The curves of Fig. 3 show how well the requirements of equation 14 are fitted by the experimental data. In the *presence* of added carbonate, all terms of equation 13 contribute due to the suppression of the diaquo intermediate, and the rate law is

$$\theta_r = \frac{1}{t^1/_2} = 1.44(k_1 + k_2K_5/h + k_3K_6h + k_4K_6K_7h/b)$$

The lack of dependence of the rate on complex concentration in presence of carbonate was confirmed by experiment.[25] Figure 4 demonstrates the inverse proportionality to free carbonate, the empirically fitted heavy curve being of the form $\theta_r = 7.9 \times 10^{-3}/b + 1.5 \times 10^{-3}$. The variation of θ_r with (H^+) is complex, but the curve drawn in Fig. 4 to fit the experimental data indicates that at low (H^+) the species $Coen_2CO_3OH$ must contribute considerably to the racemization, since this is the only one which varies inversely as (H^+).

The temperature dependence of the racemization was not adequately studied in this work. However, the data of Table I indicate an activation energy of about 23 kcal./mole in absence of carbonate, with a similar value in presence of carbonate suggested by the data of Table II. Due to the complexity of the racemization kinetics it is impossible to relate these activation energies to any specific rate constants with the data as they stand.

The exact mechanism of racemization cannot be stated unequivocally, but it clearly does not parallel the ligand exchange process. An intramolecular rearrangement must be involved, along the lines of proposals often made in this regard.[16] It is of interest that it is only at low *p*H, that is when most of the racemization is occurring through the diaquo ion, that neutral salt addition has any pronounced influence (compare Tables I and II). This is seemingly almost independent of the type of salt used. Probably for $Coen_2(H_2O)_2^{+++}$, reagents which tend to compete with the complex ion for water of solvation considerably accelerate its inversion. Further investigation of this point would be of considerable interest.

Financial assistance through Contract No. AT-(30-1)-1578 between the University of Buffalo and the U.S.A.E.C., which facilitated completion of this study, is gratefully acknowledged.

BUFFALO, N. Y.

[25] At 56.1°, with [carbonate] = 0.004 *M*, $[H^+] = 1.2 \times 10^{-9}$ *M* and [borate] = 0.05 *M*, θ_r was 3.8, 3.7, 3.7 and 3.6×10^{-3} min.$^{-1}$ for [complex] 0.0036, 0.0067, 0.0100 and 0.0127 *M*, respectively.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Effect of X-Rays on Solutions which Contain Formic Acid and Ceric Ion

BY HARRY E. SPENCER AND G. K. ROLLEFSON

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If ceric sulfate and formic acid are dissolved in 2.8 *N* sulfuric acid, they do not react appreciably under ordinary conditions. If such a solution is exposed to the radiation from an X-ray tube operated at 50 kv. and 45 ma., reaction occurs at a readily measurable rate. The principal products are cerous ion, carbon dioxide, hydrogen and oxygen. In the experiments reported in this paper it was found that these products alone sufficed to give a material balance within 10% except at high formic acid concentrations. Under the latter conditions some deviations were found which are believed to be caused by the formation of formaldehyde, although the amount of that substance formed was never enough to obtain a positive test. The effects of varying the concentrations of formic acid and of ceric ion and of adding oxygen have been studied. A mechanism has been formulated which gives a quantitative description of the experimental facts. On the basis of this mechanism the yield of radicals from the action of the radiation on water can be estimated. The yield calculated from these experiments has been compared with one calculated from some similar experiments on ferrous sulfate solutions, assuming the validity of Hart's mechanism, and the agreement found to be good.

In the study of the effects of ionizing radiations on dilute aqueous solutions it is generally assumed that the primary action of the radiation is to produce hydroxyl radicals and hydrogen atoms. The other reactions which occur are the result of reactions of these substances (or substances derived from them) with the solutes present. Normally the hydrogen atoms act as reducing agents and the hydroxyls as oxidizing agents although the latter may act as a reducing agent through some mechanism such as the formation of hydrogen peroxide. It follows that usually a solute will react with only one of the radicals. In the work described in this paper we have attempted to get clear cut reactions with both radicals by introducing two solutes, one being an oxidizing agent and the other being primarily reducing in character.[1]

The system selected for study is a solution of ceric sulfate and formic acid in 1.4 *M* sulfuric acid. In the absence of ionizing radiations there is no appreciable reaction in this solution even if it is kept for several weeks. However, if the solution is treated with X-rays from a 50 kv. tube reaction occurs with the formation of cerous ion, carbon dioxide, hydrogen and oxygen. No other products were found in detectable amounts although there was some reason to believe that a small amount of formaldehyde might have been formed in some of the experiments.

