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Sixth Technical Report

OXYGEN ATOM TRANSFER PROCESSES

March 1953

Henry Taube
University of Chicago
Department of Chemistry

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Evidence for the Exchange of Hydroxyl Radical with Water

By Otto L. Forchheimer and Henry Taube
EVIDENCE FOR THE EXCHANGE OF HYDROXYL RADICAL WITH WATER
d
Sir:

Other work has shown that the reaction of \(\text{H}_2\text{O}_4\) and \(O_3\) produces a powerful 1e-\textsuperscript{2} oxidizing agent which reacts with \(O_3\), \(\text{H}_2\text{O}_3\) as well as with less reactive substances such as \(\text{Cl}_2\textsuperscript{2-}\), \(\text{Br}_2\textsuperscript{-}\), \(\text{HOAc}\), etc.\textsuperscript{1} It has also been shown that the same species is generated by the reaction of \(\text{HO}_2\text{OH}\) with \(O_3\).\textsuperscript{2} This species has been described as the hydroxyl radical, and the decomposition of \(O_3\) which it catalyzes has been formulated\textsuperscript{3} as taking place by the steps

\[
\begin{align*}
\text{HO} + O_3 & \rightarrow \text{HO} + O_3 \\
\text{HO}_2 + O_3 & \rightarrow \text{HO} + 2O_3
\end{align*}
\]

This reaction scheme suggests a simple tracer experiment for testing exchange of \(\text{HO}\) and \(\text{H}_2\text{O}_3\) since the hydroxyl oxygen is converted to \(O_3\), which is known not to exchange readily with \(\text{H}_2\text{O}\). Hydrogen peroxide chemistry offers no similar convenient means of studying the exchange, since the hydroxyl oxygen in reaction with \(\text{H}_2\text{O}_3\) is presumably converted to water.

\[
\text{HO}_2 + \text{H}_2\text{O}_3 = \text{H}_2\text{O}_3 + \text{HO}_2
\]

This communication presents some results on the exchange of \(O_3\) with \(\text{H}_2\text{O}_3\) induced by the reaction with \(\text{H}_2\text{O}_3\). In all experiments ozonized oxygen of normal isotopic composition \((N = \text{mole fraction of } O^{18} = 2.000 \times 10^{-2})\); all isotopic compositions quoted have been normalized to this value for \(N^2\). More complete experimental results will be presented in a later report, containing also data on related systems.


d

(1) This research is supported by Office of Naval Research under contract N0-on-02025. The funds for the purchase of the mass spectrometer were supplied by the Atomic Energy commission under contract AT(11-1)-92.

(2) W. C. Bray, This Jotl.~tol., 69, 3357 (1940).


(4) W. C. Bray, ibid., 61, 2453 (1945).


d

\[
\text{HO} + O_3 \rightarrow \text{HO} + O_3
\]

\[
\text{HO}_2 + O_3 \rightarrow \text{HO} + 2O_3
\]

water enriched in \(O^{18} (N = 14.6 \times 10^{-1})\). The ratio of gas volume to liquid was approximately 5. After a time, the gas was removed, dried, and residual oxygen \(O_3\) was decomposed and the isotopic composition determined. In an experiment on the direct exchange of \(O_3\) with water, ozonized oxygen at atmospheric pressure, 7% \(O_3\) was left in contact with enriched water, 0.04 \(M\) in \(\text{HClO}_4\) for 5 days. The isotopic composition of the gas remained unchanged at 2.000 \(\times 10^{-1}\). In a typical experiment with \(\text{H}_2\text{O}_3\) present, all conditions were the same except the liquid contained \(9 \times 10^{-2} \text{M} \text{H}_2\text{O}_3\) (normal isotopic composition, \(N = 1.997 \times 10^{-1}\)). After 3 days, during which time 40% of the \(O_3\) disappeared and 80% of the \(\text{H}_2\text{O}_3\), the isotopic composition of the gas was found to be 2.030 \(\times 10^{-1}\).

