

The Lifetime of Free Hydroxyl

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The Lifetime of Free Hydroxyl

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(1) The reasons for various failures to observe the absorption spectrum of free hydroxyl radicals are discussed. (2) The absorption spectrum of OH in the electric discharge through water vapor is observed with a spectrograph of high resolving power. After interrupting the discharge, the presence of OH is traced by its absorption spectrum over time intervals up to 1/8 sec. (3) With alternating half-periods of 60 cycle a.c. cut out by a switch, the emission of OH vanishes almost entirely with the current whereas the absorption persists rather uniformly. It is concluded that the persistence of the absorption spectrum is to be attributed to a long life of OH radicals rather than a

long life of O and H atoms furnishing a fresh supply of short life OH radicals. (4) The rotational intensity distribution within the OH band at strong currents (being anomalous to a lesser extent than at faint currents) indicates the presence of free OH in the discharge. (5) For a comparison of the present result with previous estimates, leading to a much shorter life of free hydroxyl, the number per sec. of emission processes of the OH band is measured, assuming that each of these processes leads to the production of one free OH radical. (6) The process by which OH radicals are consumed is discussed.

I. PROBLEM AND PREVIOUS WORK

THE fact has been emphasized by H. N. Russell,¹ investigating absorption spectra of stellar atmospheres, that in the *visible* and *near ultraviolet* absorption spectra are to be observed preferably of *unstable* molecules, for example, the free radicals OH, NH, CN, whereas most *stable* molecules, such as H₂, N₂, O₂, CO₂, H₂O, have absorption spectra in the *extreme ultraviolet*. The reason is that most stable molecules, but not the unstable ones, have electronic configurations similar to those of the rare gases; hence they have high values of excitation energy. This preferred observation of free radicals by absorption spectra contrasts with the methods of chemical analysis. Although they have been well developed for stable molecules, there is no direct chemical test for the simplest free radicals like OH or NH. These radicals, however, play a major hypothetical part in theories of chemical reactions. Here evidently is a chance for the spectroscopist to supplement the chemical analysis of gases, that is, to observe radicals during the progress of a reaction. Although the *absorption* spectra of most simple radicals have not been observed as yet, their wavelengths can be predicted since their *emission* spectra are known as well as the spectra of stable molecules.

The OH group and its reactions present a problem of major interest because of the part

they play in the hydrogen oxygen reaction.² Furthermore, there is a particular interest in recent results of Rodebush and Wahl³ who suggest a *bimolecular* association $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$ as the principal process by which the OH radicals are consumed.

In the present paper the life of OH radicals, produced by an electric discharge through H₂O vapor as they disappear by a chemical reaction after the interruption of the discharge, is being investigated. The concentration of OH is estimated by the intensity of the absorption spectrum.

Quantitative results regarding the concentration can be derived from absorption, not from emission spectra. The reason is that within certain limits, in particular at low pressures, the *absorption coefficient*—not the intensity of the absorption line measured against the background—is proportional to the concentration of the absorbing molecules (Beer's law)⁴ whereas the intensity of the *emission spectrum* is very largely determined by other uncontrollable factors.⁵

² Cf. K. F. Bonhoeffer and P. Harteck, *Grundlagen der Photochemie*, p. 257.

³ W. H. Rodebush and M. H. Wahl, *J. Chem. Phys.* **1**, 696 (1933); cf. G. I. Lavin and F. B. Stewart, *Proc. Nat. Acad. Sci.* **15**, 829 (1929).

⁴ R. W. Wood, *Physical Optics*, 3d ed. p. 101; Macmillan Company (1934).

⁵ The method of Bay and Steiner (*Zeits. f. physik. Chemie* **3**, 149 (1929)), based on the intensity of *emission* spectra, does not apply to the OH radical, since in the electric discharges the OH is largely generated directly from H₂O so that the intensity of the OH band fails to indicate the concentration of OH.

¹ Lecture at the Harvard Observatory, 1931; *Astrophys. J.* **79**, 317 (1934).

Hence by photometry the absorption spectrum gives evidence of the concentration of the absorbing gas, but—except after special calibration—only of *relative* values, since an unknown probability of transition goes in determining the *absolute* values. It is intended to calibrate the absorption spectra thus obtained with a known partial pressure of free OH radicals and so to proceed to the measurement of the *absolute* value of their concentration. This will be attempted by thermal dissociation of H₂O vapor according to Bonhoeffer and Reichardt.⁶

For rapid reactions the absorption spectra have to be taken in snapshots. In order to secure sufficient exposure, the chemical process and the snapshot have to be repeated periodically.