Experimental Details

Materials.—The water used in all irradiations was twice distilled, first from a tin still and then from an alkaline permanganate solution in a Pyrex still. J. T. Baker 90.5% C.P. analyzed formic acid, G. F. Smith reagent grade ceric hydroxide, Baker and Adamson 95–96% C.P. sulfuric acid, and Mallinckrodt analytical grade ferrous sulfate were used without further purification.

Solutions.—Enough ceric hydroxide to make an approximately 0.2 molar stock ceric solution was dissolved in an appropriate amount of concentrated acid to make the final solution 1.4 molar sulfuric acid after dilution with twice

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[1] *Cf.* W. M. Garrison and G. K. Rollefson, *Discs. Faraday Soc.*, **12**, 155 (1952).

distilled water. This solution was passed through a sintered glass filter.

A stock solution of approximately 0.23 molar formic acid was prepared by diluting an appropriate volume of concentrated acid with doubly distilled water. The exact molarity was determined by titration with standard base. This stock solution was used to make up all solutions which contained low concentrations of formic acid. Solutions of high formic acid concentration were prepared by pipetting the appropriate amount of concentrated acid into the reaction mixture.

Ferrous solutions were prepared by dissolving the desired amount of ferrous sulfate in water, adding concentrated sulfuric acid and then diluting until the concentration of the sulfuric acid was 1.4 molar.

Analytical Methods.—The concentration of ceric salt was determined with standard arsenite using osmium tetroxide as a catalyst and ferrous *o*-phenanthroline as an indicator.[2] Concentrations of ferrous ion were determined by titration with ceric solution.[2] The formic acid content of reaction mixtures was determined by distilling *in vacuo* and condensing the vapor in a liquid nitrogen trap. The distillate was titrated with sodium hydroxide solution which had been standardized against potassium hydrogen phthalate.

Gases were dried by passing through a tube filled with magnesium perchlorate and the total amount measured in a gas buret. The composition of the gaseous mixture was determined by a mass spectrometer.

X-Rays.—The X-rays were obtained from a horizontally mounted Machlett AEG-50T tungsten target tube operated with full wave rectification. The plate current was stabilized with a Phillips milliampere stabilizer while the voltage was stabilized with a Sola transformer. The fluctuations in current and voltage did not exceed 1%. In all experiments the tube was operated at 50 pkv. and 45 ma. The only filter for the X-ray was the window of the cell.

Reaction Cell.—Several reaction cells were used but it was found that all were identical, within the limits of experimental error, as judged by the amount of cerous ion produced by a ten-hour irradiation of 100 cc. of ceric sulfate in 1.4 molar sulfuric acid. The main part of the reaction cell was made from a 200-cc. erlenmeyer flask. The window sealed on the top was a polished disk of Pyrex $^1/_{32}$ inch thick and $1^1/_{16}$ in. diameter. The diameter of the X-ray beam as it entered the cell was estimated from the brown color developed in the window to be about $^5/_8$ inch.

The solution was stirred magnetically, using a small piece of iron sealed in Pyrex as the stirrer. The temperature of the cell was controlled during the irradiation period by surrounding it with water which was maintained at 27 ± 0.5°. Introduction of the reaction mixture and degassing of the solution was accomplished through a side arm fitted with a ground joint and stopcock. Apiezon N and M greases were used for the stopcock and ground joint. The total volume of the cell and side arm was about 210 cc.

Procedures.—All glass that came in contact with the solutions to be irradiated was cleaned by soaking in chromic-sulfuric acid cleaning solution. The reaction cells were left in this mixture for at least 24 hours. After this treatment the cells were irradiated for about six hours while filled with doubly distilled water. Finally they were rinsed several times with distilled water and three times with doubly distilled water and dried under vacuum. One hundred cubic centimeters of the solution to be irradiated was pipetted into the cell, which was then connected to the vacuum line and degassed.

The solutions were degassed by attaching the cell to a vacuum line which was connected through a liquid nitrogen trap to a McLeod gage and a mercury vapor pump backed up by a mechanical pump. The gas above the solution was expanded into the evacuated line by opening the stopcock briefly and then closing it. The solution was stirred vigorously for a few minutes while the line was being evacuated and again opened to the line. This procedure was repeated several times until the pressure of the gas in the line was less than 10^{-5} mm. after each of two successive stirrings. Stirring overnight did not appreciably increase the partial pressure of air over the degassed solution. The entire degassing process usually took about two hours. After this treatment the cell was clamped into place under the X-ray tube, allowed to come to the temperature of the surrounding water-bath and irradiated.

