AIP | The Journal of Chemical Physics

Kinetics of OH Radicals as Determined by Their Absorption Spectrum1 V. A Spectroscopic Determination of a Rate Constant

O. Oldenberg and F. F. Rieke

Citation: The Journal of Chemical Physics **7**, 485 (1939); doi: 10.1063/1.1750477
View online: http://dx.doi.org/10.1063/1.1750477
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/7/7?ver=pdfcov
Published by the AIP Publishing

JULY, 1939 JOURNAL OF CHEMICAL PHYSICS VOLUME 7

Kinetics of OH Radicals as Determined by Their Absorption Spectrum[1]

V. A Spectroscopic Determination of a Rate Constant

O. OLDENBERG
Research Laboratory of Physics, Harvard University, Cambridge, Massachusetts

AND

F. F. RIEKE
Department of Chemistry, University of Chicago, Chicago, Illinois

(Received April 10, 1939)

In order to determine the efficiency with which triple collisions bring about the recombination of free OH radicals, the rate constant for the reaction must be known in *absolute* units. Consequently it is necessary to measure in absolute units the "standard concentration" on which is based the rate constant previously determined spectroscopically by Frost and Oldenberg. For this purpose the intensities of the OH absorption lines in their "standard discharge" were measured and combined with the *f* values recently published. Because of the very small width of the OH absorption lines in the discharge, Fabry-Pérot plates had to be used in order to produce absorption spectra with a resolution sufficiently high for suitable intensity measurements. It was found that the efficiency of triple collisions is higher than unity if the number of such collisions is computed from gas kinetic data. This result indicates that OH forms collision complexes which have a lifetime much greater than the duration of bimolecular collisions between stable molecules.

I. PROBLEM

In previous work[2] absorption spectra were used to measure relative concentrations of free OH produced by an electric discharge through water vapor. The result was that the concentration decays according to the law

$$1/[\mathrm{OH}]-1/[\mathrm{OH}]_0=kpt,$$

where t is the time and p the pressure of a foreign gas (either water vapor or helium), present in much higher concentration than OH. A decay curve of this type is evidence that the reaction takes place in triple collisions.[3]

It is the purpose of the present paper to measure the absolute value of the rate constant and compare the frequency of such recombination processes with the frequency of triple collisions

---

[1] Dr. V. Kondratjew kindly calls our attention to an error in the computation of the Einstein coefficients a_{ki} given in the preceding paper of this series (J. Chem. Phys. **6**, 439 (1938)). The general formula is to be corrected to $a_{ki}=g_i/g_k\times(8\pi^2e^2\nu^2)/mc\times f$. The numerical results are not changed for the most intense branch, Q_1. For the P and R branches the values for $a_{ki}\times10^{-5}$ are as follows: for $R_2(\frac{1}{2})$ to $R_2(2\frac{1}{2})$: 0.34; 0.49; 0.58, respectively; for $P_1(1\frac{1}{2})$ and $P_2(2\frac{1}{2})$: 2.40 and 1.62, respectively; for ${}^QP_{21}(1\frac{1}{2})$ to ${}^QP_{21}(6\frac{1}{2})$: 1.60; 0.78; 0.45; 0.30; 0.23; 0.18, respectively. The "*f* values" applied for the quantitative test for OH are not changed. The lifetime for the initial level of the intense line $Q_1(4\frac{1}{2})$, taking into account all 6 components originating from the same level, is 2.5×10^{-6} sec. (instead of 3.8×10^{-6}).

[2] O. Oldenberg, J. Chem. Phys. **2**, 713 (1934) and **3**, 266 (1935); A. A. Frost and O. Oldenberg, J. Chem. Phys. **4**, 642 (1936).

[3] A discussion has been given in preceding papers (references 1 and 2) of how the free hydroxyl was produced in water vapor at low pressure. The H_2O was partly dissociated by an electric discharge of brief duration, producing H and OH in equal concentrations. After interrupting the discharge the gradual disappearance of OH was traced by absorption spectra taken in snapshots; the interval between the interruption of the discharge and the snapshot was varied in multiples of 2/15 sec. up to 6/15 sec. Frost and Oldenberg, observing only *relative* concentrations of OH, found the rate of disappearance, for a given initial concentration, to be approximately proportional to the total pressure (of H_2O or added He). They inferred that OH was consumed by a trimolecular process.