In recent years there have been reports of numerous attempts to observe the *absorption* spectrum of OH in *chemical reactions* or *electric discharges*.⁷ These attempts, however, have failed,⁸ although in the electric discharge through water vapor the *emission* spectrum, connected with the normal state of the OH molecule, appears very strongly; so strongly, as a matter of fact, that the emission of OH forms one of the most annoying spectral impurities. The *absorption* spectrum of OH has been observed, however, in *thermally dissociated* water vapor at temperatures up to 1600°C by Bonhoeffer and Reichardt.⁹ The complete failure to observe the absorption spectrum of OH in chemical reactions or electric discharges led to the conclusion that, in any case, the concentration of OH is extremely small since the high reactivity limits the lives of these radicals to a very short period. Bonhoeffer and Reichardt were able to establish an upper limit for the concentration of OH present in the electric discharge through water vapor.

It seems probable that all failures to observe

the absorption spectrum of OH in reactions or discharges have in common that the experiments have been undertaken with medium sized spectroscopic instruments. To observe faint and sharp absorption lines, however, is much more difficult than is the corresponding problem for emission. A faint, sharp *emission* line, when photographed with an instrument like a medium size quartz spectrograph, *appears broader* than it actually is emitted from the source. A faint, sharp *absorption* line, however, when photographed with the same instrument, *disappears* entirely, since its observation is about equivalent to the resolution of *two closely adjacent emission* lines.¹⁰ For the most sensitive investigation of absorption spectra a spectrograph is required with a resolving power comparable with the width of the absorption lines to be observed. The great increase of sensitivity obtained by observing absorption lines with high resolving power becomes evident by the following comparison: While the quartz spectrograph fails to show any OH absorption spectrum in the electric discharge through H₂O vapor with the carbon arc furnishing the continuous background, the 21-foot grating reveals an undesirable OH absorption spectrum even without the discharge through H₂O in any carbon arc in air although operated in carefully dried air with purest carbons just baked out.

There is an essential difference between chemical processes in the discharge and other chemical processes in that the discharge produces excited and ionized states of all possible energy values, some of them much higher than the energies available in most chemical reactions. It can be assumed, however, that the *unstable* excited states of atoms and molecules radiate within so short a time interval that they are not to be observed after interrupting the discharge with the rotating disk method. *Ions and electrons* recombine very probably at such a high rate because of the Coulomb force of attraction that they may be just barely observable with the same method.¹¹ The recombination of *atoms and radicals* is probably by far the slowest process

⁶ K. F. Bonhoeffer and H. Reichardt, *Zeits. f. physik. Chemie* **139**, 75 (1928).

⁷ H. C. Urey and G. I. Lavin, *J. Am. Chem. Soc.* **51**, 3293 (1929); K. F. Bonhoeffer and T. G. Pearson, *Zeits. f. physik. Chemie* **14**, 1 (1931); W. Frankenburger and H. Klinkhardt, *Zeits. f. physik. Chemie* **15**, 440 (1932); P. Harteck, *Trans. Faraday Soc.* **30**, 139 (1934); K. H. Geib and P. Harteck, *Zeits. f. physik. Chemie* **A170**, 1 (1934).

⁸ The absorption spectrum of OH, occasionally observed in the under water spark by H. Stücklen (*Zeits. f. Physik* **30**, 27 (1924)) is an exception.

⁹ K. F. Bonhoeffer and H. Reichardt, *Zeits. f. physik. Chemie* **139**, 75 (1928); cf. E. Hulthen and R. V. Zumstein, *Phys. Rev.* **28**, 14 (1926).

¹⁰ Cf. W. H. J. Childs and R. Mecke, *Zeits. f. Physik* **68**, 353 (1931).

¹¹ C. Kenty, *Phys. Rev.* **32**, 624 (1928); L. J. Hayner, *Zeits. f. Physik* **35**, 365 (1925).

after interrupting the discharge. This chemical process is presumably the only one actually observed in the present experiment. There might be exceptional cases, however, in which this chemical process, following an electric discharge, would differ from the ordinary chemical processes if *metastable* states of a considerable lifetime are produced. Such states do exist in very pure helium and very pure mercury vapor. Since small traces of impurities, in particular hydrogen, are very efficient in destroying metastable levels, it is expected that the metastables do not play a part for any appreciable period after the interruption of the discharge through H_2O . Hence the results of the present method are directly comparable with the results of chemical methods for the investigation of the rate of chemical reactions in gases.

Since the rate of reaction is strongly affected by the temperature, it is of interest that the temperature—also a rapid change of temperature—can be observed, as well as the concentration from absorption spectra, by measuring the intensity distribution within one branch of a band.

The advantage of the method of absorption spectra over those of chemical analyses is its power to recognize free radicals and trace the progress of a fast reaction by snapshots.

II. PERSISTENCE OF OH ABSORPTION SPECTRUM

a. Apparatus

The apparatus consisted of an electric discharge through water vapor, the absorption spectrum of which is to be observed; a source for the continuous spectrum; a synchronous motor, operating the electric switch and the optical shutter; and the spectrograph (Fig. 1).

