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W. H. Rodebush and M. H. Wahl

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# The Reactions of the Hydroxyl Radical in the Electrodeless Discharge in Water Vapor

W. H. Rodebush and M. H. Wahl, *University of Illinois*

In a study of the reactions occurring in the electrodeless discharge in water vapor consistently high yields of hydrogen peroxide were obtained. A number of reactions have been studied and by a process of elimination a mechanism for the formation of hydrogen peroxide from hydroxyl has been suggested. In the course of some spectrographic investigations of the electrodeless discharge in water vapor some new bands, with heads at 3564 and 3328A, were observed which are probably due to an ionized hydroxyl. These bands were not present in the uncondensed electrode discharge but appeared in the condensed electrode discharge at low pressures.

WHEN a discharge is passed through water vapor the so-called "water" bands are excited. These bands are known to be due to the hydroxyl radical and it is supposed that an electron, having an energy of about nine volts, dissociates a water molecule into a hydrogen and an excited hydroxyl, which then emits the characteristic radiation,

$$HOH = H + OH. \qquad (1)$$
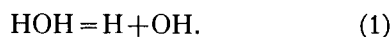
Even with the weakest discharge the hydroxyl bands are emitted with a surprising intensity. This would indicate the possibility of obtaining a high concentration of hydroxyl and numerous attempts have been made to study the reactions of this molecule. In this laboratory an attempt was made to obtain a molecular beam of hydroxyl but the attempt failed because no chemical reaction characteristic of hydroxyl was discovered and it was therefore uncertain as to whether hydroxyl itself were present in the beam. Abroad, Steiner[1] and Bonhoeffer[2] made similar attempts to study the chemical behavior of hydroxyl, likewise with negative results. Finally Bonhoeffer and Pearson[2] published an account of an unsuccessful attempt to obtain the hydroxyl bands in absorption. They reached the conclusion that the hydroxyl concentration was extremely low because of the rapid disappearance of hydroxyl by the reaction,

$$OH + OH = H_2O + O. \qquad (2)$$
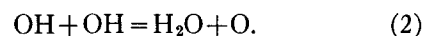
It occurred to us that if this reaction takes place, a high concentration of atomic oxygen should be present in the vapor which has passed through the discharge and it should therefore be possible to obtain a molecular beam of atomic oxygen which could be identified by well-known methods.[3] In carrying out this result however we discovered that there was very little oxygen, either atomic or molecular, present in the discharge and that large yields of hydrogen peroxide were obtained, whereas Bonhoeffer and Pearson had reported only traces of hydrogen peroxide to be formed. This made it appear doubtful that reaction (2) was occurring and made necessary a careful study of the reactions actually taking place in the water vapor discharge.

Experimental

In the study of the chemical reactions the electrodeless discharge was used. The apparatus by which the discharge was produced was essentially the same as that described in a previous article.[4] A flow system was used in all the experiments. The water reservoir was made from 5 mm Pyrex tubing which had previously been calibrated so that the amount of water used during a run could be measured. The height of the water column was followed with a cathetometer. The

[1] Steiner and Bay, Zeits. f. physik. Chemie **3B**, 149 (1929).

[2] Bonhoeffer and Pearson, Zeits. f. physik. Chemie **14B**, 2 (1931).

[3] Kurt and Phipps, Phys. Rev. **34**, 1357 (1929).

[4] Rodebush and Klingelhoefer, J. Am. Chem. Soc. **55**, 130 (1933).

flow of water vapor was regulated by a capillary leak and by the temperature of the bath surrounding the reservoir. Conductivity water was always used in the reservoir.

The discharge was produced in a 200-cc Pyrex flask. Optimum conditions for high yields of hydrogen peroxide were at pressures of 0.1 to 0.2 mm of mercury. Under best conditions the discharge had a vivid red appearance, but if the discharge was too intense blue rings appeared, which followed the turns of the coil, indicating the presence of oxygen atoms. This was confirmed by spectrographic evidence. A better yield of hydrogen peroxide was obtained when the discharge bulb was cooled by a blast of air.

It was found expedient to use a U-tube trap for collecting the sample. In the early course of the work ground glass joint traps, which necessitate the use of stopcock grease, were employed and it was found impossible to obtain consistently large yields of hydrogen peroxide. A second U-tube trap was placed in series with the first to determine if all the sample was caught in the first trap. Two runs indicated that no condensable products escaped through the first trap.