The results quoted correspond to the exchange of about one-tenth of the oxygen contained in the \(O_3\) which has decomposed. By the mechanism for decomposition which has been suggested, a maximum exchange of one-sixth of the \(O_3\) oxygen can be expected.

It should be stressed that neither the earlier data nor the present data prove that the intermediate in question is \(\text{HO}\). The present exchange data provide additional strong evidence however. \(\text{H}_2\text{O}_3\), \(O_3\), and \(\text{H}_2\text{O}\) do not exchange at all rapidly with water. Of the radicals \(\text{HO}, \text{HO}_2\), and \(\text{HO}_3\), rapid exchange seems possible only for \(\text{HO}\).

More complete experimental results will be presented in a later report, containing also data on related systems.

(5) In alkaline solution extensive exchange of ozone and water does take place.

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The Photochemical Decomposition of Hydrogen Peroxide. Quantum Yields, Tracer and Fractionation Effects

By John P. Hunt and Henry Taube
The quantum yield of the photochemical decomposition of hydrogen peroxide at relatively high light intensity is independent of the concentration of hydrogen peroxide, of acidity and of the presence in the solution of Br\(^-\), Cl\(^-\), NH\(_3\)^+ or Mn\(^{2+}\). At 25°, the limiting quantum yield at \(\lambda = 2537\) Å is 0.96 ± 0.08 and at 0° it is 0.76 ± 0.05. The primary efficiencies are taken as 1/3 of the limiting quantum yields. Tracer experiments show that the oxygen formed in the photodecomposition originates entirely in the hydrogen peroxide. The exchange between O\(_2\) and H\(_2\)O during the photodecomposition is at most very slight. The fractionation effects associated with the non-chain process for decomposition have been determined. They do not appear to be compatible with hydroxyl radicals as the sole net products of the primary act.

The original purpose of the work described in this paper was to measure the isotope fractionation effects in the reaction

\[
\begin{align*}
&\text{HO} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{H}_2\text{O} \\
&\text{H}_2\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{HO} + \text{H}_2\text{O} + \text{O}_2
\end{align*}
\]

using light acting on hydrogen peroxide to generate the radicals. The fractionation factors for these reactions are of interest in comparison with the factors which have been measured for a number of catalysts acting on hydrogen peroxide.\(^1\) In order to determine the fractionation factors in a simple way from measurement on the photodecomposition, it is necessary to choose conditions so that the total decomposition produced by the chain process be large compared to that by the separate path consisting of the chain-initiating and -terminating steps, i.e., the chains must be long. The work of others has demonstrated,\(^2\)\(^-\)\(^4\) and our experience has confirmed, the great difficulty that arises in purifying the solvent and the reagents and otherwise conducting the experiments so that the chain decomposition is restricted to some intrinsic path for the system such as is represented above. The original goal has been set aside at least for the present and, in the work reported here, we have limited our studies to conditions under which the chain decomposition is eliminated. This is achieved by using light of sufficiently high intensity\(^5\) and results in a system which is much less sensitive to impurities.

Our results on the kinetics of the photodecomposition in general confirm those obtained by Lea,\(^6\) and considerably amplify his. In addition to experiments on the quantum yield of the reaction, results obtained in tracer experiments and in the study of fractionation effects are presented and discussed with reference to mechanisms for the primary act and subsequent processes.

**Experimental**

The light source was a G.E. 4-watt germicidal lamp operating from a Sola constant voltage transformer. The light emitted in the wave length region affecting the uranyl oxalate actinometer is almost entirely 2537 Å. Shorter wave lengths are efficiently removed by the glass walls of the lamp. When a Pyrex glass filter was interposed, the effect on the uranyl oxalate actinometer was observed to be only 3% of the effect when it was omitted, thus showing that mercury lines of longer wave lengths contribute little to the light emitted. The lamp was placed in a fused quartz tube closed at one end, and this end was lowered into the neck of the reaction flask. Provision was made for sealing the quartz tube to the mouth of the flask. The flask was fitted with an entry tube for adding solutions, and an exit tube, which could be used to collect evolved gases.

