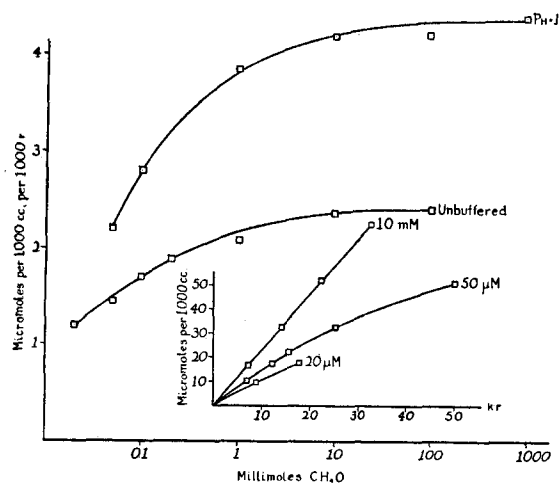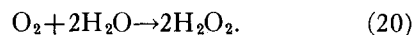

FIG. 11. Reaction concentration curves for methyl alcohol at $pH = 1$ and in unbuffered solution. Inserted: Reaction dosage curves for different concentrations of unbuffered solutions of methyl alcohol. Square, H_2.

The values of the susceptibility ratios obtained in the different mixtures vary widely. The results for acetic acid-formic acid are of particular interest. The production of gases from this system is independent of the acetic acid even when the concentration of this substance is 100 times that of the formic acid.

C. One organic component—oxygen

When water containing dissolved oxygen is irradiated, hydrogen peroxide is produced.[1, 3d, e] The reaction is:

$$O_2 + 2H_2O \rightarrow 2H_2O_2. \quad (20)$$

The production of hydrogen peroxide increases when the irradiation is carried out in the presence of organic compounds.[3d] It was suggested that
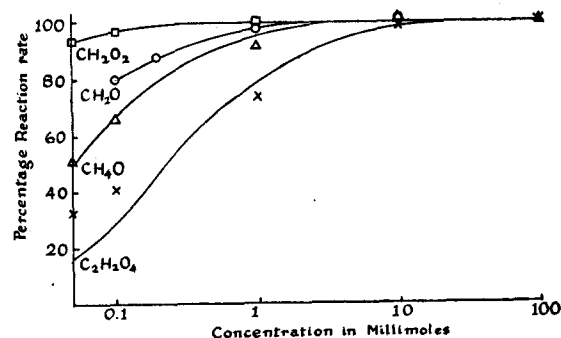

FIG. 12. Reaction concentration curves for (a) formic acid; (b) formaldehyde; (c) methyl alcohol; (d) oxalic acid. $pH = 3$.
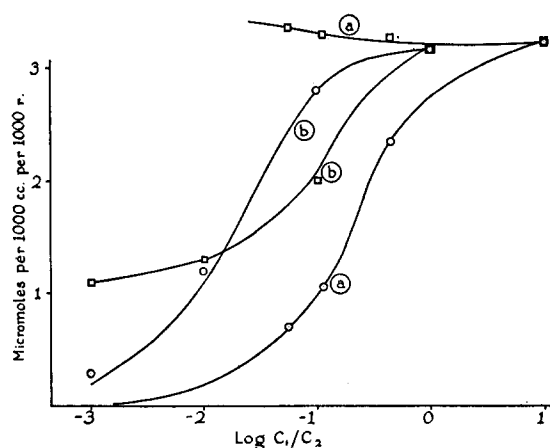
FIG. 13. Reaction log concentration ratio curves for solutions of formic acid and (a) formaldehyde; (b) acetone. Concentration of formic acid, $C_1 = 1$ mM. pH $= 3$. Square, H_2. Circle, CO_2.

this additional hydrogen peroxide results from a reaction of the oxygen with the nascent hydrogen produced by the action of the rays on the organic material. The gasometric studies which we have now carried out confirm this conclusion.

In Table II are shown the data obtained for formic acid irradiated in two concentrations, 0.03 and 1.0 mM CH_2O_2, at pH $= 3$ and at oxygen pressures of 6 cm and 70 cm of mercury.

