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A. A. Frost and O. Oldenberg

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Kinetics of OH Radicals as Determined by Their Absorption Spectrum

II. The Electric Discharge Through H₂O₂

A. A. FROST AND O. OLDENBERG, Research Laboratory of Physics, Harvard University, Cambridge, Massachusetts (Received October 5, 1936)

In order to study the kinetics of OH radicals in H_2O_2 the concentration of OH as a function of time is measured by the decay of the intensity of the OH absorption bands after interrupting an electric discharge through H_2O_2 . For each snapshot a new supply of H_2O_2 is introduced into the absorption tube and partly decomposed into OH+OH by an electric discharge of brief duration. OH radicals disappear in H_2O_2 much more rapidly than in H_2O . This indicates a bimolecular reaction OH+ H_2O_2 . The emission spectrum of OH shows abnormal rotation of OH even more strongly when excited in H_2O_2 than in H_2O , the rotation being determined not by the temperature but by the simultaneous dissociation and excitation producing the OH radicals observed.

I. PROBLEM

I N the preceding paper¹ the reaction of OH as produced in the electric discharge through water vapor has been investigated. The concentration of OH as a function of time after interrupting the discharge was traced by the intensity of the absorption spectrum taken in snapshots; the pressure, in particular of added helium was varied. The main result was that OH is largely consumed by triple collisions—probably $H+OH+M\rightarrow H_2O+M$. The interpretation of the experiments, however, was somewhat complicated by the presence of free hydrogen atoms.

There is a chance to observe a still simpler system in H_2O_2 vapor after the interruption of an electric discharge. It was found by Urey, Dawsey and Rice² that in a weak discharge through H_2O_2 the spectrum consists almost exclusively of OH bands. They concluded that in the discharge the most probable process is the dissociation of H_2O_2 into OH+OH and that very little atomic H and O are produced. This discharge, therefore, after its interruption affords an observation of the life of OH radicals when they collide largely with H_2O_2 and with much less probability with other OH radicals.

From previous results one might arrive at contradictory predictions regarding the fate of OH in H_2O_2 vapor. Rodebush and Wahl³ observed so high a concentration of H_2O_2 in the

gas pumped out of the discharge through H₂O vapor that one ought to assume as the most probable process the combination OH+OH+M \rightarrow H₂O₂+M and only a small probability that H_2O_2 thus formed is destroyed again by H or OH. On the other hand Urey, Dawsey and Rice found out that H_2O_2 is decomposed so rapidly by a weak discharge that they had to make their spectroscopic investigation with fast flowing vapor. This apparent discrepancy is probably solved by the recent assumption of Campbell and Rodebush⁴ and of Geib⁵ that in the gas pumped out of the discharge through H₂O vapor the H₂O₂ is not formed in the gas phase but in the freezing process in the liquid-air trap so that it is not exposed to decomposition. This idea is strongly confirmed by the failure, published in the preceding paper, to observe the absorption spectrum H₂O₂ after interrupting the electric discharge through H₂O in spite of an arrangement which had been made sufficiently sensitive to detect $1/100 \text{ mm H}_2O_2$.

II. EXPERIMENTAL

The experimental arrangement was largely the same as that described in previous papers. The concentration of OH was observed by the intensity of its absorption spectrum taken by snapshots in the second order of a 21-foot grating. H_2O_2 was concentrated from the commercial 30 percent solution (Superoxol) by a vacuum distillation at 0°C, the residue analyzing 95 percent

¹ A. A. Frost and O. Oldenberg, J. Chem. Phys. 4, 642 (1936).

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[•] W. H. Kodebush and M. H. Wani, J. Chem. Phys. 1, 696 (1933).

⁴ R. W. Campbell and W. H. Rodebush, J. Chem. Phys. **4**, 293 (1936).
⁵ K. H. Geib, J. Chem. Phys. **4**, 391 (1936).



FIG. 1. Discharge and absorption tube for H_2O_2 ; scale 1: 25; Q, quartz window; E, electrode; IV, inlet valve; OV, outlet valve.

 H_2O_2 by weight. However, the H_2O_2 vapor derived from this, and used in the following experiments, was only about 50 mole percent H_2O_2 as determined from vapor pressure measurements.

The H_2O_2 vapor had to be kept flowing with considerable velocity through the observation tube since otherwise the products of its decomposition would have accumulated and affected the reaction studied. On the other hand too rapid a flow was not permissible since it would carry away the OH the reaction of which was to be studied after interrupting the discharge.