In most of the experiments, the light was used without collimation, the lamp being held several centimeters above the surface of the solution. The light flux for each particular geometry was determined by replacing the hydrogen peroxide solution with an equal volume of actinometer solution.\(^6\) The geometry described required correction of the results for incomplete absorption of light when the hydrogen peroxide was at low concentration. In the worst case this correction was estimated to be 22%. Since the correction cannot be made accurately, a series of quantum yield determinations were made using a collimated light beam which was confined to the central portion of the solution. For this geometry the maximum correction amounted to only 6% and the results agreed with those obtained using full illumination. The solutions were stirred by rocking the reaction cell assembly, or by inserting a glass stirring blade. No difference in results was noted for the two methods.

Except where the influence of tap distilled water was studied, redistilled water was used. The hydrogen peroxide was Merck and Co., Inc., 30%, inhibitor free. The results at high light intensity were found to be independent of lot number of the hydrogen peroxide acid and of the redistilled water, and as the results will show are remarkably independent of the concentration of certain "catalysts."

Analyses for hydrogen peroxide were made by titration with standardized ceric sulfate solution. This was added in excess and the excess determined by titration with standardized ferrous sulfate solution using the iron orthophenanthroline indicator.

**Results**

Table I contains a summary of the experiments devoted to a study of the kinetics of the photoreaction.

No special effort was made to vary the intensity of the light. However, during the course of the work on changing the geometry, it varied ca. 2-fold, but no effect on \(\phi\) was observed. The observation that the quantum yield is substantially independent of \(\text{H}_2\text{O}_2\) further supports the conclusion that it is also independent of the rate of absorption of light since the number of quanta absorbed per unit volume changes. The rate of absorption of light was \(< 5 \times 10^9\) quanta \(\text{cm}^2\) sec. \(\text{cm}^2\) for all the experiments.

In some experiments, the effect of passing gases through the hydrogen peroxide solution was tested. When \(\text{CO}_2\) was swept through, the rate of decomposition was unaffected. The tests were made with \(\text{H}_2\text{O}_2\) at \(8 \times 10^{-3}\) M, with acid at \(10^{-4}\) M and at \(1\) M at 0°. Under the same conditions, \(\text{H}_2\) does affect the rate, enhancing it when the gas is passed at a high rate. When \(\text{H}_2\) was passed into a solution of potassium iodide after leaving the reaction vessel, only with \(\text{O}_2\) was a noticeable amount of oxidizing agent carried...
The reaction is followed by the measurement of fractionation factors which are related to the isotopic composition of water of normal isotopic composition. After the solutions of hydrogen peroxide were enriched in oxygen with Ce(IV) showed an increase in the fraction of the oxygen distil. The presence of Ce(IV) at 0.011 was found to be enriched in oxygen by 0.117 X 10^-4. The ratio of N_2 to N_2 is given by:

\[
\frac{N_2}{N_2} \frac{2(N_2 - 2N_2) - 2(N_2 - 1)}{1 - N_2}
\]

The sum and ratio of \( f_1 \) and \( f_2 \) being known, each factor can be calculated. The highest precision in measuring \( f_1 \) can be obtained by comparing \( N_2 \) after very small fractional decomposition with \( N_2 \). In this experiment, \( N_2 \) was obtained with added acid, substituting tap distilled water for the residual water introduces a chain decomposition. At 0°C with added acid, the corresponding substitution caused only a slight increase in \( f_1 \) (cf. experiments 7 and 8, Table I).

Discussion

Lea has shown that at sufficiently high light intensity (> 2.4 X 10^12 quanta 1^-1 sec^-1) when (H_2O) is ca. 0.01 M) the quantum yield for the decomposition of hydrogen peroxide approaches a limit which is independent of acidity and of the concentration of hydrogen peroxide. Our observations made in the range of high light intensity confirm these conclusions. However, the limiting value of \( \phi \) (0.98 ± 0.05) at 25°C we have measured is lower than that obtained by Lea, 1.39 ± 0.11. We are unable to account for the difference.

