iodine molecules was over two hundred in these experiments.

It would seem necessary to conclude that the difference in the quantum yields of gaseous products in Fluorochemical 0–75 and perfluorodimethylcyclobutane solvents is due mainly to a difference in the quenching efficiencies of the two solvents. Studies of the photolysis of acetone in mixtures of the two solvents have been made, but since the data do not fit any simple quenching mechanism, the results are inconclusive and will not be reported in further detail. The photolysis of acetone in completely fluorinated Fluorochemical 0-75 should be useful in establishing whether or not quenching is responsible for the difference in the quantum yields in these fluorinated solvents. We are presently engaged in carrying out these experiments.[20]

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PITTSBURGH, PA.

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Tracer Experiments on the Oxidation of Oxalic Acid

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The exchange of oxygen between oxalic acid and the solvent water at 25° follows the rate law, Rate (g. atom l.$^{-1}$ min.$^{-1}$) = 7.4×10^{-3} $(H_2C_2O_4)$ + 4.4×10^{-2} $(H_2C_2O_4)(H^+)$. When oxalic acid is oxidized by Ce(IV) or hypochlorous acid, none of the oxygen in the CO_2 originates in the solvent or oxidizing agent. When H_2O_2 is the oxidizing agent, approximately $^2/_3$ atoms of oxygen for each CO_2 are derived from the oxidizing agent. No evidence was found for exchange between CO_2 and $C_2O_4^{=}$ induced by the oxidation of $C_2O_4^{=}$ by Mn(III).

Many kinetic measurements have been made on reactions in which oxalic acid or its ions in water reacts with oxidizing agents, but important problems of mechanism remain unsolved in many of the systems. Some of these can be resolved by oxygen-tracer experiments, which in principle can answer questions such as these: Is oxygen from the solvent incorporated into the CO_2 which is evolved? Is oxygen transferred to oxalate from the oxidizing agent on reaction? We are reporting the results of such oxygen-tracer experiments with selected oxidizing agents as the principal theme of this paper. Results on the related study, the exchange of oxygen between oxalate and water, are also reported, as well as those obtained in a search for evidence of a free radical intermediate in the oxidation of oxalate by Mn(III).

Part A. Oxygen Exchange between Oxalate and Water

Experimental

Solutions of oxalic acid of normal isotopic composition in normal water were prepared at three acidities. Each solution was mixed with O^{18}-enriched water at 25°, the temperature at which the exchange reaction took place. Samples were withdrawn at intervals, rapidly cooled to 0° and oxidized with acidic Ce(IV). The CO_2 produced was swept from the solution with a stream of N_2, dried and condensed for isotopic analysis. This method of isotopic assay anticipates the results which properly belong in the next section and are there reported. These results prove that Ce(IV) liberates CO_2 from oxalic acid in water without change in the isotopic composition of the oxygen. The small exchange that does take place can be attributed to direct exchange between CO_2 and solvent during the time the CO_2 stays in solution.

Results

The data, consisting of the isotopic composition of the CO_2 as a function of time, were treated in the usual way, plotting $2.3 \log (N_\infty - N_0)/(N_\infty - N_t)$ against t to determine the exchange specific rate k for an experiment (N's represent the atom fraction O^{18} at the times defined by the subscripts). Then for each experiment a value of R, the rate of exchange in g. atom of oxygen per liter per minute is calculated using the equation[1]

$$R = k\,\frac{4(H_2O)[\text{oxalic}]}{(H_2O) + 4[\text{oxalic}]}$$

The values R for the three sets of concentration conditions are summarized in Table I. Throughout, total stoichiometric concentrations are represented by formulas enclosed in brackets, actual concentrations allowing for the distribution among various equilibrium forms, by the formulas in parentheses.

TABLE I

THE RATE OF EXCHANGE OF OXYGEN BETWEEN OXALATE AND WATER

(Concentrations recorded are stoichiometric)

$[H_2C_2O_4]$	$[Na_2C_2O_4]$	$[HClO_4]$	Rate, g. atom l.$^{-1}$ min.$^{-1}$
0.100	...	1.00	4.6×10^{-3}
.100	...	..	4.2×10^{-4}
.050	0.050	..	1.98×10^{-5}

To interpret these rate data, the equilibrium compositions of the solutions must be calculated, taking into account the two equilibria

$$H_2C_2O_4 = H^+ + HC_2O_4^- \qquad K_1$$

$$HC_2O_4^- = H^+ + C_2O_4^- \qquad K_2$$

At the two higher acidities, only the first equilibrium is important. The values of K_1 for all of the conditions were calculated from the equation

$$\log K_1 = \log K_1^0 - \log \frac{\gamma_{H^+}\gamma_{HC_2O_4^-}}{\gamma_{H_2C_2O_4}}$$