After irradiation the cell was connected to the vacuum line again and the gas pumped off in a manner similar to that before irradiation except that a Toepler pump was used to transfer the gas from the cell through a magnesium perchlorate drying tube into a gas buret. The total amount of gas was measured and it was expanded into a bulb for mass spectrographic analysis. The solution left in the cell was analyzed for ceric content and in some cases for formic acid by the methods already described.

In some experiments oxygen was added to the reaction system after the initial degassing. Identical results were obtained with two different procedures. One method involved adding the oxygen directly from the tank to the volume above the degassed solution in the cell. The solution was stirred vigorously for several hours before it was irradiated. The other technique consisted of bubbling the oxygen successively through sodium hydroxide solution, distilled water, and the reaction mixture. This was done for about 15 minutes before the 100-cc. sample was taken for irradiation. After introduction of the sample into the reaction cell the gas above the liquid was pumped off quickly and replaced with oxygen from the tank to the desired pressure. Then the solution was stirred vigorously for a few minutes before irradiation.

Experimental Results and Discussion

The only products which were found in measureable amount were hydrogen, oxygen, carbon dioxide and cerous ion. A consideration of the amounts of these substances formed showed that the results can be expressed as a combination of three net reactions

$$2Ce^{+4} + HCOOH = 2Ce^{+3} + CO_2 + 2H^+ \qquad (A)$$

$$4Ce^{+4} + 2H_2O = 4Ce^{+3} + 4H^+ + O_2 \qquad (B)$$

$$2H_2O = 2H_2 + O_2 \qquad (C)$$

In writing these equations we have simply indicated the oxidation state of the cerium although it may actually be in the form of a sulfate complex. The validity of the statement that these reactions represent the complete change which occurs as a result of radiation is shown by the balance of the number of equivalents oxidized with the number reduced. Thus in Table I for solutions with no formic acid present, it is necessary to consider only reactions (B) and (C) and it is apparent that the balance for a single experiment is usually within 10% in spite of the great sensitivity of this balance to errors in the analysis. That the fluctuations are caused by experimental errors is supported by considering the totals for all the experiments listed in the table. It shows 1209 microequivalents reduced and 1192 oxidized. Similarly, in Table II, where all three net reactions must be taken into account, the total number of equivalents oxidized is 3037 as compared to 3063 reduced. The agreement of the totals for Table III is not quite as satisfactory (3766 compared to 3563), but this is the result of the relatively large number of equivalents oxidized in the experiments with high formic acid concentrations. This discrepancy is probably real and it was thought that it might be caused by formaldehyde formation. Such an explanation was suggested by Fricke, Hart and Smith[3] who found a similar behavior in aqueous solutions of formic acid at low *p*H. In an attempt to get a positive test for formaldehyde, a solution of 0.938 molar formic acid and 0.01866 molar ceric sulfate was irradiated for ten hours. The solution was distilled and

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(2) H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," D. Van Nostrand Co., New York, N. Y., 1940.

(3) H. Fricke, E. J. Hart and H. P. Smith, *J. Chem. Phys.*, **6**, 229 (1938).

the distillate tested for formaldehyde by the chromotropic acid, *p*-phenylenediamine and bisulfite tests given by Feigl.[4] The first two tests showed that the formaldehyde concentration was less than 0.001 molar but in blank tests it was found that these would not show 0.0001 molar. The third test was inapplicable because it was found in a blank test that formic acid of this concentration gave a positive test. It was found that the material balance improved when oxygen was added to the system. This effect is probably the result of the elimination of side reactions.

TABLE I

TEN HOUR IRRADIATIONS OF CERIC SOLUTION WITH NO FORMIC ACID PRESENT

Initial (Ce^{+4}), mmoles/l.	μmoles produced Ce^{+3}	H_2	O_2	μ equiv. Reduced	Oxidized
6.73	117				
6.73	117				
9.97	118	28.7	41.9	175	168
9.97	120	30.4	42.3	181	169
9.97	119	27.5	43.7	174	176
9.97	118	23.1	49.9	164	200
9.97	124	26.9	43.1	178	172
4.99	117	25.0	43.1	167	172
4.99	116	26.8	33.8	170	135