After a run had proceeded the desired length of time and the sample frozen out in the liquid air-cooled trap, the apparatus was shut off from the pumps by a large stopcock. The vacuum was broken, drawing the air slowly through a liquid air trap so no moisture would be carried into the trap containing the sample. When the pressure within the apparatus was atmospheric the sample was permitted to melt. The trap was then cut off, weighed, and the sample titrated with 0.1 N. potassium permanganate. After a thorough rinsing the trap was dried and reweighed. The sampling process was carried out as hurriedly as possible in order to minimize decomposition of peroxide. A set of representative data is given in Table I.

TABLE I.

	Millimols water used	Mol % water converted to hydrogen peroxide and hydrogen	Mol % water converted to hydrogen and oxygen
1	18.67	50.5	4.9
2	18.50	50.8	4.6
3	18.77	48.8	2.0
4	20.30	58.2	2.6

Effect of surface

The reaction tube was filled with Pyrex tubing so that the surface-volume ratio was increased more than fivefold. There was no increase in yield of peroxide, showing that the peroxide forming reaction is not influenced by the surface of the confining vessel. Results are given in Table II.

TABLE II.

Surface volume (cm)	Time (min.)	Wt. sample (g)	Wt. H_2O_2 (g)	% H_2O_2 in sample
2.09	75	0.60	0.318	53.0
11.80	60	0.45	0.221	49.0

From time to time during the course of this work it was noticed that the peroxide yields were lowered whenever the glass became very warm. The reaction tube was placed in an ice bath and several runs made to determine if decomposition occurred when the wall was at room temperature. There was no variation in the yield of peroxide.

Effect of distance

A study was made of the yield of hydrogen peroxide as a function of the distance between the discharge bulb and the trap. The results are shown in Table III.

TABLE III.

Distance (cm)	Wt. % H_2O_2 in sample	Distance (cm)	Wt. % H_2O_2 in sample
160	50.2	17	50.0
100	50.7	3	52.0
40	51.6	3*	47.0

* This run was made with a very high rate of flow.

Action of catalysts

By the action of a silver screen catalyst, an attempt was made to destroy the active species at varying distances down the reaction tube and determine what effect it would have on the peroxide yields. As soon as the discharge was turned on the catalyst became hot and some metal evaporated to the walls of the tube, causing it also to be catalytically active. Analysis of the sample showed only a very small fraction of a percent of peroxide present. It seemed plausible

that, even if the peroxide were formed before it reached the catalyst, it would be decomposed by the hot metal. A concentrated solution of hydrogen peroxide (85 percent) was prepared by the method given by Rice, Reiff and Kilpatrick.[5] The vapor from this solution was passed through the apparatus, which was entirely free of any catalyst, and a sample collected and analyzed. This procedure was repeated with the catalyst in the reaction tube. The sample in the first case tested about 65 percent by weight of peroxide and in the latter only 3 percent, showing that practically a quantitative decomposition of peroxide was brought about by the catalyst. A chemically deposited silver mirror was found to be equally effective for the decomposition of peroxide.

Taylor and Lavin[6] found that dehydrogenation catalysts, such as zinc chromite, were selective for atomic hydrogen recombination but did not destroy the hydroxyl molecules. The discharge bulb and reaction tube were coated with a similar dehydrogenation catalyst, copper chromite, and a discharge run on water vapor. The collected sample showed no peroxide present.

It would be very desirable to know whether the hydrogen peroxide is formed in the vapor immediately after the latter leaves the discharge or only by condensation in the liquid air trap. A possible method for detecting hydrogen peroxide vapor is the photography of the ultraviolet absorption spectrum. The absorption spectrum of hydrogen peroxide vapor was found by Urey, Dawsey and Rice[7] to be continuous in the region from 2150 to 2750A. An attempt was made to obtain the absorption spectrum of peroxide as formed in the water vapor discharge. The discharge bulb was placed near a long absorption tube but arranged so the discharge would not be photographed. Quartz windows were sealed on each end of the absorption tube. A small hydrogen arc was used as a source of continuum and was found to give consistently reproducible intensities. Several plates were taken with the discharge in operation but no

noticeable absorption was obtained. A blank run was made passing the vapor from a concentrated solution of peroxide through the absorption tube and several pictures were taken. A very small amount of absorption was indicated. The partial pressure of peroxide in these blank runs was about 10 times greater than that occurring in the water vapor discharge. It is evident that the partial pressure of peroxide as found in the water vapor discharge is too small to give any noticeable absorption.