Contrasting the results obtained when formic acid and oxygen are irradiated together against those obtained, when these substances are irradiated separately, we notice (1) the production of hydrogen peroxide and the consumption of oxygen increase; (2) the production of carbon
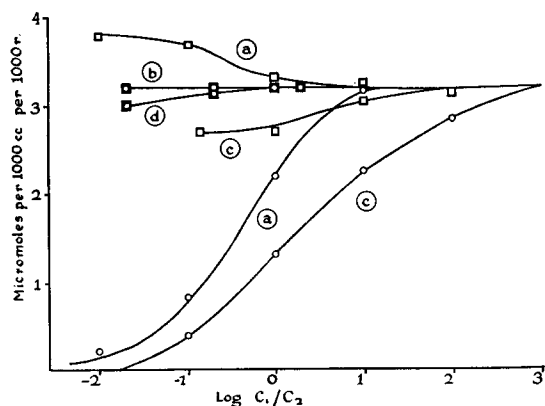

FIG. 14. Reaction log concentration ratio curves for solutions of formic acid and (a) methyl alcohol; (b) acetic acid; (c) caproic acid; (d) benzene. Concentration of formic acid, $C_1 = 1$ mM. pH $= 3$. Square, H_2. Circle, CO_2.
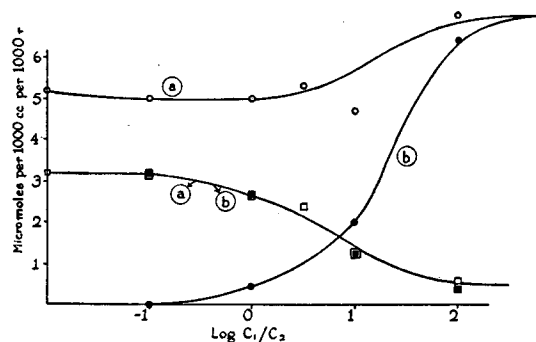

FIG. 15. Reaction log concentration ratio curves for solutions of oxalic acid and (a) formic acid (Square, H_2; Circle, CO_2); (b) methyl alcohol (filled square, H_2; filled circle, CO_2). Concentration of oxalic acid, $C_1 = 1$ mM. pH $= 3$.

dioxide and of hydrogen decreases, but the decrease of the hydrogen is greater than that of the carbon dioxide; (3) the increase in the hydrogen peroxide production ΔH_2O_2, the increase in the oxygen consumption ΔO_2 and the amount by which the hydrogen differs from the carbon dioxide $\Delta H_2 = [CO_2] - [H_2]$, are equal, as far as the accuracy of the data allows one to judge. This is shown by the following tabulation:

6 cm O_2 1.0 mM HCOOH $\quad \Delta H_2 = 2.1 - 0.8 = 1.3\ \mu M$;
$\Delta O_2 = 2.2 - 1.1 = 1.1\ \mu M$; $\quad \Delta H_2O_2 = 3.4 - 2.2 = 1.2\ \mu M$;

6 cm O_2 0.03 mM HCOOH $\quad \Delta H_2 = 1.6 - 0.5 = 1.1\ \mu M$;
$\Delta O_2 = 2.1 - 1.1 = 1.0\ \mu M$; $\quad \Delta H_2O_2 = 3.2 - 2.2 = 1.0\ \mu M$;

70 cm O_2 1.0 mM HCOOH $\quad \Delta H_2 = 2.0 - 0.4 = 1.6\ \mu M$;
$\Delta H_2O_2 = 3.7 - 2.2 = 1.5\ \mu M$.

These results can be explained by assuming (1) Reaction (20) takes place at the same rate as when formic acid is not present. (2) Formic acid is decomposed to hydrogen and carbon dioxide but the rate of this reaction is lower than when oxygen is absent. (3) The quantity ΔH_2 of the

TABLE II. *Irradiation of formic acid in the presence of oxygen at 6 cm and 70 cm Hg and at pH = 3. The initial production or consumption of gases is given in micromoles per 1000 cc and per 1000 r.*

MILLI-MOLES HCOOH	GAS FREE		OXYGEN AT 6 cm Hg				OXYGEN AT 70 cm Hg			
	CO_2	H_2	CO_2	H_2	O_2*	H_2O_2	CO_2	H_2	O_2*	H_2O_2
1.0	3.2	3.2	2.1	0.8	2.2	3.4	2.0	0.4	—	3.7
0.03	2.7	2.7	1.6	0.5	2.1	3.2	—	—	—	—
0	—	—	—	—	1.1	2.2	—	—	1.1	2.2

* Consumed.

hydrogen from this reaction combines with oxygen to form hydrogen peroxide according to:

$$H_2 + O_2 \rightarrow H_2O_2. \qquad (21)$$
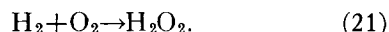
(4) This reaction (21) accounts for the increased production of hydrogen peroxide and increased consumption of oxygen.