TABLE II

IRRADIATIONS OF CERIC, FORMIC ACID SOLUTIONS WHICH WERE ANALYZED FOR FORMIC ACID CONCENTRATION

Mmoles/l. Initial Ce^{+4}	HCOOH	Final HCOOH	μmoles produced Ce^{+3}	H_2	O_2	CO_2	Hr. radiated	μ equiv. Reduced	Oxidized
9.42	9.4	..	512	78.0	93.0	126	22	668	624
9.42	9.4	8.1	443	63.3	87.6	115	20	568	580
9.42	9.4	8.3	447	64.9	88.0	116	20	577	588
6.27	4.81	4.03	384	66.3	85.8	73.5	20	488	490
6.27	4.81	4.21	287	46.6	60.7	57.2	15	370	357
6.27	4.81	4.37	190	32.1	43.2	45.0	10	254	263
6.27	4.81	4.50	104	17.2	21.4	24.5	5	138	135

TABLE III

TEN HOUR IRRADIATIONS OF CERIC, FORMIC ACID SOLUTIONS

Mmoles/l. initially Ce^{+4}	HCOOH	Ce^{+3}	μmoles produced H_2	O_2	CO_2	μ equiv. Reduced	Oxidized
4.99	11.73	232	32.5	43.9	69.7	297	315
9.97	11.73	230	38.2	39.4	65.4	306	288
19.94	11.73	240	26.7	43.4	69.5	293	313
9.97	5.85	191	32.4	41.0	48.3	256	261
9.97	23.45	274	52.5	39.4	108.1	379	374
39.97	11.74	231	28.9	47.1	66.7	289	322
39.97	23.45	268	45.5	40.3	78.5	359	318
38.47	234.5	346	74.1	39.3	225.4	494	608
38.53	117.3	348	51.5	43.8	186.3	451	548
38.55	46.9	327	50.6	41.9	125.7	439	419
O_2 or air added in various amounts (results independent of O_2 added)							
9.97	23.45	265	29.4	46.7	77.9	324	343
9.97	23.45	270	26.8	34.8	82.8	324	305
19.94	11.73	231	25.3	44.0	59.0	282	294
38.53	117.3	359	30.7	39.0	120.6	420	396
38.53	117.3	361					
38.47	234.5	407	35.6	35.3	142.8	478	427
38.47	234.5	385	29.8	37.1	132.8	446	414
38.47	234.5	396					
38.47	234.5	402					
38.55	46.9	306					
9.68	1173	417					
9.68	1173	417					
9.68	704	413					
19.27	938	419					
9.64	469	412					

A survey of the data presented in the tables shows that the production of hydrogen is dependent on the formic acid concentration. The amount produced is a linear function of the concentration of the formic acid but is never less than about 27 μ-moles. Eight irradiations without formic acid present yielded an average of 26.9 ± 1.5 μmoles of hydrogen for a ten-hour irradiation. The extrapolation of the lines shown in Fig. 1 to zero formic acid gives a value close to 27 μmoles. It is assumed therefore that this number represents the amount of hydrogen produced by a path which is not affected by the addition of the solutes used in these experiments.

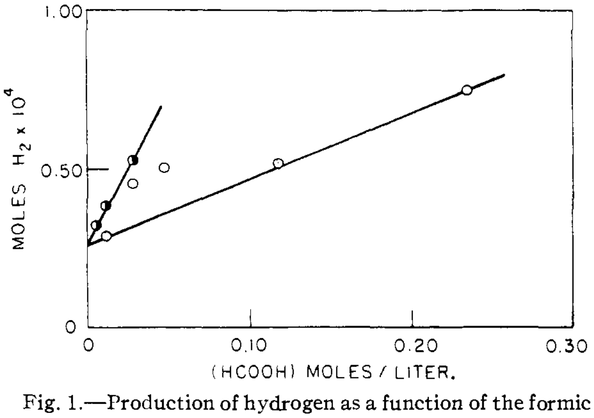

Fig. 1.—Production of hydrogen as a function of the formic acid concentration. The two lines correspond to different concentrations of ceric ion.

The production of oxygen in all solutions was found to depend solely on the time of irradiation. The average amount produced in nineteen irradiations in which no oxygen was added originally was 42.1 ± 2.3 μmoles in ten hours. The average for six experiments in which oxygen was added initially was 39.5 ± 3.8. The latter figure represents the difference between relatively large numbers and therefore is not as accurate as the former.