Since it was not possible to determine either exactly where the hydrogen peroxide is formed or what the mechanism is by which it is formed there remained only the alternative of settling the mechanism by a process of elimination. Accordingly a number of chemical reactions which might produce hydrogen peroxide were tried out.

Condensation of oxygen atoms with water in the trap

Water vapor was rapidly drawn through the apparatus and frozen out in the trap, taking care to obtain a reasonably uniform layer of water on the walls of the trap. A discharge was then run with oxygen, at about 0.2 mm pressure, and a sample collected over a period of 60 minutes. The sample gave no reaction with potassium permanganate indicating the absence of hydrogen peroxide. It did have an ozone odor and colored a solution of potassium iodide. Three different trials indicated the same results.

The apparatus was changed so that the distance between the discharge bulb and the trap was about 1.6 meters. In traversing this distance the oxygen atoms would have completely disappeared, so that there would be no possibility of a reaction involving oxygen atoms in the trap. A run of some hours' duration was made with the water vapor discharge and a sample collected. Titration with permanganate showed the sample to be 50.2 percent by weight peroxide. The possibility of a condensation reaction in the trap involving oxygen atoms appears to be excluded.

Reaction of hydrogen atoms with oxygen

The oxygen was introduced into the active species from the hydrogen discharge a short distance from the discharge bulb, taking pre-

[5] Rice, Reiff and Kilpatrick, J. Am. Chem. Soc. 48, 3019 (1926).
[6] Taylor and Lavin, J. Am. Chem. Soc. 52, 1910 (1930).
[7] Urey, Dawsey and Rice, J. Am. Chem. Soc. 51, 1371 (1929).

cautions to prevent back diffusion of the oxygen into the bulb. The spectrum of the discharge did not change on admittance of the oxygen into the reaction tube so it was assumed that back diffusion was negligible. The flow of gases was measured by gas burettes and regulated by capillary leaks. Results are shown in Table IV.

TABLE IV.

No.	Time (min.)	Flow of gas (cc./min. at atmos. conditions) H₂	O₂	Wt. sample (g)	Wt. H₂O₂ (g)	% H₂O₂ in sample
1	98	22.0	1.30	0.70	0.022	3.1
2	80	15.5	3.70	0.06	0.0002	0.33
3	110	6.3	1.15	0.06	0.039	64.5
4	60	14.0	1.10	0.05	0.020	40.0

At the higher rates of flow the yields were very noticeably decreased, but, the reaction tube in the region of the entrance of the oxygen became very warm. It was consistently observed in the course of this work that whenever the glass became heated the yield of peroxide was always decreased.

Reaction of oxygen atoms with hydrogen

Several trials were made, employing different rates of flow, but in no case was any appreciable amount of hydrogen peroxide present. Usually one to three drops of standard permanganate would give a pink coloration. Good yields of water were obtained and a small amount of ozone was noted. The heating effect in the reaction tube was quite small.

Reaction of oxygen atoms with water

Runs were made varying the pressure of oxygen in the discharge bulb and the rate of flow of water vapor but no trace of peroxide was found in any of the samples. Because of the small sample obtained runs of several hours duration were made. Small amounts of ozone were detected.

Reaction of hydrogen atoms with water

No evidence of any sort of a reaction was noticed. No peroxide was found in the samples and there was no heating effect at the entrance of the water vapor into the active species from the hydrogen discharge.

Reaction of the active species from the water vapor discharge and oxygen

A discharge was run on the water vapor and the oxygen added to the active species in the reaction tube. The results are given in Table V. The weight of the sample is larger than the amount of water used in each measurable case. Beside the reactions occurring in the water vapor discharge the reaction between hydrogen atoms and oxygen molecules occurs, and it was found to yield both peroxide and water.

TABLE V.