With this arrangement only very faint absorption spectra of OH were observed. They disappeared entirely after a short time interval. It was questionable, however, whether this failure was caused by inadequate conditions or by the real disappearance of OH. Therefore a fresh supply of H₂O₂ at a definite pressure was introduced for each snapshot of the absorption spectrum. The direction of flow was arranged such that impurities emanating from the electrodes were swept away. The following cycle of operations was carried out automatically with the aid of magnetically operated valves. First the absorption tube was pumped out through short and wide tubes by a very rapid pump (Cenco Hypervac), next the stopcock to the pump closed, H₂O₂ of the proper pressure admitted and partly decomposed by a discharge of about 350 ma (current density 20 ma/cm²) lasting for 1/120 of a second, and finally the absorption spectrum of OH was taken in a snapshot at a time interval after the discharge that could be varied. This whole process that needed about 4 seconds was repeated 4500 times in order to secure sufficient exposure of the photographic plate.

Because of the long total time required for the exposure it was found convenient to take during

the same run two exposures corresponding to two different time intervals between discharge and absorption measurement. This was done by using a rotating sector which allowed light to get into the grating spectrograph through two different portions of the same slit at different times. Since during these experiments the astigmatism of the spectral lines from a concave grating was almost completely removed by a cylindrical lens, the two adjacent portions of the slit formed adjacent portions of the spectral lines.

It is known that H₂O₂ decomposes when in contact with metals or stopcock grease. The aluminum electrodes therefore were kept away from the absorption tube by the arrangement illustrated in Fig. 1. The gas valves only schematically indicated in Fig. 1 were built as shown in Fig. 2. The movable glass core C containing a piece of soft iron, sealed in a closely fitting glass tube, rested by its weight on the flange Fof a glass tube. The flange F and the ring forming the bottom of C were both ground and polished optically flat, as tested with interference methods.⁶ No grease was applied. Only very little gas leaked through this valve when closed. A test showed that the H₂O₂ was not decomposed by flowing through this value. It must be kept in mind that its purpose was only



FIG. 2. Greaseless valve, magnetically operated, with optically flat contact; scale 1: 2; C, glass core; F, flange.

⁶ We appreciate the accurate work of Mr. D. W. Mann and Mr. H. W. Leighton who made the valves. to separate the absorption tube for a few seconds from adjoining tubes which contained pressures different by a few millimeters. When opened by the magnet it offered an outlet much wider than most commercial stopcocks. (This valve must be connected so that when closed the gas pressure acts downward on the core C. The strength of the magnet required to open it depends upon the pressure difference.) A synchronous motor with various switches on its axis operated the following five devices: the current through the H_2O_2 vapor (with the aid of a thyratron as a relay), the hydrogen discharge that gave the continuous background for the absorption spectrum, the two magnets for inlet and outlet valve, and finally a sector disk that excluded from the spectrograph the emission spectrum from the flash through the H₂O₂ and admitted only the light for the absorption spectrum.

The absorption spectrum when resolved into rotational lines indicates relative concentrations of OH by a photometric procedure described in the preceding paper.

III. RESULTS

After interrupting the discharge through H_2O_2 the absorption spectrum of OH disappeared at a rate very much higher than in the discharge through H₂O While in H₂O the absorption of OH could be traced as long as 0.4 sec., in H_2O_2 under similar conditions it was much fainter and disappeared within 1/100 sec. That OH is certainly produced in the discharge is shown by the fact that the OH emission from the discharge through H_2O_2 was even stronger than the OH emission from an H₂O discharge under the same conditions of pressure and current.

Since the main feature of the new experiment consists of the presence of ample H_2O_2 , it is most plausible to assume that the rapid disappearance of OH is caused by a bimolecular reaction with H_2O_2 . This experiment gives no evidence of the product of this reaction. The rate is too high for accurate measurement with the rotating sector. On the other hand it is certain that only a small fraction of all collisions $OH + H_2O_2$ lead to a reaction.

By observing the continuous absorption spectrum of H_2O_2 it was found that a half-period of rather weak current is sufficient to decompose largely the H₂O₂. This agrees with the statement of Urey, Dawsey and Rice that the emission spectrum of H₂O₂ shows its characteristic feature only if the vapor is rapidly flowing. Since a tendency towards the formation of H₂O is to be assumed, it is plausible that the same process takes place in the vapor $OH + H_2O_2 \rightarrow H_2O + O_2H$ that has been discussed in great detail by Haber and Weiss⁷ and by Kornfeld⁸ for the decomposition of H_2O_2 in solution.

IV. Abnormal Rotation of OH Caused by DISSOCIATION OF H₂O₂

In the electric discharge through water vapor a striking difference has been observed between the intensity distributions in emission and absorption.⁹ In absorption only a few rotational quanta appear in each branch corresponding to approximately room temperature. In emission, however, very high rotation is indicated by the long extension of each branch, entirely unrelated to the temperature of the gas; the well-known sharp edge 3064 by which this band is easily identified in emission disappears completely in absorption since its rotational energy value considerably exceeds the thermal value.