The amount of cerous ion produced is independent of the concentration of the ceric irradiated but both it and the carbon dioxide production depend on the formic acid concentration. Since cerous ion is formed both according to reaction (A) and reaction (B) it is necessary to make a correction for any change in the extent to which reaction (B) occurs. It has been mentioned that the production of oxygen is constant but that that of hydrogen increases when formic acid is added. This effect can be expressed as an increase in reaction (C) with a corresponding decrease in (B). Although in many of the experiments this correction is not large the data plotted in Fig. 2 have been corrected in accordance with these observations. When two or more points were obtained under the same condi-

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(4) F. Feigl, "Qualitative Analysis by Spot Tests," Nordemann Publishing Co., New York, N. Y., 1939.

tions the average was used for plotting. All the results in this plot are for ten hour exposures. The line shown is drawn to fit the equation

$$Ce^{+3} = 117.9 + 2(CO_2 - (H_2 - 27))$$

The value of the intercept, 117.9, is the number of micromoles of cerous ion produced when no formic acid is present. The two points which appear well off the line were obtained at high formic acid concentrations under conditions, already mentioned, where the material balance was not good and are therefore not considered as good tests of the stoichiometry. Since complete analyses were not made for the last points included in Table III no correction of the carbon dioxide value was made in plotting them. It is apparent, however, from an inspection of the points immediately preceding these in the table that the correction if made would be small.

In order to explain the observations which have been given we have considered the following list of reactions

$$H_2O \longrightarrow H + OH \quad (1)$$
$$2OH \longrightarrow H_2O_2 \quad (2a)$$
$$2H \longrightarrow H_2 \quad (2b)$$
$$H + O_2 \longrightarrow HO_2 \quad (3)$$
$$Ce^{+4} + H \longrightarrow Ce^{+3} + H^+ \quad (4)$$
$$Ce^{+4} + H_2O_2 \longrightarrow Ce^{+3} + HO_2 + H^+ \quad (5)$$
$$Ce^{+4} + HO_2 \longrightarrow Ce^{+3} + H^+ + O_2 \quad (6)$$
$$H + OH \longrightarrow H_2O \quad (7)$$
$$HCOOH + OH \longrightarrow H_2O + HCOO \quad (8)$$
$$HCOOH + H \longrightarrow H_2 + HCOO \quad (9)$$
$$Ce^{+4} + HCOO \longrightarrow Ce^{+3} + CO_2 + H^+ \quad (10)$$
$$OH + HCOO \longrightarrow H_2O + CO_2 \quad (11)$$
$$OH + HO_2 \longrightarrow H_2O + O_2 \quad (12)$$
$$H + H^+ \longrightarrow H_2^+ \quad (13)$$
$$H_2^+ + OH \longrightarrow H_2O + H^+ \quad (14)$$

The reactions 1–7 and 12–14 represent the possibilities in the absence of formic acid and reactions 8–11 are the additional ones introduced by the presence of formic acid. Reaction 1 is in accord with the usual assumption that the essential effect of the ionizing radiation on the water is to break it into hydrogen and hydroxyl radicals which may then enter into reactions with the solutes or react in accordance with reactions 2a, 2b and 7. It is apparent from our results that there is always some hydrogen formed no matter how high a concentration of oxidizing solute we may have present. This hydrogen may be thought of as having been formed by reaction 2b in regions where the concentration of these radicals is high.[5] The corresponding amount of hydrogen peroxide formed by reaction 2a would react with ceric ion in our experiments and hence not be detected. Although these two reactions are always possible, the failure to influence the limiting amount of hydrogen formed by the concentration of the solutes added suggests that the peroxide and hydrogen instead of being formed by 2a and 2b may be formed by the reaction of an activated water molecule with another molecule of the solvent.[6]