No.	Time (min.)	Wt. H₂O₂ used (g)	Flow O₂ (cc./min.)	Wt. sample (g)	Wt. % H₂O₂ in sample
1	90		0.83	0.160	53.1
2	90		2.20	0.160	47.2
3	45	0.372	1.13	0.410	55.3
4	60	0.532	1.13	0.588	55.0

Effect of premixing hydrogen and water vapor

The hydrogen was added to the water vapor before passing into the discharge bulb. Two trials were made and in each case the yield was about the same as in the water vapor discharge. (See Table VI.) This indicates that there is very little oxygen present with which the hydrogen may react.

TABLE VI.

Time (min.)	Flow of H₂ (cc./min.)	Wt. H₂O used (g)	Wt. sample (g)	Wt. H₂O₂ (g)	% H₂O₂ in sample
60	1.50		0.150	0.070	46.6
60	1.86	0.436	0.421	0.206	48.8

Effect of premixing oxygen and water vapor

Several runs were made and in each case the sample, which was larger than the amount of water used, tested about 50 percent peroxide. It appears that neither oxygen atoms nor mole-

TABLE VII.

No.	Time (min.)	Flow of O₂ (cc./min.)	Wt. H₂O used (g)	Wt. sample (g)	Wt. H₂O₂ (g)	% H₂O₂ in sample
1	40	2.30		0.12	0.059	49.7
2	45	1.34	0.336	0.362	0.164	45.3
3	40	0.715	0.337	0.350	0.187	51.6

cules participate in ·the peroxide forming re-
action, for if they did the yield of peroxide should
have been noticeably increased. (See Table VII.)

Spectrographic studies

The spectrum of the electrodeless discharge in
water vapor was photographed with a Hilger
quartz spectrograph (E38) with Eastman 40
plates. An exposure of a few seconds gave the
well-known water bands at 3064 and 2811A and
in addition some hitherto unreported bands. The
strongest of these had a head at 3564A and was
degraded toward the red. A fainter band had a
head at 3328A. In order to ascertain if possible
why these bands had not been previously ob-
served the emission spectrum of water vapor
was photographed in a Wood tube with alu-
minum electrodes. With a 60 cycle discharge no
trace of the bands was obtained but with a
condensed discharge the new bands came out
very strongly at pressures in the neighborhood
of 0.1 mm. At higher pressures they disappeared.

Several plates were made of the bands on a
large spectrograph with a dispersion of 3A per
mm. Preliminary assignments were made but the
analysis proved to be very difficult and was not
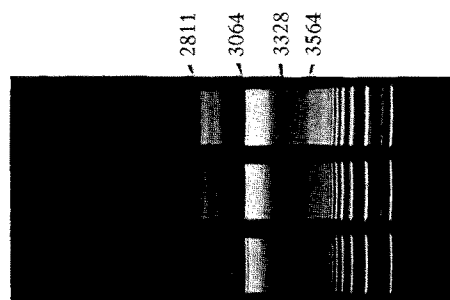carried further.[8] The bands have a hydride

FIG. 1. Electrodeless discharge. 0.1 mm pressure.

structure and since they appear only in the con-
densed discharge are to be attributed to an
ionized radical. As water of high purity was used
to supply the vapor it seems probable that the
carrier is OH^+.

These bands always appear with a condensed
discharge at pressures low enough for the dis-
charge to have a red color. At higher pressures
the discharge is bluish white and these bands are
not obtained.

The spectrum of the electrodeless discharge at
low pressures, taken on a small Hilger spectro-
graph is shown in Fig. 1. In Fig. 2 the same
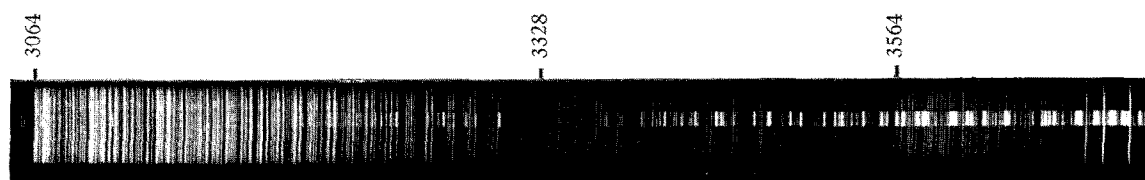spectrum is shown with large dispersion. The

FIG. 2. Electrodeless discharge. 0.1 mm pressure.

new bands at 3564 and 3328A are easily seen as
well as the well-known hydroxyl bands. Figs. 3,
4 and 5 are photographs of the discharge in
water vapor in a Wood tube, with aluminum
electrodes. The new bands appear only at low
pressures and when a condensed discharge is
used.