The decrease in carbon dioxide shows us to what extent the effect of the rays on formic acid is suppressed by the presence of the oxygen and it is given in the following tabulation:

6 cm O_2 1.0 mM HCOOH $\Delta CO_2 = 3.2 - 2.1 = 1.1 \mu M$ CO_2,

0.03 mM HCOOH $\Delta CO_2 = 2.7 - 1.6 = 1.1 \mu M$ CO_2,

70 cm O_2 1.0 mM HCOOH $\Delta CO_2 = 3.2 - 2.0 = 1.2 \mu M$ CO_2.

The decrease in carbon dioxide is independent of the formic acid concentration and of the oxygen pressure and equals $\Delta CO_2 = 1.1 \mu M$. This value equals the rate at which oxygen is consumed when it is irradiated alone.

Apparently the formic acid decomposition can be only partially suppressed by adding oxygen. This result takes on a special significance when we note that water activated with ultraviolet light causes the decomposition of formic acid, but it has no effect on oxygen. Possibly, therefore, the reason for the inability of oxygen to completely suppress the formic acid reaction may be that the x-ray activated water molecules, which act on formic acid, do not all react with oxygen.

We are indebted to D. M. Gallagher for his assistance during the greater part of this work.

The Near Ultraviolet Bands of Acetylene

SHO-CHOW WOO, TA-KONG LIU, T. C. CHU AND WU CHIH
National Research Institute of Chemistry, Academia Sinica, Shanghai, China
(Received February 28, 1938)

The present investigation is a part of the program of a series of studies aiming at a satisfactory analysis of the near ultraviolet spectrum of acetylene. The spectrum of C_2H_2 at room temperature and 300°C was taken with a Bausch and Lomb large quartz spectrograph. The spectrum extends from λ2430A down to the ultraviolet limit of the instrument. More than 1000 bands and lines have been measured. Most of the bands revealed intensification at elevated temperature. Some of them have been partially resolved into rotational lines with alternating intensities. Seven main progressions all with frequency difference ~1050 cm^{-1} have been found. Only the bands of three of the progressions showed no intensification at higher temperature. From the differences between these bands, a frequency 580 cm^{-1} has been observed. Weaker bands on the red side of stronger ones have been proved through temperature variation to be due to transitions from the excited $2v_5''(E_g)$ level in the ground state. Through a tentative assignment, $2v_5' = 1050$ cm^{-1} and $v_4'(E_u) = 580$ cm^{-1} and the empirical selection rules, all of the bands in the seven progressions can be satisfactorily explained. Other possible assignments and the nature of the electronic transition have also been briefly discussed.

THE complexity of the ultraviolet spectra of polyatomic molecules usually prevents a complete analysis in the present state of knowledge. Attempts toward simplification have been made by working with those molecules which possess a structure of high symmetry. For this reason, we have recently been working mainly on molecules which are considered to be of the symmetrical and collinear type. Acetylene is particularly suitable in this category since its structure and fundamental frequencies in the ground state have been thoroughly investigated through the infra-red and Raman spectrum measurements. Unfortunately, no satisfactory analysis which makes use of these results in the ground state has been attained, in spite of the numerous investigations[1] made in recent years.

[1] (a) J. Stark and P. Lipp, Zeits. f. physik. Chemie **86**, 36 (1913); (b) H. Hese, A. Rose and R. Gräffin Zu Dohna, Zeits f. Physik **81**, 745 (1933); (c) G. Kistiakowsky, Phys. Rev. **37**, 276 (1931); (d) M. A. Jonesco, Comptes rendus **199**, 710 (1934); (e) M. A. Jonesco, Comptes rendus **200**, 817 (1935); (f) H. Göpfert, Zeits. f. wiss. Phot. **34**, 156 (1935); (g) It is uncertain if the bands beginning at λ2070A found by Herzberg (Trans. Faraday Soc. **27**, 378 (1931)) are a continuation of the system here discussed, since the distances between the main bands were found to be 1365 and 865 cm^{-1}, which are quite different from what we have found here.