Rodebush, Wende, and Campbell (W. H. Rodebush, C. W. J. Wende, and R. W. Campbell, J. Am. Chem. Soc. **59**, 1924 (1937)) discussed in detail the possible reactions that might take place in the electric discharge through H_2O; their conclusion was that most of the hydroxyl disappears by the trimolecular association

(1) $\mathrm{H+OH+M\rightarrow H_2O+M}$.

In addition, the reaction

(2) $\mathrm{OH+OH+M\rightarrow H_2O_2+M}$

may take place. Against reaction (2) the objection may be raised that Frost and Oldenberg (A. A. Frost and O. Oldenberg, J. Chem. Phys. **4**, 781 (1936)) failed to detect by its absorption spectrum any H_2O_2 so formed. This failure, however, was not considered as definitely excluding reaction (2) because it is explained if a rapid decomposition of H_2O_2 takes place when H and OH are present; in this case the H_2O_2 would be present in only a very small concentration even though it were formed rapidly by reaction (2).

Kondratjew (V. Kondratjew, Acta Physicochem. U. S. S. R. **8**, 315 (1938)), on the other hand, estimated that reaction (2) is much more probable than (1). He based this conclusion on the idea that the mean life of a "collision complex" (a colliding pair ready to be stabilized by a collision with a third body) is longer the more complicated the resulting molecule. The outstanding difficulty for the application of this argument is the present uncertainty in as computed from kinetic theory. (Mulliken[4] has recently made a quantum-mechanical calculation of the f value of OH and arrived at a result which is in substantial agreement with our measurement.)

As may be seen from the above equation, the reaction constant k has the dimensions of $([OH]\cdot p\cdot t)^{-1}$; its magnitude therefore is dependent on the units in which [OH] is measured (p and t being directly measured in the conventional units). At the time the experiments of Frost and Oldenberg were performed it was not possible to use the absorption spectrum as a measure of the *absolute* concentration of OH since the transition probabilities were not known. It was possible, however, to make *comparisons* with a certain arbitrary standard in which the concentration of OH was *reproducible*, being defined by pressure of H_2O and electric current, although the value of the concentration was *unknown*. Such measurements are sufficient to give the order of the reaction, but they lead to a value of the rate constant which contains the arbitrariness inherent in the standard. In order to obtain the rate constant in absolute units, so that it may be compared with the results of kinetic theory, we have undertaken an absolute calibration of the arbitrary standard used by Frost and Oldenberg.

The first step in the calibration of the "standard concentration" was to determine the transition probabilities (or the related "f values") of the OH absorption lines. For this purpose a known concentration of OH was produced by thermal dissociation of water vapor and the intensities of the absorption lines were measured. The result, reported in a preceding paper[5] was that the transition probability for the well-known 3064 band of OH is unexpectedly small—f values of the order of magnitude of 2×10^{-4}. This result was confirmed by the reinterpretation[6] of recent measurements by Avramenko and Kondratjew.[7]

The second step in the calibration—the principal subject of the present paper—is to measure the absolute intensity of the absorption spectrum produced by the standard. As defined by Frost and Oldenberg the "standard concentration" is that in the discharge, under certain conditions of pressure and current, immediately after the discharge current has been interrupted. By the application of the f values just mentioned, the concentration of OH, in molecules/cc, is then computed. This second step requires a special technique because at the low pressure and temperature of the discharge the OH lines are exceedingly narrow.