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[8] Professor F. W. Loomis of the Department of Physics
has undertaken the analysis of these bands. A preliminary
note, reporting their discovery was published; J. Am.
Chem. Soc. 55, 1742 (1933).

Stewart and Lavin[9] have reported that they
obtained the OH bands in emission apparently
as an afterglow from the dark part of the tube
30 cm from the discharge. This point was in-
vestigated and it was found that under ordinary
conditions a faint discharge travelled throughout
the apparatus which gave the hydroxyl bands
with considerable intensity. When elaborate pre-
cautions were taken in the way of shielding to

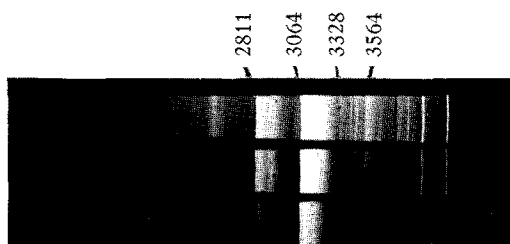[9] Stewart and Lavin, Proc. Nat. Acad. Sci. 15, 829 (1929).

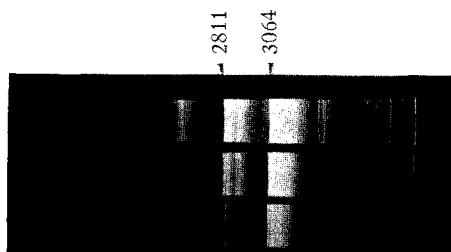FIG. 3. High frequency electrode discharge. 0.1 mm pressure.

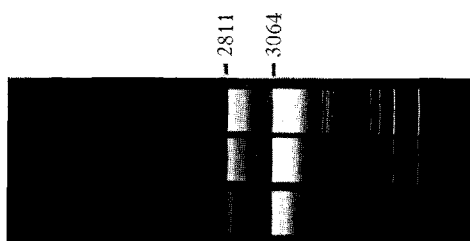FIG. 4. High frequency electrode discharge. Several mm pressure.

FIG. 5. 60 cycle electrode discharge. 0.1 mm pressure.

prevent the discharge, no trace of the hydroxyl bands appeared after fifteen minutes exposure on the small spectrograph.

DISCUSSION

The reaction mechanism proposed by Bonhoeffer and Pearson to account for the disappearance of hydroxyl cannot be correct since large amounts of hydrogen peroxide were obtained in these experiments. The difference in the experimental results is undoubtedly due to the fact that the electrodeless discharge was used and the powerful catalytic action of traces of sputtered metal avoided.

The failure of Bonhoeffer and Pearson to obtain the absorption spectrum should not be difficult to explain. On the other hand we are inclined to agree with their conclusion that hydroxyl disappears by some one fast reaction mechanism so that its concentration is always low and the molecule is not available for other reactions. A low concentration of hydroxyl is not inconsistent with a high intensity of emission of the hydroxyl bands since it is the *water molecule which is excited to give the hydroxyl bands*. We suspect that the reaction by which hydroxyl disappears is the rapid homogeneous bimolecular condensation to hydrogen peroxide,

$$OH + OH = H_2O_2. \tag{3}$$
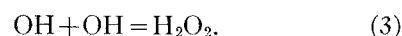
The energy liberated here is about 41 large calories. This amount of energy would correspond to the excitation of the hydroxyl to the fifth vibrational state and the disposal of this energy does not seem to be a serious obstacle to the reaction.

Heterogeneous reactions do not occur rapidly unless adsorption takes place upon the walls of the vessel and experience has shown that minimum of catalytic wall activity is obtained when considerable amounts of water vapor are present. Since large concentrations of hydrogen atoms were shown to reach the liquid air trap the wall activity was certainly slight. The only alternative to bimolecular reactions are those taking place in triple collisions and these must of necessity be slow reactions.