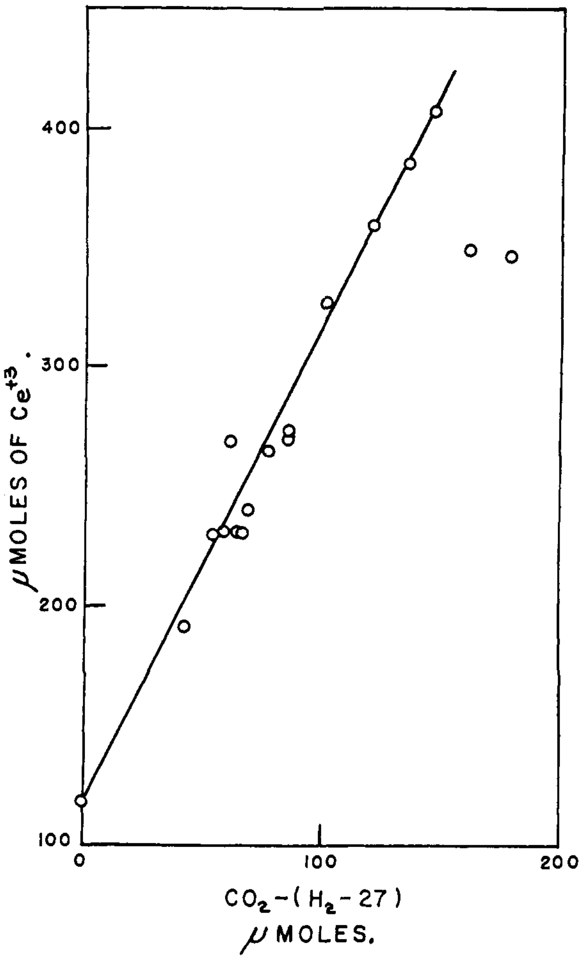

Fig. 2.—Correlation of amounts of cerous ion and carbon dioxide produced by irradiation for ten-hour periods.

It is possible to draw some qualitative conclusions concerning the relative importance of the various reactions mentioned. The competition between reaction 8 and reactions 7, 12 and 14, causes the dependence of the amounts of cerous ion and carbon dioxide produced on the concentration of formic acid. Similarly, the lack of dependence of the rate of production of cerous ion on the ceric concentration means that the reactions of the ceric ion with the various intermediates do not compete with the other reactions which may involve these same intermediates. No competition is indicated for reaction 5. The close correlation between the extra amount of ceric ion reduced and the amount of formic acid oxidized when the latter substance is introduced into the system indicates that reaction 11 must be negligible compared to 10. With regard to the other reactions it can be said that the reactions with ceric ion are too slow to enter the competition in the small elements of volume where the ions are formed but once a radical gets out of this track the principal method whereby it is destroyed is by a reaction with the ceric ion.

It has been pointed out that at high formic acid concentrations there is a noticeable discrepancy between the number of equivalents oxidized and those reduced. The addition of oxygen to the reacting system tended to reduce this discrepancy but did not

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[5] A. O. Allen, *Discs. Faraday Soc.*, **12**, 79 (1952); also, A. O. Allen, *Radiation Research*, **1**, 85 (1954).

[6] J. Weiss, *Ann. Rev. Phys. Chem.*, **4**, 143 (1953).

otherwise affect the reaction. We believe that the role of the oxygen is to bring about the oxidation of some side products, such as formaldehyde, although we have not been able to establish the nature of those products. Of course another possibility is that the oxygen prevents the formation of formaldehyde or other side product.

The problem of expressing the results in a mathematical form differs from that encountered in the usual kinetic study in that the intermediates are not formed in a uniform manner throughout the solution but are distributed at relatively high concentrations along the paths taken by the electrons produced by the X-ray. Under such conditions the possibility must be considered that the concentrations of the radicals will change not only because of the reactions indicated in the mechanism but also because of the tendency of the radicals to diffuse out of the regions in which they were formed. In order to obtain an equation to apply to our data it is only necessary to obtain the total effect corresponding to integration from zero to infinity with respect to time. We have carried out such calculations on the basis of two limiting assumptions with respect to the diffusion process. First, we have assumed that the diffusion out of the original zone can be neglected; for the second method we assumed that the diffusion was fast with respect to the reactions in the mechanism so that the radicals, instead of being distributed uniformly in the reaction zone, are in a Gaussian distribution about the axis of a cylinder.[7] Both treatments lead to the same equation, which leads us to believe that the diffusion effect is not important in determining the final state.

The results can be expressed in accordance with the first method with the aid of the following simplifying assumptions: (1) the reaction of the hydroxyl radical takes place in small isolated volumes of solution with no overlap of the volumes; (2) concentrations within any one of these volumes can be represented by some average concentration at any time, *t*; (3) the concentration of hydroxyl radical is equal to the sum of the concentrations of atomic hydrogen, HO_2, and H_2^+; (4) the rate constants for the reactions 7, 12 and 14 are essentially equal; (5) in the presence of oxygen (a condition which necessarily prevails most of the time) hydrogen atoms react with oxygen to form HO_2 rather than with formic acid. The third of these assumptions is equivalent to saying that we do not consider that it is important whether a hydrogen atom is free or has formed one of the other possible intermediates. On the basis just given we may write

$$-\,\mathrm{d(OH)}/\mathrm{d}t = k_8(\mathrm{HCOOH})(\mathrm{OH}) + k_7(\mathrm{OH})^2 \quad \text{(I)}$$

Since the formic acid changes relatively little during the irradiation its concentration may be treated as a constant and the above expression integrated to give

$$(\mathrm{OH}) = (\mathrm{OH})_0 k_8(\mathrm{HCOOH})e^{-k_8(\mathrm{HCOOH})t}/k_8(\mathrm{HCOOH}) + k_7(\mathrm{OH})_0(1 - e^{-k_8(\mathrm{HCOOH})t}) \quad \text{(II)}$$