The discharge tube with large nickel electrodes and quartz windows, containing water vapor, afforded a column of 1.27 m length and 5 cm diameter for the absorption experiment. The electrodes, fastened in side tubes, had a distance of 10 cm from the main body of the tube which served as the absorption tube. Before the final experiments the glass walls were carefully freed of sputtered metal. "Conductivity water," distilled several times in high vacuum, was used.

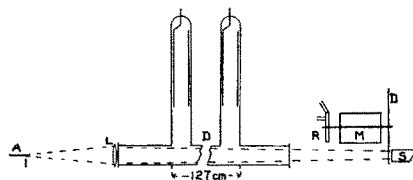


FIG. 1. Absorption experiment. A, carbon arc; L, quartz lens; D, discharge tubes; M, synchronous motor; R, revolving switch; D, sector disk; S, slit of spectrograph.

The source for the continuous spectrum offered an unexpectedly difficult problem. At 3100 Å the hydrogen discharge tube, emitting a perfectly uniform spectrum, gave an intensity, even with the highest current density obtainable, far inferior to the carbon arc. The carbon arc in air, however, was useless since it contributed a pronounced absorption spectrum of OH. By various experiments it was found that this absorption spectrum was due to the combustion in air of hydrogen compounds serving as binding material for the carbons. The carbon arc in flowing nitrogen, carefully dried, was applied. Its spectrum, however, was not quite continuous because of superimposed nitrogen bands, nor was its intensity quite uniform with time because of the irregular shaping of the carbon electrodes.

A synchronous motor carried on its axis a brass and Bakelite sector disk as a switch. It connected the discharge tube with the secondary of a transformer in most experiments for a half-period of 60 cycles a.c. and disconnected the tube for the next half-period or three half-periods. During this time interval the chemical recombination was investigated by the absorption spectrum. In order to determine the maximum time interval through which the absorption spectrum of OH could be traced, the speed of the revolving switch was reduced by gears to one-fifth of its former rate, the switch transmitting one full period of current and cutting out nine full periods.

An optical sector disk of Bakelite rotating on the same axis with the switch, immediately in front of the slit of the spectrograph, screened off the inevitable radiation emitted from the water vapor during the electric discharge running and let through only emission flashes of the continuous spectrum passing the water vapor within

short time intervals after interrupting the discharge. By varying the phase difference between electrical and optical sectors and observing the intensity of the absorption spectrum, decaying after the discharge, the lifetime of the OH molecules was investigated. With an optical sector of 12° , each individual flash lasted 1/900 sec.

A 21-foot Rowland concave grating served as a spectrograph. Its mounting had recently been rebuilt in a constant temperature room in the basement of the new Research Laboratory of Physics by Professor F. H. Crawford and Mr. D. W. Mann. Its second order at 3100Å has a resolving power of 0.014Å. On the other hand, the width of OH lines, when computed on the basis of the Doppler broadening at 400°C , is only 0.005Å, considerably smaller than the resolving power. Hence an apparatus with higher resolving power would afford a still more sensitive spectroscopic test for OH radicals. In order to secure the highest resolving power a narrow slit and the fine grain Eastman IV-0 plates were used in spite of their very small speed.

Since an intermittent continuous spectrum was to be photographed with very high dispersion on slow photographic plates, a serious difficulty was expected from the lack of light intensity. Hence the experiment started from a systematic comparison of the various methods by which the intensity of illumination could be increased, in particular by compensating for the astigmatism. The results were published in a previous paper.¹² A cylindrical lens in front of the grating proved useful.¹³ The times of exposure, including intermissions, were of the order of magnitude of 30 minutes.

b. Results

By using the apparatus described, the absorption spectrum of OH radicals came out clearly. (Fig. 2.) It was strongest when the water vapor pressure was high (2 mm) and the current strong. Because of the inevitable intense emission spectrum of the discharge, it was best observed immediately after the interruption of the current.

It could be traced down to about 0.3 mm. At a pressure of 2 mm, by means of the slow interrupter, its decaying intensity could be followed after the interruption over the full period of 1/8 sec. Within this interval a considerable decay was observed (Fig. 3). The figure, however, does not express an average lifetime of OH radicals since it is largely dependent upon the sensitivity of the test. The time interval of 1/8 sec. holds for favorable conditions.

In order to compare the absorption spectra during the discharge and after the interruption, care must be taken that during the discharge the emission spectrum is faint as compared with the continuous background or else it would mask the absorption spectrum. Hence a small current (30 ma) through the water vapor and, in order to secure sufficient absorption, rather high pressure (2 mm) was applied. The intensity of absorption was not much stronger during the discharge running than after the interruption. Hardly any change was noticed within one half-period—in agreement with the total persistence of absorption observed as amounting to many half-periods of 60-cycle current.