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(1) A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 11.

with $K_1{}^0 = 5.36 \times 10^{-2}$ [2] and $\gamma_{H^+}\gamma_{HC_2O_4^-}$ assumed to be given by $\gamma_{H^+}\gamma_{Cl^-}$. The values of $\gamma_{H^+}\gamma_{Cl^-}$ were taken from Harned and Owen.[3] The value of K_2 which is needed for the experiment at lowest acidity was estimated as 1.34×10^{-4} from $K_2{}^0 = 5.18 \times 10^{-5}$ [4] and activity coefficients calculated by the equation

$$\log \gamma = \frac{-0.509Z^2\mu^{1/2}}{1 + 0.328 \times 10^8 a_i \mu^{1/2}}$$

where the values of a_i were taken from Kielland's table.[5]

The results of the calculations for the three solutions are summarized in Table II.

TABLE II

EQUILIBRIUM COMPOSITIONS OF THE SOLUTIONS

Soln.	$K_1 \times 10^2$	$K_2 \times 10^4$	$(H_2C_2O_4)$	(H^+)	$(HC_2O_4^-)$
1	8.2	..	0.0925	1.008	0.0075
2	8.5	..	0.041	0.059	.059
3	8.5	1.34	2.65×10^{-3}	2.43×10^{-3}	.0923[a]

[a] $(C_2O_4^{=}) = 5.1 \times 10^{-3}$.

It is found that the results for the three experiments cannot be accounted for by a single exchange path, but that a two term rate law is required, $R = k_1(H_2C_2O_4) + k_2(H_2C_2O_4)(H^+)$. When the coefficients k_1 and k_2 are chosen as 7.4×10^{-3} min.$^{-1}$ and 4.4×10^{-2} M^{-1} min.$^{-1}$, the values of R calculated for the three sets of concentration conditions are 4.8×10^{-3}, 4.1×10^{-4} and 1.99×10^{-5}, in good agreement with those observed.

The rate of exchange is slow enough to ensure success of tracer experiments requiring differentiation between solvent oxygen and oxalate oxygen.

Part B. Tracer Experiments on the Oxidation of Oxalate

General Procedure.—In the oxygen tracer experiments it is essential to remove the product CO_2 rapidly so as to minimize the exchange of oxygen with solvent. This was done by sweeping a continuous stream of N_2 through the solution during the reaction. The stream of gas then was passed through a trap immersed in Dry Ice–methanol to condense out water vapor, and through a trap cooled by liquid nitrogen to condense carbon dioxide. For the reactions with hypochlorous acid, an additional trap, containing solid potassium iodide and cooled by Dry Ice–methanol, was interposed between the two traps already described.

Oxidation by Ce(IV).—The solution for reaction was made up in water enriched in O^{18}. It contained 0.014 M $Ce(HSO_4)_4$, 0.57 M H_2SO_4 and 0.014 M $H_2C_2O_4$ (this reagent was of normal isotopic composition). The temperature of reaction was 0°; the reaction did not take place instantly but was substantially complete after 10 minutes.

When compared to a sample of CO_2 prepared by oxidizing oxalate of ordinary isotopic composition in water of ordinary isotopic composition, the CO_2 was found to be enriched in O^{18} by a factor of 1.046. The enrichment factor for the solvent was 3.91. Thus only 1.6% of the oxygen atoms in the CO_2 formed are derived from the solvent. It is likely that this exchange is not a property of the oxidation mechanism but takes place after the CO_2 is formed. This conclusion is indicated by experiments in which Na_2CO_3 is acidified in enriched water, and in water of normal isotopic composition (keeping conditions as far as possible similar to those in the oxidation experiments), and comparing the isotopic composition of the two samples of CO_2. Exchange of the order of 2 atom % is observed in such experiments.

Oxidation by Hypochlorous Acid.—In these experiments, the oxidizing agent and solvent were at exchange equilibrium[6] but the oxalate had a different isotopic composition.

The solution of HOCl was prepared by passing Cl_2 into a solution of silver nitrate until a slight excess was present, then filtering off the silver chloride. Preliminary experiments showed that under the conditions chosen for the tracer experiments (0°, ~0.015 M HOCl, 0.022 M $H_2C_2O_4$), more than 95% of the reducible chloride had disappeared during the 3 minutes allowed for the reaction. In the tracer experiment, with the solvent enriched in O^{18} by the factor 3.21, the CO_2 liberated from oxalate of normal isotopic composition was found to be enriched by the factor 1.042. Thus only about 1.8% of the oxygen atoms in the CO_2 originate in the solvent. As in the experiment with Ce(IV) as the oxidizing agent, this slight mixing of oxygen isotopes can be attributed to exchange of the product CO_2 with solvent.

