## Summary

1. The oxidation-reduction potentials of the pentavalent-trivalent columbium system were measured with a mercury electrode in an atmosphere of hydrogen at 25°. Three concentrations of sulfuric acid, 3.14 *M*, 5.91 *M* and 9.87 *M* were used. The concentration of columbium in Tables I, II, III and V expressed as $Cb_2O_5$ was 0.024 *M*. In Table IV it was 0.012 *M*.

2. The trivalent columbium was found to be a strong reducing agent which increased markedly as the concentration of acid increased.

3. A valence of three was confirmed for the reduced state.

4. The average calculated normal electrode potentials for the three concentrations of acid, respectively, are: −0.3730, −0.3849 and −0.4261.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

# PHOTOCHEMICAL STUDIES. VII. THE PHOTOCHEMICAL DECOMPOSITION OF FORMIC ACID LIQUID AND VAPOR

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The fact that formic acid decomposes under the influence of ultraviolet radiation has been known for many years. Thiele[1] found that the product of photochemical decomposition of the anhydrous acid was largely carbon dioxide, together with small amounts of oxygen, carbon monoxide and other gases. Berthelot and Gaudechon[2] state that long wave lengths (250 to 350 m$\mu$) cause the formation of water and carbon monoxide, while shorter wave lengths cause the formation of carbon dioxide and hydrogen. Allmand and Reeve,[3] in a recent careful investigation of the photochemical decomposition of formic acid in aqueous solution, find that wave lengths below 350 m$\mu$ are effective and that practically the only gas formed is carbon dioxide. They think that the hydrogen (which would be formed simultaneously) is used in reducing formic acid to formaldehyde and other products. These authors also made accurate studies of the quantum efficiency and found the latter to be nearly independent of concentration but to depend on the wave length, being greater for short wave lengths.

Little work has been done on the photochemical decomposition of formic acid vapor. Ramsperger and Porter[4] have made a study of the absorption spectrum. They find that two types of molecule, HCOOH and $(HCOOH)_2$, exist in the vapor state and that each absorbs below about

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[1] Thiele, *Ber.*, **40**, 4914 (1907).

[2] Berthelot and Gaudechon. *Compt. rend.*, **151**, 478 (1910).

[3] Allmand and Reeve, *J. Chem. Soc.*, **129**, 2852 (1926).

[4] Ramsperger and Porter, THIS JOURNAL, **48**, 1267 (1926).

260 mμ. They exposed vapors of formic acid to radiation from the quartz mercury arc lamp until decomposition was complete. Under these conditions carbon monoxide and water formed 64% of the mixed products and carbon dioxide and hydrogen 36%. No details of the method of analysis and no measure of the quantum efficiency were given. Bates and Taylor[5] have studied the photochemical decomposition of formic acid vapor sensitized by excited mercury. They find that the sensitized reaction proceeds much more rapidly (400 times) than the unsensitized reaction and that of the products uncondensed by liquid air, 76% were carbon monoxide and 24% hydrogen.

Other work has been done but need not be mentioned at this time.

## I. Experimental Procedure and Results

**A. Decomposition of the Vapor.**—The formic acid used in these experiments was prepared by the method of Schlesinger and Martin[6] by drying with boron trioxide. In part of the experiments phosphorus pentoxide was used as the drying agent. The formic acid used was outgassed after it had been admitted to the vacuum line. The line was first thoroughly flamed out with the highest vacuum obtainable and the formic acid distilled in with liquid air. The line was again evacuated with the formic acid frozen. The formic acid was then distilled from one trap to another and the evacuation repeated. This was continued until the amount of gas removed by a Toepler pump into a volume of 210 cc. was less than $10^{-4}$ mm. No excess liquid was present except in two of the preliminary runs.

After exposure to the radiation the formic acid was condensed with liquid air and the decomposition products remaining in the gas phase were removed by the Toepler pump. These consisted entirely of hydrogen and carbon monoxide. The formic acid was then distilled with liquid air and the free gas removed by the Toepler pump. This process was repeated until distillation liberated a negligible amount of gas. Carbon dioxide snow and ether ($T = -77°$) was then substituted for liquid air and the process repeated. Under these conditions carbon dioxide (and small amounts of water vapor) were removed by the Toepler pump.

Monochromatic light was not used in these experiments. The light intensities were measured by a thermopile calibrated by a standard source of radiation furnished by the Bureau of Standards. A perforated sheath was placed over the mercury arc lamp to approximate a point source of radiation. The light was made into a slightly diverging beam by means of a quartz lens, passed through a quartz cell 2 cm. in thickness containing water and then through a tube 92 cm. in length fitted with transparent quartz ends. The intensity was measured when the vapor was in the tube and when the vapor was condensed in liquid air. The difference gave the deflection due to the light absorption. The area of the spot was not very definite due to the fact that monochromatic light was not used, since the index of refraction of the quartz in the lens varies with wave length.