The abnormal rotation observed in emission has been explained by the assumption that in the excitation process a fast electron which must have at least 9.0 volts, dissociates the H₂O and excites the OH in one process. The energy with which H and OH' separate is determined not by the temperature but instead by properties of potential curves describing the structure of normal and excited H₂O.¹⁰

In the electric discharge through H_2O_2 , according to Urey, Dawsey and Rice, we similarly assume one process of dissociation and excitation of one of the OH. Since we are dealing with a dissociating molecule of a structure entirely different from H₂O we ought to expect some other value of abnormal rotation although we are unable to predict the value in one or the other case.

⁷ F. Haber and J. Weiss, Proc. Roy. Soc. London A147, 332 (1934).

⁸ G. Kornfeld, Zeits. f. physik. Chemie B29, 205 (1935).

 ⁹ O. Oldenberg, Phys. Rev. 46, 210 (1934).
 ¹⁰ O. Oldenberg, Phys. Rev. 37, 1550 (1931).

The experiment described above offers good conditions for such an observation since a brief electric discharge is sent through H₂O₂ vapor and then the partly decomposed vapor is pumped out and replaced by fresh vapor so that the OH band observed is certain to originate from dissociating H₂O₂.

A comparison of the OH bands in H₂O and H_2O_2 actually shows a distinct difference in abnormal rotation. For equal intensities at the low rotational lines in H_2O_2 , the tail representing the highest rotation is more intense than in H₂O. This result confirms the idea of the origin of abnormal rotation of OH.

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Solvent Action on Optical Rotatory Power

CHARLES O. BECKMANN AND KARL COHEN,* Department of Chemistry, Columbia University, New York City (Received July 28, 1936)

A general theory of the optical rotatory power of liquids is developed. The method of C. G. Darwin, supplemented so that the fundamental quantities $s_{\alpha\beta\gamma}$...[†] which appear there are related to the properties of the molecules comprising the medium, is followed. The optical properties of a molecule are given by a set of tensors $\sigma'_{\alpha\beta\gamma\dots}$. The concept of deformation leads naturally to a simple relation between the $\sigma'_{\alpha\beta\gamma...}$'s and the field acting on the molecule. The electrostatic field of the dipoles of the surrounding mole-

SECTION 1

THE problem of the solvent action on optical rotatory power dates back to within a few years of the discovery of natural gyration itself by Biot.¹ His early work on solutions (1815–1832) led Biot² to invent the quantity "specific rotation" which he believed to be characteristic for a particular optically active substance. He concluded from these experiments that each molecule possesses the property of rotating the plane of polarized light a definite amount and that "the active molecules (solute) merely disperse themselves among the inactive molecules (solvent), as if in free space, without suffering from them any action which modifies their rotatory power appreciably."3 In subsequent experiments however, it was found that all active substances show variations of specific rotation with solvent. concentration and temperature.

The earliest explanation of this solvent action,

cules is computed for the limiting cases of imperfect gases and dilute solutions, for molecules of simple geometrical configuration. This field is identified with the solvent field. For these idealized systems, the rotatory power of a molecule in various solvents is determined in terms of quantities characteristic of the solvents. The resulting equations are controlled by comparing with the behavior of actual liquids.

the tautomerism theory, was closely associated with anomalous rotatory dispersion. Historically, the tautomerism theory arose from studies on tartaric acid. Biot found that tartaric acid solutions not only exhibited a strong solvent effect, but also showed anomalous rotatory dispersion, so-called because the dispersion curve showed a maximum in the visible region. He artificially produced the dispersion anomaly by measuring simultaneously two substances with simple dispersion but opposite rotations.⁴ This suggestive idea was explicitly formulated, and applied to the solvent effect, by Arndtsen⁵ in 1858. He concluded that anomalous dispersion is caused by the existence of two forms of tartaric acid in solution, varying proportions of the two forms being responsible for the changes of rotation with concentration. The variation of the proportions was later considered to be due to a shift in an equilibrium between the two forms.⁶

Confirmation of the existence of tautomers was obtained from the work on mutarotation in

^{*} Adapted from a dissertation submitted to Columbia University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

 $[\]sigma_{\alpha\beta\gamma}$... in Darwin's notation.

 ¹ J. B. Biot, Mém. acad. sciences 15, 93 (1838).
 ² J. B. Biot, Mém. acad. sciences 13, 39 (1835).
 ³ J. B. Biot, Ann. chim. phys. (3) 36, 258 (1852).

⁴ J. B. Biot, Comptes rendus 2, 543 (1836).

 ⁵ A. Arndtsen, Ann. chim. phys. (3) 54, 403 (1858).
 ⁶ T. M. Lowry and T. W. Dickson, Trans. Faraday Soc.
 10, 96 (1914); T. M. Lowry and P. C. Austin, Phil. Trans. Roy. Soc. A222, 249 (1922).