II. EXPERIMENT

A. Choice of method

In determining the intensity of a narrow *absorption* line a very great difficulty arises from the effect of the spectrograph on the absorption observed. The intensities of *emission* lines, no matter how narrow, are easily obtained by using a slit wide enought to give flat-topped lines; the final resolving power of the spectrograph need be only great enough to separate neighboring lines. However, this method fails for absorption lines since a narrow absorption line practically disappears when a spectrograph of poor resolving power is used; both adjacent sides of the continuous background overlap and thus swallow the line. Simple considerations show that for the detection of absorption lines the sensitivity increases with the resolving power of the spectrograph up to the point where the true contour of the lines is resolved; moreover for the direct measurement of the absorption coefficient within the line—which is directly proportional to the concentration of absorbing particles—the resolving power must actually be great enough to show the true width of the line. Since in the discharge tube the OH absorption lines are so narrow that the 21-foot grating is not quite adequate for the latter purpose, we have resorted to Fabry-Pérot plates with a still higher resolving power.

---

the computation of the mean lives of complexes. Kimball (G. E. Kimball, J. Chem. Phys. **5**, 310 (1937)) has given a classical treatment of the problem, but his results have been criticized by Kassel (L. S. Kassel, J. Chem. Phys. **5**, 922 (1937)), who indicated that the inclusion of additional factors greatly reduces the mean lives predicted by the theory. Hence neither this theory nor our observation determines conclusively whether it is reaction (1) or (2) which results from triple collisions.

[4] R. Mulliken, J. Chem. Phys. **7**, 14 and 20 (1939); Astrophys. J. **89**, 283 (1939).

[5] O. Oldenberg and F. F. Rieke, J. Chem. Phys. **6**, 439 (1938).

[6] O. Oldenberg and F. F. Rieke, J. Chem. Phys. **6**, 779 (1938).

[7] L. Avramenko and V. Kondratjew, Acta Physicochimica **8**, 567 (1937).

One can easily estimate that a line 0.01A wide (approximately the width of the OH lines at 300°K and low pressure) which absorbs 50 percent at its center, when observed with an instrument of resolving power of 1A (medium sized quartz spectrograph), will produce a broadened depression of the continuous background amounting to only $\frac{1}{2}$ percent, which is entirely unobservable. With a resolving power of 0.015A (large grating) the depression will be approximately 30 percent. Hence, for the qualitative observation of OH absorption lines in the discharge, and for the matching of lines of equal intensity,[8] the 21-foot grating is a suitable instrument, even though it does not give the true value of the absorption coefficient at the center of the line.

While thus the broadening of an absorption line *by the poor quality of a small spectrograph* is apt to make the line unobservable, broadening *within the absorbing gas* by temperature or pressure may have the opposite effect. Here we must differentiate between the *absorption coefficient* $\alpha(\nu)$ and the *absorbed intensity* $1-e^{-l\alpha}$ (l = length of absorbing layer). The *absorption coefficient* α as a function of the wave number ν behaves the same way as the intensity of an emission line: in the case of Doppler broadening it follows a curve of the type $y=e^{-x^2}$ which, for high temperature, becomes lower and broader so that the same $l\int\alpha d\nu$ is maintained. Also the effect of pressure broadening is the same on the absorption coefficient as on the intensity of emission, although for pressure broadening the shape is not exactly represented by a curve of the type e^{-x^2}. However, for the *absorbed intensity* $(1-e^{-l\alpha})$ as a function of ν, a simple analysis leads to the following result: When we consider a given number of absorbing molecules (given $l\int\alpha d\nu$) the broadening of an absorption line by temperature or pressure will really increase the amount of energy taken away from the continuous background (represented by $\int(1-e^{-l\alpha})d\nu$). This increase disappears only in the limit of weak absorption lines. Hence for the measurement of absorption, artificial broadening is advantageous. For example, the total absorption (the "f value") of the resonance line 2537 of Hg, which is exceedingly narrow under ordinary conditions, could be measured with a quartz spectrograph by Füchtbauer, Joos, and Dinkelacker[9] in a high pressure chamber with 50 atmospheres of a foreign gas.

This advantage was used in our calibration experiment in which the total pressure of 1 atmos. broadened the lines of OH, of which only 0.35 mm was present. Under this condition the second order of a 21-foot grating proved sufficient. Far more difficult, however, is the present problem, the measurement of the OH absorption spectrum in the discharge tube near room temperature, because the *temperature* broadening is smaller in the ratio $1/\sqrt{5}$ and the *pressure* broadening practically disappears. (No broadening by the *electric current* takes place, as the absorption line is photographed after interruption of the discharge.)