The intensity distribution within the absorption band was very different from the one within the well-known OH emission band. The strong heads, characteristic in emission, disappeared in absorption. The reason is that in *absorption* the molecular rotation is low, mainly determined by the temperature, whereas in *emission* much higher rotational quanta come out with great intensity. The process exciting the abnormal rotation in emission has been discussed in a previous paper.¹⁴

Up to the present no quantitative photometric work, comparing concentrations of OH, could be carried through since the source of the continuous spectrum, the carbon arc in N_2 , contributed traces of OH absorption spectra in a rather erratic way. It is easy to recognize the OH absorption due to the *discharge* which is unlike the one caused by the *arc* because of the widely different widths of the lines and intensity distributions of rotation. For photometric work, however, a perfectly uniform background is

¹² O. Oldenberg, J. Opt. Soc. Am. **22**, 441 (1932); cf. G. Dieke, J. Opt. Soc. Am. **23**, 274 (1933) and J. B. Green and R. A. Loring, J. Opt. Soc. Am. **24**, 348 (1934).

¹³ W. J. Humphreys, Astrophys. J. **18**, 324 (1903); E. Gehrecke, Zeits. f. Instr. Kde. **31**, 217 (1911).

¹⁴ O. Oldenberg, Phys. Rev. **46**, 210 (1934).

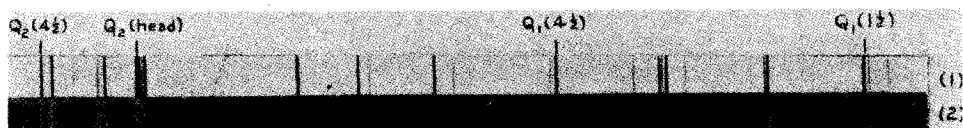


Fig. 2. Spectra of OH radicals (enlargement 9-fold); part of band 3064; (1) emission; (2) absorption.

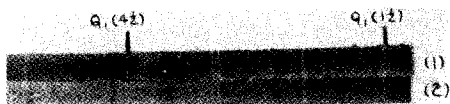


Fig. 3. Decay of absorption spectrum-after interruption of discharge; (1) 1/300 sec.; (2) 1/8 sec. after interruption.

indispensable. Therefore, only the estimate given above of the persistence of the OH absorption spectrum can be made as yet.

III. NATURE OF THE LONG LIFE PARTICLES

As described in the preceding section, the absorption spectrum of OH radicals can be traced over a period as long as 1/8 sec. after the discharge is interrupted. This, however, does not necessarily indicate a correspondingly long life for the free OH radicals. Bonhoeffer and Pearson, discussing the afterglow, suggested an alternative; namely, that the long lives of the *O* and *H* atoms by slow recombination produce a fresh supply of OH radicals over a considerable period of time; these radicals are assumed to have a much shorter life. This is analogous to the persistence of the *molecular* emission spectrum in the well-known afterglow of nitrogen which is ascribed not to the long life of the molecules but to slowly recombining atoms.¹⁵

a. Lifetime not attributed to the recombination of O and H atoms

First, we shall compare the various possibilities of slow recombination of O and H atoms with the spectroscopic observations.

(1) *Triple collisions forming OH*'. Bonhoeffer and Pearson investigated various processes by which the band spectrum of OH might be excited. They proved by experiments that *in the discharge* the emission of OH is largely due to

dissociation of H_2O and excitation of OH in one process (impact by fast electrons of 9 volts or more). This process has recently been confirmed by an independent argument.¹⁶ The *afterglow* of the OH bands, however, discovered by Lavin and Stewart¹⁷ must originate from another excitation process since outside of the discharge no fast electrons are present. Bonhoeffer and Pearson proved that H atoms in O_2 or O atoms in H_2 fail to excite the OH band but that H and O atoms when mixed produce the OH band with high intensity. They concluded that the afterglow is caused by $O+H \rightarrow OH'$, the energy of combination changing largely to excitation of OH; for known reasons triple collisions have to be assumed. Furthermore, they assumed a relatively short life of the OH radicals, estimated to 10^{-3} sec.

This theory, which well explains previous results, is to be correlated with the absorption spectra described. The underlying hypothesis (short life of OH, long lives of O and H forming a fresh supply of OH) leads us to predict that any change in the *supply formed per sec.* will be followed by a change in the *concentration* of OH within a time limited approximately by the life of OH ($\sim 1/1000$ sec.). Therefore a somewhat slower fluctuation of the supply ought to be accompanied by a corresponding fluctuation of the concentration. The cutting out of alternate half-periods of 60 cycle a.c. will cause a fluctuation of the discharge by which this theoretical prediction will be tested. By spectra taken in snapshots we can trace both the supply formed per sec. and the concentration. The *supply* is to be traced since all formation processes mentioned in the theory lead to *excited* OH radicals (during the discharge running by dissociation of H_2O into $OH'+H$ as the process of major probability

¹⁶ O. Oldenberg, Phys. Rev. **46**, 210 (1934).

¹⁷ G. I. Lavin and F. B. Stewart, Proc. Nat. Acad. Sci. **15**, 829 (1929).