In this expression $(\mathrm{OH})_0$ is the initial concentration of hydroxyl radicals. Similarly we may write for the formic acid

$$-\,\mathrm{d(HCOOH)}/\mathrm{d}t = k_8(\mathrm{HCOOH})(\mathrm{OH}) \quad \text{(III)}$$

Substituting the value for (OH) given by II and integrating with respect to time from zero to infinity gives

$$\Delta(\mathrm{HCOOH}) = (k_8/k_7)(\mathrm{HCOOH}) \ln (1 + k_7(\mathrm{OH})_0/k_8(\mathrm{HCOOH})) \quad \text{(IV)}$$

The number of molecules of formic acid reacting per molecule of hydroxyl (excluding those which form peroxide by 2a) is obtained by dividing both sides of equation IV by $(\mathrm{OH})_0$ to give

$$\begin{aligned}\text{Yield HCOOH} &= \Delta(\mathrm{HCOOH})/(\mathrm{OH})_0 \\ &= (k_8(\mathrm{HCOOH})/k_7(\mathrm{OH})_0) \ln (1 + k_7(\mathrm{OH})_0/k_8(\mathrm{HCOOH})) \\ &= ((\mathrm{HCOOH})/K) \ln (1 + K/(\mathrm{HCOOH})) \quad \text{(V)}\end{aligned}$$

In the last form $K = k_7(\mathrm{OH})_0/k_8$.

It is possible to express the formic acid yield in terms of the amount of cerous ion produced. The increased production of cerous ion in the presence of formic acid is caused by a combination of reactions 8 and 10 in the proposed mechanism. The limit in the amount of cerous produced as the concentration of formic acid is increased indefinitely corresponds to a condition under which all the hydroxyl radicals (except those used in 2a) react in accordance with 8. Under these conditions the total amount of cerous ion formed minus the amount formed in the absence of formic acid is twice the number of hydroxyls reacting. Expressed in micromoles, $\mathrm{Ce}^{+3} - 117.9$ is a measure of the number of hydroxyls reacting with formic acid and the ratio of this quantity to the limiting value is the fraction of the hydroxyls which react with formic acid in any given experiment, *i.e.*, it is what we have called the formic acid yield. Hence

$$(\mathrm{Ce}^{+3} - 117.9)/(\mathrm{Ce}^{+3}{}_{\mathrm{limit}} - 117.9) = ((\mathrm{HCOOH})/K) \ln (1 + K/(\mathrm{HCOOH}))$$

which may be rearranged to

$$(\mathrm{Ce}^{+3} - 117.9)/((\mathrm{HCOOH}) \ln (1 + K/((\mathrm{HCOOH})) = (\mathrm{Ce}^{+3}{}_{\mathrm{limit}} - 117.9)/K \quad \text{(VI)}$$

This equation involves experimentally measurable quantities and the parameter *K*. It was found that the numerical value of the left hand side of the equation showed the expected constancy if *K* was taken as 0.060 and the numerator of the right-hand side taken as 310. Table IV shows the test of the equation and the data are represented graphically in Fig. 3.

TABLE IV

$\dfrac{\mathrm{Ce}^{+3}{}_{\mathrm{limit}} - 117.9}{0.060}$ calcd. from eq. VI.

HCOOH, moles/l.	Ce^{+3}, 117.9 μ moles	$\dfrac{\mathrm{Ce}^{+3}{}_{\mathrm{limit}} - 117.9}{0.060} \times 10^{-2}$
0.00586	73.1	51.5
.01173	115.1	54.2
.02345	151.4	50.9
.0469	198.6	51.4
.1173	242.4	50.0
.2345	279.6	52.3
.469	294.1	52.1
.704	295.1	51.2
.938	301.1	51.8
1.173	299.1	51.0
	Av.	$51.7 \pm 0.7 \times 10^2$

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[7] J. Weiss, *Disc. Faraday Soc.*, **12**, 161 (1952).

Equation VI may also be derived by assuming that the radicals are contained in a cylinder with a Gaussian distribution around the axis of the cylinder.[7] Otherwise the assumptions are essentially the same and the factors in the final equation have the same physical significance.