Water absorbs practically all of the infra-red beyond 1.4μ. The infra-red intensity of a quartz mercury arc lamp is relatively low. In addition, while the authors were unable to find any data on formic acid vapor, most simple organic compounds in the vapor state do not possess infra-red absorption bands between 1.4μ and 0.7μ. The error due to infra-red

[5] Bates and Taylor, This Journal, **49**, 2438 (1927).

[6] Schlesinger and Martin, *ibid.*, **36**, 1589 (1914).

should not exceed 10%. From a consideration of the absorption spectrum and the energy distribution of the quartz mercury arc lamp as determined with a quartz spectrograph, the average wave length absorbed by the vapor was taken to be 250 ± 10 mμ.

The average of ten determinations gave 6.6 × $10^{12}$ molecules uncondensed by liquid air formed per erg absorbed or 0.52 molecule per quantum with an average deviation from the mean of 0.16. In addition 0.39 molecule (with an average deviation of 0.10) not condensed by carbon dioxide snow and ether but condensed by liquid air was formed per quantum. The measurement of the light intensity was the most probable source of error since it involved the difference between two quantities. It would seem, however, that the quantum efficiency of the decomposition of the vapor is on the average less than unity.

**B. Decomposition of the Liquid.**—It is exceedingly difficult to measure the decomposition of anhydrous liquid formic acid because some thermal decomposition is unavoidable. However, the gas formed by thermal decomposition is uncondensed by liquid air, while the main gas formed by photochemical decomposition is condensed by liquid air but not at −77°. This agrees with the statement made by Allmand and Reeve for solutions, that the main gas evolved by photochemical decomposition is carbon dioxide.

Light intensity measurements were made by placing the thermopile in front and in back of the cell. By use of the change in area of the beam in traversing the cell and the decrease in deflection due to the empty cell, it was found that 15% of the radiation from the arc lamp (after passage through 2 cm. of water) was absorbed by 3.1 cm. of liquid formic acid. The average wave length is taken as 300 mμ since the mercury line of greatest intensity in the region of strong absorption is at 313 mμ. The coefficient $k$ in the equation $I = I_0^{-kl}$ ($l$ is thickness in cm.) increases from 0.42 at 300 mμ to about 1.5 at 250 mμ. (Measurements made with rotating sector in conjunction with quartz spectrograph.) Seven determinations gave 0.46 molecule condensed by liquid air but uncondensed by carbon dioxide snow and ether per quantum absorbed with an average deviation of 0.16.

Five runs with light transmitted by Pyrex glass were made. From a consideration of the absorption coefficients of the liquid and the fact that of the ultraviolet lines transmitted by Pyrex glass by far the most intense are at 366 mμ and 313 mμ, the average wave length was taken as 330 mμ. The average number of molecules of gas condensed by liquid air but not at −77° formed per quantum absorbed was 0.14 with an average deviation of 0.04.

Allmand and Reeve found the quantum efficiency for decomposition of formic acid in solution to be about 2.7 at 260 mμ and 1.0 at 300 mμ. A very rough calculation shows that the quantum efficiency is about 1.1 on the average for those wave lengths transmitted by quartz but not by Pyrex glass. Since the average wave length in this case is nearer 300 mμ than 250 mμ, the quantum efficiency is not greatly different from that found by Allmand and Reeve for solutions.

## II. Discussion of Results

The results of Ramsperger and Porter[4] and of Bates and Taylor[5] indicate that formic acid may decompose either directly or through the agency of excited mercury into carbon monoxide and water or into carbon dioxide and hydrogen. If these two primary reactions occur, measurement of the number of molecules of hydrogen and carbon monoxide together (both uncondensed by liquid air) would give an indication of the number of molecules of formic acid vapor decomposed. One run was made in which hydrogen to a pressure of 0.2 mm. was added. Normally, with the light intensity used, a pressure increase (with liquid air around the trap) of 0.03 mm. would have been observed. Actually the pressure change was negligible but showed, rather, a slight diminution. This may indicate that hydrogen is capable of reducing formic acid under the conditions of the experiment with formation of a product condensed by liquid air.

From the data of Ramsperger and Porter[4] it can be shown that at 25° and a total pressure of 39 mm. (the approximate conditions in the above experiments) over 95% of the pressure is exerted by the bimolecular form. Since the absorption coefficient of this form is higher than for the monomolecular form, nearly all of the radiation is absorbed by $(HCOOH)_2$. While sufficient resolution was not used by Ramsperger and Porter to make an analysis of the absorption spectrum of the vapor, the absorption seems to be continuous and to increase in intensity with frequency. Whether a definite low frequency limit to the absorption exists or not cannot be ascertained. The heat of dissociation of the bimolecular form is about 14,000 calories per mole. This would correspond to a wave length of $2\mu$. This wave length may be absorbed. The ultraviolet absorption may cause the dissociation of the bimolecular form as follows: $(HCOOH)_2 = HCOOH + HCOOH^*$, where $HCOOH^*$ represents an activated molecule. The monomolecular form should then absorb at slightly longer wave lengths in the ultraviolet than the bimolecular form, since the heat of dissociation is small compared to the total energy absorbed. The activated molecule may decompose either directly or upon collision. Little information can be obtained on this point from the absorption spectrum measurements. While the error in the above experiments may be fairly large, the low value of the quantum efficiency indicates that direct dissociation probably does not result.