¹⁵ G. Cario and J. Kaplan, Zeits. f. Physik **58**, 769 (1929).

and as afterglow between discharges by $O+H \rightarrow OH^*+M$; hence each formation process of an OH radical is accompanied by an emission process of the OH band. Therefore, by measuring the intensity of the emission spectrum we actually register the supply formed per sec. of OH radicals. On the other hand, independently of any theory, by the absorption spectrum we can also observe the *concentration* of OH present. The theory under discussion predicts that the concentration of OH will fluctuate at the same rate as supply formed per sec. This becomes equivalent to the absorption spectrum of OH fluctuating at the same rate as the emission spectrum. This prediction is to be tested by snapshots of emission and absorption spectra during and between discharges.

With the same discharge through water vapor and the same sector disk and interrupter, letting through and cutting out alternate half-periods, and with a quartz spectrograph, the *emission* of OH was compared during and between discharges. It faded to an inferior order of magnitude after the interruption. For example, approximately the same photographic effect was produced *during* the discharge in 1/2 sec. and *between* discharges in 5 hours, the ratio being about 1:40,000. Therefore according to the theory under discussion—concentration rapidly changing with supply formed per second—we expect a striking decay of the concentration after the interruption. The absorption spectrum of OH, however, indicating the concentration, persisted during the intermission of one half-period without any striking decay as discussed above (II 2). This contradicts the theoretical prediction based on a very short life of OH, but long lives of O and H.

(2) *Triple collisions forming OH*. Secondly, we must consider $O+H$ combining in triple collisions leading to OH instead of OH^* . (In this case we cannot estimate the supply formed per sec. of OH from the intensity of emission.) There are two arguments against this process. Bonhoeffer and Pearson actually proved that two streams of gases, one containing H atoms, the other O atoms when flowing together, emit OH bands with high intensity. Hence the very small intensity of these bands, observed during the intermission, indicated that no large concentration of

both atoms is present. Hence we fail to explain the absorption between discharges by the formation of OH from O and H. The other argument leading to the same conclusion is as follows: Granted that some OH radicals are supplied during and between discharges by recombination of O and H atoms, we still positively know that during the discharge another powerful source of OH radicals exists, the simultaneous dissociation of H_2O and excitation of OH by electron impact. Hence we should expect the concentration of OH to be considerably stronger *during* than *after* discharges—contrary to the observation. Therefore, the long lifetime of 1/8 sec. cannot be attributed to O and H atoms forming short life OH radicals. This argument applies against the catalytic effect of the wall as well as against triple collisions in the gas.

b. Lifetime attributed to OH radicals

Since the formation of OH from the atoms is excluded by the arguments just given, the plausible conclusion is that the persistence of the absorption spectrum of OH observed is due to a correspondingly long life of OH radicals.

Another argument against a very short lifetime of OH radicals is given by the fluorescence radiation of H_2O vapor, sensitized by Hg vapor. When excited by the Hg resonance line 2537 the OH band 3064 is strongly emitted.¹⁸ The energy of 4.9 volt electrons, corresponding to the line 2537, is unable to dissociate the H_2O molecule and excite the OH radical in one process; hence we must assume two consecutive processes. It is most plausible to assume one impact of the second kind leading to dissociation of H_2O into $OH+H$ and another to excitation of OH. The second process is probable only if an appreciable concentration of OH has been built up by the effect of the first process; or in other words, if the OH radicals have an appreciable lifetime.

c. Contribution of decomposing H_2O_2

In addition to the association of $OH+OH$, suggested by Rodebush and Wahl as the main reaction by which OH radicals *disappear*, one

¹⁸ E. Gaviola and R. W. Wood, Phil. Mag. **6**, 1292 (1928). Under somewhat different conditions (a few mm H_2O vapor, sensitized fluorescence), Gaviola and Wood estimated the lifetime of free OH to the order of magnitude of 1/100 sec.

must consider the effect of another process *regenerating* these radicals. According to Geib H_2O_2 is decomposed by H atoms probably in the following process $\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{OH}$.¹⁹ Is there a chance that the persistence of the absorption spectrum is caused by the slow liberation of OH radicals in this process from H_2O_2 , while the radicals themselves have a much shorter life? Since so large a concentration of H_2O_2 was observed by Rodebush and Wahl among the gases pumped out of the discharge, it is hard to assume that a still much larger amount of H_2O_2 was originally produced which would give rise to the full amount of OH observed in the absorption spectrum. Moreover it is hard to assume that OH is stored up and bound in the shape of H_2O_2 from which it is gradually liberated only for very brief moments by H atoms, and yet the permanent concentration of *free* OH is so high, over a considerable period of time, that its absorption spectrum is well observable. It is probable, therefore, that the lifetime of OH observed in the absorption spectrum is largely determined by the real life of OH slowly recombining.