The observation that \( \phi \) decreases as markedly as it does when the temperature falls proves that the limiting value of \( \phi \sim 1.0 \) at 25°C cannot be attributed to a primary efficiency of unity. Two mechanisms which are consistent with the requirement on the primary efficiency, with the kinetics of the change and which otherwise appear reasonable are

\[
\begin{align*}
1 & \quad \text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{HO}_2 \\
2 & \quad \text{HO}_2 + \text{H}_2\text{O} = \text{HO}_2 + \text{H}_2\text{O} \\
3 & \quad 2\text{HO}_2 = \text{H}_2\text{O}_2 + \text{O} \\
\end{align*}
\]

(1) and (2) followed by (3) and (4) as above.

A reaction scheme in which the products of the primary act are H and H_2O has been considered but rejected because changing the concentration...
of oxygen over a wide range has no effect on the rate. Oxygen competes effectively against \( \text{H}_2\text{O}_2 \) for hydrogen atoms,\(^1\) and would therefore cause a decrease in \( \phi \) if hydrogen atoms were present.

Both mechanisms I and II are consistent with the tracer experiments. By each mechanism a limiting value of \( \phi \) is reached which is twice the primary efficiency. The primary process can be considered in terms of the scheme

\[
\begin{align*}
\text{H}_2\text{O}_2 + h & \rightarrow \text{H}_2\text{O}_2^* \\
\text{H}_2\text{O}_2^* & \rightarrow \text{H}_2\text{O}_2 + \text{H}_2 \\
\text{H}_2\text{O}_2 & \rightarrow \text{dissociation, } h
\end{align*}
\]

\( \text{H}_2\text{O}_2^* \) represents the activated entity, whether an electronically excited species or radicals trapped in a solvent cage. Using the limits of \( \phi \) as establishing the primary efficiencies as 0.49 and 0.38 at 25 and 0°C, respectively, \( k_p/k_d \) at the two temperatures is 0.93 and 0.61. If the temperature coefficient of \( k_d \) is assumed to be unity, the activation energy corresponding to dissociation to effective products is 2.9 kcal. This value seems reasonable in comparison with \( \alpha \), 7 kcal, for the corresponding process for bromine and the value for chlorine (wave length dependent) of \( \alpha \), 3 kcal.\(^2\) In all cases, the values represent lower limits for the activation energies of the dissociation steps.

Even if hydroxyl radicals are assumed to be formed as primary products of the absorption of light (mechanism I), it is not unreasonable to suppose that they can undergo reaction in the solvent cage to form the products \( \text{H}_2\text{O} + \text{O} \) (mechanism II). "Escape from the solvent cage" on this interpretation means formation of these products in competition with recombination and deactivation. Good evidence that the reaction of hydroxyls to form \( \text{H}_2\text{O} + \text{O} \) takes place has been presented by Hardwick.\(^3\)

The fact that substances such as \( \text{Br}^- \) and \( \text{Cl}^- \) which are known to react with \( \text{HO}^+ \) do not affect the quantum yield does not prove that \( \text{HO}^- \) is absent. The effect of the reaction

\[
\text{HO} + \text{Br}^- \rightarrow \text{OH}^- + \text{Br}
\]

for example, may merely be to replace reaction 3 by

\[
\text{Br} + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{Br}^- + \text{HO}_2
\]

Similarly with \( \text{Mn}^{++} \), the formation of \( \text{Mn}^{+++} \) would be followed by

\[
\text{Mn}^{+++} + \text{H}_2\text{O}_2 \rightarrow \text{Mn}^{++} + \text{HO}_2 + \text{H}^+
\]