The question now arises as to whether all of the products found by Ramsperger and Porter[4] and by Bates and Taylor[5] result from the primary reaction. In solution and in the anhydrous liquid only one type of decomposition seems to result. The following possibilities may be considered.

(*a*) The monomolecular form may decompose in one manner and the bimolecular form in another. This would necessitate a large quantum efficiency for the decomposition of the monomolecular form and a relatively small one for the decomposition of the bimolecular form. Increase in the percentage of the monomolecular form by lowering of the pressure from 39 mm. to 18 mm. did not affect appreciably the ratio of gas uncondensed by liquid air to that condensed by carbon dioxide snow and ether.

(*b*) The activated molecules may decompose in two manners for the reasons given by Bates and Taylor.[5]

(*c*) The primary decomposition may be into carbon dioxide and monatomic hydrogen. The heat of the reaction is small (of the order of four thousand calories) and the production of monatomic hydrogen is possible. Production of formaldehyde might result by the action of the monatomic hydrogen on another molecule of formic acid. The formaldehyde might then decompose. By this mechanism the quantity of hydrogen should be equal to the quantity of carbon monoxide unless the hydrogen were partially used up. Formaldehyde was tested for but not found in the condensed formic acid vapor remaining after the gases had been removed by a Toepler pump with carbon dioxide snow and ether around the trap. The small amount of carbon monoxide in the gases given off from solutions[3] indicates that formaldehyde, if formed, does not decompose rapidly in solution due to the screening effect of the formic acid or to polymerization. Evidence is not satisfactory on these various points.

(*d*) It is possible that the bimolecular form might decompose directly into formaldehyde, carbon dioxide and water, the formaldehyde decomposing into carbon monoxide and hydrogen. The excess of carbon monoxide over hydrogen found by previous observers could be explained by reducing action of the hydrogen.

It seems not impossible, therefore, that the primary reaction in both liquid and vapor state may lead to the formation of carbon dioxide. While the errors in the determination of the quantum efficiencies are large, they are of the same general magnitude.

If the activated state for the vapor is the same as for the liquid, one might expect the heat of vaporization to be related to the effective frequencies for decomposing the liquid and vapor by the formula $\Delta H = Nh(\nu_1 - \nu_2)$, where $\Delta H$ is the heat of vaporization, $h$ is Planck's constant and $\nu_1$ and $\nu_2$ are the frequencies necessary to cause decomposition of the liquid and vapor, respectively. It is not possible to test this formula accurately with the present data due to difficulty in choice of frequency but we may say qualitatively that the formula does not give the wrong order of magnitude.

The authors wish to express their appreciation to Mr. W. E. Vaughan for aid in performing part of these experiments.

## Summary

1. The number of molecules of gas uncondensed by liquid air formed per quantum absorbed has been determined for the photochemical decomposition of both liquid and gaseous formic acid. A similar determination of the number of additional molecules uncondensed by carbon dioxide snow and ether has been made.

2. The quantum efficiency increases with frequency in the case of the liquid. The vapor absorbs only at short wave lengths and variations of frequency were not made.

3. Possible mechanisms for the reaction have been discussed.

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# THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. VIII. THE ELECTRIC MOMENT AS A VECTOR QUANTITY

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Electric moment data for a number of molecules, organic and inorganic in nature, have been presented in the previous papers of this series.[2] The moments have been calculated from dielectric constant and density data for suitable binary mixtures, using the Debye modification of the Clausius–Mosotti Law. The purpose of the present article is to give the results of further experimental work in this field and to suggest the significance of these data.

The apparatus used for the determination of the dielectric constants of the binary mixtures was designed and constructed especially for the purpose by the author. It has been very briefly described in a previous article.[2e] Dielectric constant and density determinations were made at 25°, using a carefully regulated thermostat and observing the usual precautions for precision work. In every case the solvent used was benzene.

## Purification of Materials

All substances used for the measurements herein reported were subjected to a careful purification. For that purpose the customary methods of crystallization or distillation or both were resorted to. It is considered unnecessary to give the outline of the method for each particular substance—suffice it to say that in no case did the observed physical constants,

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[1] National Research Council Fellow in Chemistry.

[2] (a) Williams and Krchma, This Journal, **49**, 1676, 2408 (1927); (b) Williams and Allgeier, *ibid.*, **49**, 2416 (1927); (c) Williams and Ogg, *ibid.*, **50**, 94 (1928); (d) Williams and Schwingel, *ibid.*, **50**, 362 (1928); (e) Williams and Weissberger, *ibid.*, **50**, 2332 (1928).