IV. ESTIMATE OF CONCENTRATION OF OH FROM THE EMISSION SPECTRUM

The absorption spectra described indicate only relative values of the concentration of OH under different conditions. They fail, however, to give evidence of the OH concentration as compared with the concentration of H_2O molecules. For the stationary concentration caused by a heavy current, the emission spectrum indicates an appreciable concentration of OH in the following experiment.

In a previous paper it was pointed out that the excitation process (*simultaneous* dissociation of H_2O and excitation of OH) leads to a characteristic *abnormal* rotation of the radiating OH, observed by the intensity distribution in the band spectrum. Conversely, we can recognize

¹⁹ K. H. Geib, Zeits. f. physik. Chemie **A169**, 166 (1934). Mr. N. D. Smith called my attention to the possible effect of this reaction on the lifetime of OH. The next reaction, suggested by Geib, $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$ does not agree with the results of Rodebush and Wahl who proved the absence of atomic O from the discharge through H_2O vapor (cf. Section VIa). The alternative $\text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$ seems preferable. Since, however, this reaction regenerates half the H_2O_2 just decomposed, the yield of the first reaction would be higher than computed by Geib.

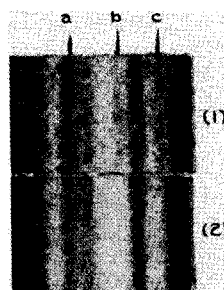


FIG. 4. Part of OH band (negative, quartz spectrograph, enlargement 55-fold). (1) weak current; (2) strong current. Abnormal rotation is pronounced at weak current; the following lines are enhanced; $a = R_1(17\frac{1}{2})$ and $R_2(15\frac{1}{2})$; $b = R_2(14\frac{1}{2})$; $c = R_2(13\frac{1}{2})$; rotational quantum number 3 or 4 would be most probable according to the temperature.

this excitation process from the strongly *abnormal* intensity distribution observed. On the other hand, free OH radicals in the discharge tube are certain to contribute a band of *normal* intensity distribution in emission since the absorption spectrum reveals normal rotation of the unexcited OH radicals present. (Section II b.) Therefore we may expect for a very small current (hardly any free OH present, hence all excited OH originating directly from H_2O) the greatest abnormal rotation and, on the other hand, for a very strong current a tendency towards normal rotation (smaller intensity of the very high rotational quanta) provided that an appreciable part of the intensity is due to free OH radicals present under the action of the current.

For a test the intensity distributions are compared for currents of 3 ma and 250 ma by spectra taken on the same plate, and with the same times of exposure in order to make them comparable, the intensity with the heavy current being reduced by dense gauze screens. Actually, as expected, heavy currents tend to reduce the high rotational lines. This effect can best be observed on lines of an R branch which have neighboring wavelengths although they belong to widely different rotational quanta (Fig. 4). This observation proves that for strong currents the partial pressure of OH radicals is appreciable. Since in the discharge the OH radical is preferred by its small energy of excitation (4.0 volts), a small concentration of free OH would be sufficient for the observed effect. In this argument the

unknown contribution of H_2O_2 to the spectrum is neglected.

V. THE RATE OF PRODUCTION OF OH BY THE PROCESS $\text{H}_2\text{O} + e \rightarrow \text{OH} + \text{H}$

It might seem unsatisfactory to attribute the persistence of the OH absorption, observed as 1/8 sec., to the long life of OH radicals (Section IIb) since all previous papers agree to a very short life of OH, estimated to 1/1000 sec. The reason for this discrepancy must be discussed.²⁰

The main argument for a short life has been that the striking intensity of the emission band 3064 indicates a supply of OH formed per sec. so rich that its absorption spectrum could be expected to be observable with the quartz spectrograph (Section I).²¹ It is difficult, however, to base this estimate of intensity upon a correct comparison. The observation shows only that the intensity of 3064 is strong when compared to other spectra.

The following comparison seems preferable: Assuming that each emission process of the band 3064 indicates the production of one OH radical and furthermore, assuming a lifetime as long as 1/8 sec. (Section IIb), the intensity of the emission band, measured in absolute units, leads to the *concentration* of OH (= number produced per sec. \times lifetime) as far as it is produced by this observed process. This concentration is to be compared with a reasonable minimum concentration required for an absorption spectrum. The previous estimates (leading to a *short* life of OH) make us believe that this measurement of supply combined with a *long* lifetime of OH would lead to a concentration so high as to render the previous failures to observe the absorption spectrum inexplicable.

For this estimate the total number per sec. of emission processes of the band in the whole dis-

charge must be measured. The densitometer trace of the band—with proper calibration of the photographic plate—yields a curve representing intensity in *arbitrary* units as a function of wavelengths. The emissive power of the surface of the discharge is obtained in *absolute* units from a quantitative comparison with the black body radiation at the same wavelength.²² (In order to take the spectra of the discharge and the black body at 1415°K on the same plate with the same time of exposure, the intensity emitted from the discharge was reduced by the factor 950.) By integration over the whole surface of the discharge the total energy or number of quanta emitted per sec. from the whole discharge can be derived; that is, the total number of OH radicals generated per sec. by this observed process, the yield of which is to be estimated.