without necessarily producing a change in quantum yield. Evidence that \( \text{Fe}^{+++} \) does participate, although affecting \( \phi \) only slightly at low concentration, is that \( f_o \) and \( f_j \) change when \( \text{Fe}^{+++} \) is added. The changes in the fractionation factors prove that new substances are reacting with \( \text{H}_2\text{O}_2 \) when \( \text{Fe}^{+++} \) is present. When tap distilled water replaces redistilled water, a chain decomposition of hydrogen peroxide is initiated. The values of \( f \) are different from those observed when the limiting quantum yield is observed, and show that new intermediates are involved. It is very doubtful that these are \( \text{HO} \) and \( \text{H}_2\text{O}_2 \) and they are presumably formed from some impurity, dissolved or solid, in the tap distilled water. The experiments with \( \text{Fe}^{+++} \) added are difficult to evaluate quantitatively. At \( 10^{-4}A \text{M} \) \( \text{Fe}^{+++} \) only 3% of the light is absorbed by \( \text{H}_2\text{O}_2 \); however, the quantum yield is decreased by only 40%. A question of interest which will require more data to be settled is whether light absorbed by \( \text{Fe}^{+++} \) is also photochemically effective. If \( \text{Fe}^{+++} \) acts as an efficient internal filter, it must act also to increase the chain length since it produces a relatively slight change in \( \phi \) when present in sufficient amount to absorb nearly all the light. The decrease in \( \phi \) produced by \( \text{Ce}^{+++} \) may be due to an internal filter action.

It is of interest to consider the measured values of \( f_o \) and \( f_j \) in relation to mechanism I and II. For mechanism I, \( f_o = f_o f_i \) and \( f_j = f_j \). \( f_i \) describes the discrimination between isotopic forms of \( \text{H}_2\text{O}_2 \) in reaction (1), \( f_o \) in reaction (3) and \( f_j \) describes the isotope discrimination when \( \text{HO}_2 \) forms \( \text{O}_2 \). On the basis of mechanism I, the fractionation of isotopes in forming water takes place only in the primary act (\( \text{HO} \) once formed yields water with no further isotope discrimination). The observations on \( f_j \) are inconsistent with this mechanism since it provides no way of explaining the change of \( f_j \) with acidity. Further, the magnitude of the fractionation effect in low acid (\( f_j = 0.977 \)) seems too great to be attri-

### Table II

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<th>( \text{H}_2\text{O}_2 ) added</th>
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<th>( \phi_o )</th>
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<td>0.815</td>
<td>0.988</td>
<td>0.600  0.960</td>
</tr>
<tr>
<td>0.06</td>
<td>1.00</td>
<td>25 ± 1</td>
<td>0.679</td>
<td>0.991</td>
<td>0.995  0.992</td>
</tr>
<tr>
<td>0.06</td>
<td>1.00</td>
<td>25 ± 1</td>
<td>0.697</td>
<td>0.991</td>
<td>0.995  0.992</td>
</tr>
<tr>
<td>0.06</td>
<td>1.00</td>
<td>25 ± 1</td>
<td>0.740</td>
<td>0.991</td>
<td>0.993  0.993</td>
</tr>
<tr>
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<td>1.00</td>
<td>25 ± 1</td>
<td>0.67</td>
<td>0.991</td>
<td>0.968  0.61</td>
</tr>
<tr>
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<td>1.00</td>
<td>25 ± 1</td>
<td>0.687</td>
<td>0.981</td>
<td>0.951  0.966</td>
</tr>
</tbody>
</table>

\[10^{-4} \text{M} \text{Fe}^{+++}\]

The transition from the limiting decomposition to the chain decomposition has been discussed by Lea. The slight trend in $\phi$ with concentration of hydrogen peroxide (Table I, experiments 1-4 and 5-7) is presumably due to a residual chain decomposition, which diminishes as the peroxide concentration decreases. It is by no means certain that the chain decomposition which sets in is carried by HO and HO$_2$. The difficulty that has been experienced in obtaining reproducible data when the chain lengths are long makes it questionable to assume that the chain carriers are these radicals in any particular case. The fractionation factors $f_0$ and $f_1$ should be useful in characterizing the intermediates in future work. They have the advantage over rate measurements that they are independent of chain length, and are affected only by changing the identity of the intermediates. Thus an accidental inhibitor that acts only by breaking chains will affect the quantum yield but not the values of $f_0$ and $f_1$. It is assumed in these remarks that the chains are long enough so that the principal path for decomposition of H$_2$O$_2$ is by the chain mechanism.

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