The total production of hydroxyl radicals in the ceric–formic acid system and hence the total radical pair yield expressed in micromoles is twice the amount of oxygen produced plus one-half the increase in the production of cerous ion caused by the addition of the formic acid. The numerical value is 2 × 42 plus one-half 310 for a total of 239. A corresponding calculation can be made for the oxidation of ferrous solutions by dissolved oxygen using the same radiation. In that case, if we accept Hart's[8] mechanism, the total amount of ferrous ion oxidized (ferric ion formed) is given by the number of hydroxyls reacting with the ferrous ion plus twice the number of moles of peroxide formed by the reaction we have listed as 2a, plus three times the number of HO_2 radicals (formed by the reaction 3 in our mechanism). If we combine this statement with the fact that the total numbers of hydrogen atoms and hydroxyl radicals formed must be equal we find that the total number of radical pairs produced is one-fourth the sum of the number of moles of ferric ion and six times the amount of hydrogen formed. In a ten-hour irradiation of such a ferrous solution in our reaction cell we found that the amount of ferric produced was 719 micromoles and the hydrogen was 35.3. These values lead to a radical yield of 233, which we consider to be in excellent agreement with the one obtained for the ceric–formic system. This agreement may be taken as lending support to both mechanisms and to the idea that under the limiting conditions all of the radicals produced are entering into secondary reactions.

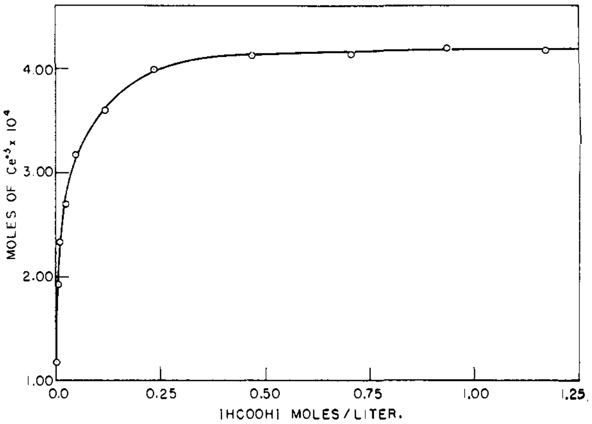

Fig. 3.—Cerous ion produced as a function of the formic acid concentration.

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[8] E. J. Hart, THIS JOURNAL, **73**, 1891 (1951).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, SIR JOHN CASS COLLEGE]

The Kinetics and Mechanism of the Reaction of Formaldehyde with Dimedone. Part I

BY D. SPENCER AND T. HENSHALL

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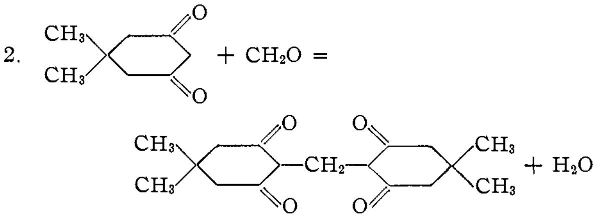
A kinetic study has been made of the reaction between dimedone and formaldehyde under both acid and alkaline conditions. The reaction has been shown to be of the first order with respect to both reactants. The reaction rate is considerably affected by the hydrogen-ion concentration of the solution, and reaches a maximum value at *p*H 8.5. A reaction sequence based on an ion-polar molecule interaction has been proposed. From this, on analysis, a rate equation has been derived which is in close agreement with the experimental results over the *p*H range of 1 to 14.

The reaction between dimedone (5,5-dimethylcyclohexanedione-1,3) and formaldehyde is represented stoichiometrically as a simple condensation of one molecule of formaldehyde with two molecules of dimedone by the elimination of one molecule of water according to



(I)

The nature of possible intermediates in this reaction is suggested[1] by the closely related, though often considerably more complex condensation products of formaldehyde with phenols in which, under certain conditions, almost quantitative yields of methylene compounds similar in structure to I can be obtained.

Moreover, a quantitative analytical study of the reaction of dimedone and formaldehyde,[2] in which the amounts of I precipitated in a given time from buffer solutions containing known amounts of the aldehyde with a slight excess of dimedone were determined, showed (a) that a theoretical yield of product was obtained only at *p*H 4.6 and (b) that in solutions more acid than this, the yield of product diminished rapidly, even on allowing the reaction mixture to stand for many days.

The lower yield of I obtained above *p*H 4.6 may be reasonably interpreted as a solubility effect; but the decrease in yield in more acid solutions could not be accounted for unless it be assumed that the rate of formation of I decreased rapidly with in-

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[1] J. F. Walker, "Formaldehyde," Reinhold Publ. Corp., New York, N. Y., 1944.

[2] J. H. Yoe and L. C. Reid, *Ind. Eng. Chem., Anal. Ed.*, **13**, 238 (1941).