With a lifetime of 1/8 sec. a concentration of 4×10^{15} OH radicals per cm^3 results, or of 1 OH radical, as produced by the process considered, among 8000 H_2O molecules. (Apart from the uncertainty of the estimate caused in particular by the rather uncertain lifetime, it is easy to explain why the total concentration of OH must be considerably higher than the contribution of one process estimated here.) The result is that the intensity of the OH band observed in absolute units combined with a lifetime as long as 1/8 sec. does not lead to absurdly high values of the concentration of OH.

VI. PROCESSES IN THE DISCHARGE THROUGH H_2O VAPOR

a. Reactions consuming OH radicals

The reactions by which OH radicals disappear have been much discussed. It seems that the chemical processes are simpler in the electric discharge through water vapor than in the photochemical or thermal combination of H_2 and O_2 . The reason is that in the discharge at moderate currents no free oxygen is formed. This is proved by the following three arguments: (1) Rodebush and Wahl proved by the Stern-Gerlach experiment that free O atoms are absent from the gases flowing out of the discharge. (2) They found no molecular oxygen in the discharge. (3) As re-

²⁰ The estimate of Bonhoeffer and Pearson, based on the idea that a considerable fraction of the total electric energy serves for producing OH^\cdot , need not be discussed here since it leads only to a lower limit of the lifetime of OH.

²¹ From the failure to observe the absorption spectrum Bonhoeffer and Pearson derived the concentration of OH as being less than 0.03 mm. It must be taken into account that the calibration of an absorption spectrum at four times the temperature and about five hundred times the pressure of the discharge cannot be quite accurate unless the spectrograph has very large resolving power, since in a medium size spectrograph a narrow line has a much larger tendency to escape from observation than a broad one.

²² I am obliged to Dr. F. F. Rieke for the construction of the black body.

ported in Section III, the afterglow was exceedingly faint (in agreement with the results of Rodebush and Wahl and of Stoddart).²³ Its intensity, however, is known to be high if both O and H are present. Since there is no doubt about the presence of H, it follows that O is absent.²⁴ The conclusion agrees with the result of Stoddart who enhanced the afterglow by introducing O₂ to the H₂O vapor. Hence in the discharge through H₂O vapor with moderate current we are allowed to discard the consideration of O or O₂.

Among the gases pumped out of the discharge Rodebush and Wahl found a large concentration, about 50 percent, of H₂O₂. (Considering that H₂O₂ decomposes by the effect of the electric current as well as in the presence of H atoms, the concentration of H₂O₂ originally formed must have been still higher.) They explained previous failures to observe H₂O₂ by the catalytic effect of metal sputtered in the discharge tube, decomposing the H₂O₂. After a detailed discussion of all possible reactions leading to H₂O₂ they concluded that it is formed from OH+OH and that this is the main reaction by which OH disappears.

Harteck proved that the reaction by which OH disappears is homogeneous.²⁵ The rate of this reaction, however, seemed to bring in a difficulty.

²³ E. M. Stoddart, Phil. Mag. [7] 18, 410 (1934).

²⁴ The absence of free oxygen might be interpreted by the assumption that in the electric discharge at moderate energies of electrons, OH radicals (as well as N₂ molecules) have a tendency to become excited or ionized rather than dissociated. This is to be expected from the high relative intensity of the 0-0 band emitted by the neutral molecule and the small change of internuclear distance that takes place by ionization. The values of these distances were kindly communicated to me by Professor F. W. Loomis; they are for the neutral molecule $r' = 1.022$, $r'' = 0.979$ and for the ionized molecule $r' = 1.139$ and $r'' = 1.027$. The absence of free oxygen is not easy to reconcile with the observation of G. von Elbe (J. Am. Chem. Soc. 55, 62 (1933)), who found free oxygen in H₂O₂+H₂ when illuminated with the light of the zinc spark. It has been proved by Urey, Dawsey and Rice (J. Am. Chem. Soc. 51, 1371 (1929)) that the intense zinc lines around 2100Å excite the OH band in the fluorescence of H₂O₂. Hence OH is certainly produced. Nevertheless, the interpretation of the experiment is not unique since the continuous absorption spectrum of H₂O₂, observed between 2000 and 3100Å is caused by the superposition of different processes; for instance light of 3100Å, just coinciding with the band, clearly cannot produce dissociation of H₂O₂ and simultaneous excitation of OH which are produced by 2100Å. The light of the zinc spark, therefore, is certain to produce other additional particles, making the interpretation rather uncertain.

²⁵ Cf. K. F. Bonhoeffer and T. G. Pearson, Zeits. f. physik. Chemie 14, 5 (1931).