The above reaction mechanism should be very rapid, causing the disappearance of hydroxyl immediately after leaving the discharge. About 50 percent of the water is converted to hydrogen peroxide. It is not likely that much more than 50 percent of the water molecules are dissociated in the first place and there are reactions which could account for the reconversion of considerable amounts of hydrogen peroxide to water. With a more intense discharge a considerable amount of atomic oxygen is produced probably by the dissociation of free hydroxyl. But at moderate intensities the amount of oxygen produced is negligible. The results of Bonhoeffer and Pearson who obtained only traces of hydrogen peroxide are accounted for by the presence of particles of metal sputtered from the electrodes.

Our experiments show that hydrogen peroxide vapor is decomposed quantitatively by small amounts of exposed metal surface into water and oxygen.

The evidence for the above reaction is negative and falls into two classes. First, one must assume that if hydrogen peroxide were not formed by simple, rapid, mechanism that competing reactions would take place. The most important of these is the reaction with atomic hydrogen.

$$H + OH = H_2O - 115 \text{ cal.} \qquad (4)$$
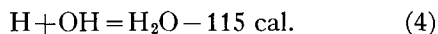
The energy to be disposed of here is probably too large to permit a bimolecular mechanism.

Finally it is necessary to consider other possible reactions by which hydrogen peroxide may be formed. It is necessary to consider only those mechanisms which are sufficiently simple to be inherently probable. There are two mechanisms which form hydrogen peroxide directly.

$$O + H_2O = H_2O_2 - 33 \text{ cal.} \qquad (5)$$

$$OH + H_2O = H_2O_2 + H + 72 \text{ cal.} \qquad (6)$$
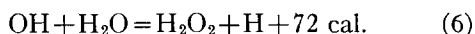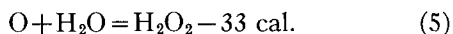
The first reaction is inherently improbable as it involves a change from a triplet to a singlet state and it was shown in this work not to take place either in the main part of the apparatus or in the liquid air trap. The second reaction cannot take place because of the large amount of heat absorbed.

It was shown in this work and has been shown previously by Bates[10] and others that atomic hydrogen reacts with molecular oxygen to give hydrogen peroxide by some mechanism which is presumably complex and hence not very rapid. There are two mechanisms by which molecular oxygen might be formed.

$$OH + OH = H_2 + O_2 \qquad (7)$$

$$OH + OH = H_2O + O.$$
$$O + O = O_2 \qquad (8)$$
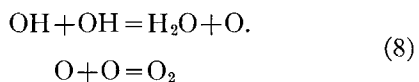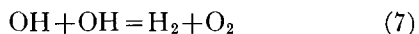
The first reaction has a high heat of activation

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[10] Bates and Salley, J. Am. Chem. Soc. **55**, 110 (1933).

since the reverse reaction has a high heat of activation and the heat of reaction is small. The second mechanism is controverted by the experimental evidence as to the concentration of atomic oxygen. Furthermore the formation of molecular oxygen by these two steps must be exceedingly slow. Also to produce a 50 percent conversion to hydrogen peroxide 100 percent dissociation of water molecules would be necessary. There is reason to believe as has been mentioned that the conversion to hydrogen peroxide is much greater than observed since the reaction

$$H + H_2O_2 = OH + H_2O$$
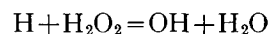
must take place to some extent particularly on the walls of the trap.

The experiment with the discharge only three cm from the trap with a flow rate of 9 meters per second shows that the reaction probability per collision from hydroxyl by (3) must be of the order 10^{-3}. It is unlikely that any competing reaction can be found which is as fast.

There is of course no direct proof that the condensation of hydroxyl does not take place on the walls of the trap and undoubtedly this reaction does take place to some extent. The fact, however, that no variation in yield of peroxide with distance of trap or rate of flow was observed, is most easily explained by assuming the disappearance of hydroxyl by a gas phase reaction which is faster than any competing reaction.

If we assume that the new bands observed are due to OH^+ then the fact that they appear only at low pressures tends to confirm the hypothesis of the reaction mechanism. While the absolute amount of hydroxyl present will decrease with decreasing pressure the relative amount will increase and this will result in the formation of an increased amount of OH^+. This conclusion can only be true if the disappearance reaction for hydroxyl is of second or higher order.

The authors wish to express their gratitude to Professor F. W. Loomis for the loan of spectrographic equipment and for advice in the interpretation of spectra.