Hydrogen Peroxide as Oxidizing Agent.—The reaction of hydrogen peroxide with oxalate is accelerated by acid,[7] and under conditions which make the reaction conveniently rapid, the exchange of oxygen between oxalic acid and solvent is also rapid. The tracer experiment therefore was done having oxalate and water at exchange equilibrium, but with the oxidizing agent differing from them in isotopic composition.

The oxalic acid was brought into exchange equilibrium with water enriched in O^{18} by keeping the solution, which also contained 1 M $HClO_4$, at 25° for 5 days. The tracer experiment was done using a solution of composition 2.3 M $HClO_4$, ~ 1.3 M H_2O_2 and 0.05 M $H_2C_2O_4$. The reaction was allowed to proceed for 30 minutes at 25°, and the carbon dioxide formed was removed continuously. The enrichment ratio of the CO_2 was found to be 2.430, while that of the oxalate before reaction was 3.09. If no allowance is made for exchange of CO_2 with solvent, the number of peroxide oxygens introduced for each molecule of CO_2 is calculated as 0.63.

An experiment using Na_2CO_3 as source of carbon dioxide, designed to check on the exchange to be expected for CO_2 under the present experimental conditions, showed this to amount to 3.8 atom %. When correction is made for the exchange of CO_2 with solvent, the number of peroxide oxygens introduced for each molecule of CO_2 is calculated as 0.68.

Part C. A Test for Induced Exchange between CO_2 and Oxalate

Numerous researches[8-10] provide evidence for a radical being formed on the oxidation of oxalate by certain reducing agents. This radical is presumably CO_2^- or $C_2O_4^-$. Either radical might be expected to catalyze the exchange of $C_2O_4^-$ with CO_2, as for example by

$$CO_2{}^* + CO_2{}^- \rightleftharpoons C_2O_4{}^{*-}$$

$$C_2O_4{}^{*-} + C_2O_4{}^- \rightleftharpoons C_2O_4{}^{*-} + C_2O_4{}^-$$

The reaction of Mn(III) with $C_2O_4^{=}$ was chosen as one likely to involve a radical as intermediate.[11-13] It is to be recorded at the outset that no evidence for induced exchange was obtained. This negative result in no way affects published conclusions concerning the mechanism of the Mn(III)–oxalate reaction and is worthy of record only as providing a point of departure for other work on this question which may be undertaken.

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(2) L. S. Darken, THIS JOURNAL, **63**, 1007 (1941).

(3) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 2nd Ed., 1950, p. 547.

(4) H. S. Harned and L. D. Fallon, THIS JOURNAL, **61**, 3111 (1939).

(5) J. Kielland, *ibid.*, **59**, 1675(1937).

(6) M. Anbar and H. Taube, *ibid.*, **80**, 1073 (1958).

(7) W. H. Hatcher and G. W. Holden, *Trans. Roy. Soc. Can.*, **18**, (III) 231 (1924); **21**, (III) 237 (1927).

(8) R. O. Griffith and A. McKeown, *Trans. Faraday Soc.*, **28**, 752 (1932).

(9) H. F. Launer, THIS JOURNAL, **54**, 2597 (1932); **55**, 865 (1933).

(10) G. H. Cartledge, *ibid.*, **63**, 906 (1941).

(11) H. Taube, *ibid.*, **69**, 1418 (1947); **70**, 1216, 3928 (1948).

(12) F. R. Duke, *ibid.*, **69**, 2885 (1947).

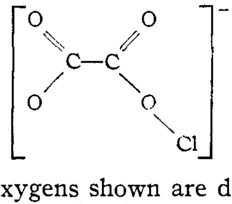
(13) S. J. Adler and R. M. Noyes, *ibid.*, **77**, 2036 (1955).

Our experiment was done in the following way. The reaction flask was fitted at the top with a ground glass joint and a stopcock and was provided with two compartments which served to keep the reactant solutions separate until the time of mixing. One compartment held a solution containing $KMnO_4$ and H_2SO_4 (20 ml., 0.10 M $KMnO_4$, 1.3 M H_2SO_4) and the other a solution containing oxalic and Mn^{++} (28.5 ml., 0.26 M $H_2C_2O_4$, $\sim$ 0.35 M $MnSO_4$). CO_2 enriched in C^{14} (the amount contained in 0.050 g. of $BaCO_3$, specific activity of 1.5×10^{-3} curie $g.^{-1}$) was introduced into the evacuated space above the solution, and the system allowed to equilibrate for a day at room temperature. It is estimated that approximately $^1/_2$ of the CO_2 was dissolved in the solution. The solutions were mixed, and after the color of Mn(III) had been discharged, the solution was degassed. The residual oxalate was oxidized by Ce(IV), and the CO_2 liberated counted in an ionization chamber. The counting rate was found not to differ significantly from that for normal CO_2. This result shows that less than 1% of the total active carbon had been introduced into the residual oxalate. On random distribution of the C^{14} dissolved as CO_2 with other forms of C in the solution, $\sim$35% of the total C^{14} would have been expected in the residual oxalate.