B. Optical arrangement

The Fabry-Pérot plates were of fused quartz; for use in the ultraviolet (3000A) they were aluminum coated by evaporation.[10] In order to increase the intensity of the light transmitted, the Fabry-Pérot plates were modified in the manner described by Machler and Fisher.[11] The strips in the coating of the first plate were produced by a coarse wire grating in contact with the plate during the evaporation. The plate separation was 12 mm. This gives practically the maximum resolving power that can be applied because a still greater separation, although increasing the theoretical resolving power, would lead to so narrow a distance between adjacent orders (smaller than 0.42 cm^{-1}) that the width of the emission lines used for a background would cause overlapping. The adjustment of the plates was checked between exposures. The resolving power was estimated at 5×10^5 (0.065 cm^{-1}) by photographing sharp lines of a cooled mercury arc. This is 2.2 times as high as the theoretical resolving power of the second order of the 21-foot grating of this laboratory. The theoretical resolving power of Fabry-Pérot plates leads to this figure if 6.4 is taken as the number of effective reflections.

The Fabry-Pérot plates were used in conjunction with a Hilger E1 spectrograph[12] with a dispersion of 5.2A/mm at 3000A.

The spectroscopic apparatus was placed in the constant temperature room built for the 21-foot grating in the basement of the laboratory.

C. Background

A difficulty arose because of the small range—only 0.42 cm^{-1}—between adjacent orders of the spectrum. Since the quartz spectrograph, even the large Hilger E1, is unable to separate out so narrow a spectral range from a *continuous* spectrum, no such spectrum could be used as a background for the absorption experiment. This

---

[8] A. A. Frost, D. W. Mann and O. Oldenberg, J. Opt. Soc. Am. **27**, 147 (1937).

[9] C. Füchtbauer, G. Joos, and O. Dinkelacker, Ann. d. Physik **71**, 204 (1923). A pressure as high as 50 atmos. may produce an appreciable change of the f value. No effect like that has ever been observed for our pressure range of 1 atmos.

[10] For help in coating the plates we are obligated to Dr. H. M. O'Bryan, who built the apparatus for vacuum evaporation.

[11] R. C. Machler and R. A. Fisher, J. Opt. Soc. Am. **25**, 315 (1935).

[12] The Littrow mounting of this instrument necessitates a slight tilt of the lens which causes astigmatism. Since the interference fringes appeared horizontally, sharp fringes could be obtained on the photographic plate only if the fringe system was focused in a plane about a cm from that of the slit.

spectrograph, however, is well able to separate *individual lines* of the intense Q branches of the OH band. Hence this band itself, emitted by a heavy discharge through water vapor, was used as a background.

The emission discharge tube, built as the conventional tube for a strong hydrogen discharge, showed strong self-evacuation when operated with H_2O vapor. Therefore, in order to keep conditions constant the water vapor had to be kept flowing from a container, kept at 0°C, through the discharge tube capillary and CO_2 trap to the pump. Since each exposure of the absorption spectrum was made in flashes through a rotating sector disk, the emission discharge was interrupted in between by a rotating switch and relays; thus a current as strong as 2 amp. through a rectangular capillary (cross section 1×5 mm^2) could be used for the flashes.

The OH band proved to be only slightly susceptible to broadening by current. In spite of the high current density mentioned, we failed to make the emission lines sufficiently broad so that the absorption to be studied would appear as narrow dark lines on the background of broad emission lines. However, the loss of intensity by absorption at the middle of the lines was easily observed.

Since the *absorption* band has *thermal* distribution of rotational energy while the *emission* band shows *abnormal* rotation[13] far exceeding the thermal value, the absorption effect is restricted to a few lines close to the zero line. The tail of the emission band, representing the abnormal rotation, can be followed up to the rotational line $29\frac{1}{2}$, and served as a check as to whether, in the two exposures to be compared—with and without an absorber—the background remained constant.