Rodebush and Wahl found the concentration of H₂O₂, pumped out of the discharge and condensed in a liquid air trap, to be independent of the time interval of the flow between discharge and trap, even for intervals as short as 1/300 sec. They inferred that the process OH+OH→H₂O₂ is finished within a still shorter time. Considering this high rate of reaction, they discarded the idea of a triple collision and rather assumed a bimolecular association.²⁶ The argument for this rather unusual process becomes questionable, however, when considering the longer lifetime of OH reported in Section IIb. Instead, the following alternative, which was mentioned by Rodebush and Wahl themselves, seems preferable. It is assumed that the combination of OH+OH→H₂O₂ goes on in the gas as well as within the liquid air trap so that for the measurement of the H₂O₂ concentration it does not matter whether a molecule is formed before or during condensation. Because of the reported much longer life of OH there is no argument left in favor of a bimolecular association. Consequently, the usual assumption of a triple collision for the process within the gas seems preferable. The experiments reported above are not sufficiently quantitative as yet to give direct evidence of the order of the reaction by which OH disappears.

More questionable than the homogeneous reactions discussed are the reactions of OH on the wall. Urey and Lavin²⁷ discovered the high reactivity of H₂O vapor when partly dissociated by an electric discharge. The present results agree with their assumption that OH radicals can be pumped out over considerable distances from the discharge. Yet it seems difficult to attribute the reactivity of the gas mixture to one or the other particle, for instance OH, formed in the discharge. According to Rodebush and Wahl it is true that in pure glass vessels only H, OH and H₂O₂ are produced by the discharge. But since H₂O₂ decomposes readily in the presence of a

²⁶ A triple collision is fundamentally required for the association of two atoms (like H+H); not, however, for the association of two radicals forming a fouratomic molecule (like OH+OH→H₂O₂). A process of this type without a triple collision was reported by Farkas and Harteck (K. F. Bonhoeffer and P. Harteck, *Grundlagen der Photochemie*, p. 257). The probability was estimated on the basis of wave mechanics by N. Rosen (J. Chem. Phys. 1, 319 (1933)).

²⁷ H. C. Urey and G. I. Lavin, J. Am. Chem. Soc. 51, 3290 (1929).

catalytic surface, oxygen also must be taken into consideration. There seems to be no chance to investigate individual effects of one or the other particle since Stoddart reports a failure to separate the hydroxyl from atomic hydrogen and oxygen.

b. Survey of processes in the discharge through H₂O vapor

There is no doubt about the principal primary process taking place in the discharge, the water molecule being broken up by electron impact: $\text{H}_2\text{O} + \text{electron} \rightarrow \text{OH}^\cdot + \text{H}$. (Instead of OH, the H atom might become excited; or both particles might be formed in their normal states.²⁸) Since at moderate currents free atomic or molecular oxygen does not play a part, the processes to follow are the combinations of the particles mentioned, namely, $\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$ and $\text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$. The following competing associations must be considered: $\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$ obviously takes place but at a lower rate, or else the concentration of H₂O₂ could not be so high as actually observed in glass tubes with no metal present. For the same reason the reaction $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$ is supposed to have a lower rate; moreover, it would lead to atomic oxygen, the absence of which has been proved. The H₂O₂ formed in the discharge is partly broken up again by $\text{H}_2\text{O}_2 + \text{H} \rightarrow \text{H}_2\text{O} + \text{OH}$. The reaction $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ is known to have an energy of activation ≥ 14 kcal. so that it does not take place at room temperature.²⁹

A fundamental uncertainty is unavoidable in

discussing processes in discharges. Excited atoms and molecules are being produced which, due to the high energy content of their *electronic structure*, might have a special reactivity, so high that even during the life of the excited state reactions are probable. Obviously the processes after the interruption of the discharge are easier to correlate to known chemical processes.

In the combination of H₂ and O₂, started by photochemically produced H atoms, H₂O₂ is formed, too. If the most recent theory is correct, in this photochemical experiment the H₂O₂ is formed over the intermediate compound HO₂ by association of H atoms with O₂ molecules.³⁰ It is of interest that in the electric discharge through H₂O vapor the formation of H₂O₂ takes place by an entirely different process.

The main results of the present paper are as follows: As a test for free OH radicals absorption spectra taken in snapshots were applied. They indicate in particular the change of concentration with time. The lifetime of free OH radicals is much longer than previously assumed, so long that no bimolecular association must be assumed for the process by which they disappear. Attempts will be made to obtain quantitative results by photographic photometry and to search for free OH radicals in other reactions.

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²⁸ J. Franck, H. Kuhn and G. Rollefson (Zeits. f. Physik **43**, 155 (1927)) describe analogous processes caused by absorption of light.

²⁹ W. Frankenburger and H. Klinkhardt, Zeits. f. physik. Chemie **15**, 436 (1932).

³⁰ K. H. Geib, Zeits. f. physik. Chemie **A169**, 161 (1934); K. F. Bonhoeffer and P. Harbeck, *Grundlagen der Photochemie*, p. 262.