Discussion

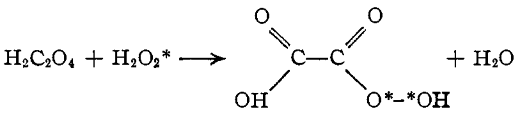
The oxygen-tracer result obtained for the oxidation of oxalate by Ce(IV) is not unexpected. There is no particular reason to suppose that solvent oxygen, or oxygen originating in the coördination shell of the Ce(IV) need be transferred to $C_2O_4^=$ to bring about its oxidation. It is nevertheless reassuring to observe that indeed no oxygen is transferred, and a number of mechanisms which might be considered for the reaction are definitely eliminated by the observation.

The tracer experiment with ClO^- is rather more instructive because ClO^- is known to transfer oxygen in certain oxidation–reduction reactions (partial transfer when $SO_3^=$[14] is reducing agent, essentially complete with NO_2^-[1]). The work of Griffith and McKeown[15] shows that in solutions as acidic as those used in our work, the composition of the activated complex is $HOCl{\cdot}HC_2O_4^-$ (but, as usual, leaving the activated complex undefined with respect to labile solvent molecules). The tracer result we have obtained shows that the activated complex does not decompose to form $CO_3^=$, which would otherwise be a reasonable possibility for an activated complex of the composition given. Conceivably, then, the activated complex has the structure

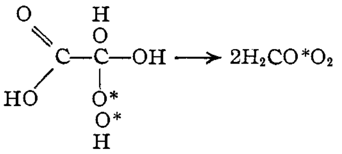


where all the oxygens shown are derived from the oxalate and the reaction is consummated by electron flow so that $2CO_2 + Cl^-$ are the immediate products of the reaction. It is also possible that $ClCO_2^-$ is an intermediate product; our tracer result would require this species to decompose to $Cl^- + CO_2$ rather than hydrolyzing to $CO_3^= + 2H^+ + Cl^-$.

The most interesting tracer result obtained in this study is for the reaction of H_2O_2 with oxalic acid. The fact that the reaction with H_2O_2 is slow unless the solution is strongly acidic fits in with the theory that the reaction requires substitution of OH by OOH.



as has been postulated for the reaction of H_2O_2 in acid with sulfite[16] and nitrite.[17] The tracer result can be understood by assuming that the peroxalic acid decomposes to CO_2 and $CO_3^=$ (no per oxalic acid is detected in $H_2C_2O_4$–H_2O_2 mixtures).[7] Two-thirds of an atom of peroxide oxygen would be lost in the transformation of $CO_3^=$ to CO_2, and the average number of peroxide oxygens left per CO_2 would be $(2 - {}^2/_3)/2 = 0.67$, which is very close to the observed result. An alternative interpretation[18] which explains the tracer result is that an intermediate on the way to peroxalic acid decomposes as



and the carbonic acid decomposes as before. The two formulations can be distinguished by using doubly labeled hydrogen peroxide. A third possibility, that peroxalic acid decomposes to $CO^*O_2^= +$ CO^*O, does seem to be eliminated by the present tracer result.

In principle, the reaction of oxalic acid with hydrogen peroxide, requiring as it does substitution in a carboxyl group, can afford a test of the mechanism of oxygen exchange. This kind of application has been made in the NO_2^-–H_2O_2 reaction.[17] The reaction of hydrogen peroxide with oxalic acid is, however, so slow compared to the exchange that a similar test of mechanism probably can not be made for this reaction. According to the data of Hatcher and Holden, at 25° in 3 M H_2O_2 the rate of oxidation of oxalic acid at unit stoichiometric concentration would be *ca.* 0.8×10^{-3} M $min.^{-1}$, which is only $^1/_5$ of the measured rate of exchange. Thus the effect of H_2O_2 in competing for an intermediate common to the exchange and oxidation reactions could hardly be distinguished from the effect it might exert merely as changing the properties of the solvent. As the acidity increases, the disparity in rates appears to become even greater.

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[14] J. Halperin and H. Taube, THIS JOURNAL, **74**, 375 (1952.)

[15] R. O. Griffith and A. McKeown, *Trans. Faraday Society*, **28**, 518 (1932).

[16] J. Halperin and H. Taube, THIS JOURNAL, **74**, 380 (1952).

[17] M. Anbar and H. Taube, *ibid.*, **76**, 6243 (1955).

[18] This suggestion was made to us by Dr. Ronald Breslow.