With ideal resolving power it would have been possible to determine how the original intensity distribution of the emission line was modified by the absorber; this would have led to the *complete contour* of the absorption line. The actual resolving power, however, corresponded to an interval only slightly less than the half-value width of the absorption line. Consequently it seemed preferable to measure only intensities *at the centers of lines* with and without an absorber and thus determine only the central value of absorption. This measurement is sufficient since it is safe to assume that the absorption line, observed at low pressure after interrupting the discharge, has only the Doppler broadening corresponding to the temperature of the gas. (The pressure broadening had been measured for one atmosphere of a foreign gas and was computed to be only 1.6 percent of the Doppler broadening which is negligible.)

Since the resolving power was barely adequate, a correction was applied to the measurements; this was computed using the method described by Slater.[14] A contour was assumed for the emission line, and contours computed and plotted for various values of absorption. By applying the correction to both the unabsorbed line and the absorbed lines, observed values of central absorption could be correlated with the true values. The corrections, shown in Table I, were less than 5 percent and for the weak absorptions dealt with here were found to be rather insensitive to the width assumed for the emission line.

This method differed from the "line absorption" applied by Avramenko and Kondratjew,[7] although they, too, employed the emission lines as a background. However, they measured the loss of *total intensity* of the emission line, using a spectrograph of small resolving power; furthermore they presupposed the exclusive action of *pressure* broadening.

D. Electrical arrangement and procedure

The electrical arrangement was largely the same as described by Frost and Oldenberg. A synchronous motor operated the switches through gears. A rotating switch, controlling the grid of a

TABLE I.

(1) J	(2) I_t/I_0 OBSERVED	(3) I_t/I_0 CORR. FOR LACK OF R.P.	(4) I_t/I_0 CORR. FOR SECTOR WIDTH	(5) I_t/I_0 COMPUTED FROM $Q_1(6\frac{1}{2})$	(6) N_{OH} (CM^{-3})	(7) p_{OH} (MM)
$1\frac{1}{2}$	0.58	0.54		0.64		
$5\frac{1}{2}$	0.67	0.63		0.67		
$6\frac{1}{2}$	0.80	0.77	0.72		1.1×10^{14}	0.0035

Results of absorption measurements.—I_t = transmitted intensity; I_0 = incident intensity; N_{OH} = concentration of OH (cm^{-3}); p_{OH} = partial pressure of OH (mm mercury). Correction for sector width directly applied to $Q_1(6\frac{1}{2})$ (column 4); for a check, the values for $Q_1(1\frac{1}{2})$ and $Q_1(5\frac{1}{2})$ were computed (column 5) from $Q_1(6\frac{1}{2})$; they are to be compared with column 3.

---

[13] O. Oldenberg, Phys. Rev. **46**, 210 (1934).

[14] J. C. Slater, Phys. Rev. **25**, 783 (1925).

thyratron, passed the current (about 180 m amp., current density 9.5 m amp./cm^2) through the absorption tube for three half-periods of current. This current produced the concentration of OH as it was arbitrarily adopted as a standard by Frost and Oldenberg, and was to be determined by the present experiment. Meanwhile a sector disk protected the slit of the spectrograph. Immediately after interrupting this discharge, the sector opened the light path and the snapshot of the absorption spectrum was taken for 8/45 sec. This procedure was automatically repeated every 8/15 sec. through two hours.[15]

In the next exposure the spectrum of the background was taken with no preceding current through the absorption tube. The constancy of the intensity was checked at the tail of the band, which is, as explained above, not subject to absorption. For the conventional photometric procedure intensity marks were printed with uniform illumination of the slit by a Hg arc with the same time of exposure and the same sector disk, intensity steps being provided along the slit by an additional fast sector disk. The photometric work was done on the densitometer built at this laboratory by Dr. F. H. Crawford and Mr. D. W. Mann.

III. COMPUTATION

The individual line is described by the absorption coefficient as a function of the frequency $\alpha_\nu = \alpha_0 e^{-\beta(\nu-\nu_0)^2}$. The constants of this formula are determined as follows: The broadening is due only to the Doppler effect (0.097 cm^{-1} at 300°C); this leads to the constant $\beta = 0.326 \times 10^{-18}$ cm^2. The constant α_0 of each spectral line (the maximum absorption coefficient of the line) was measured by the usual procedure of photographic photometry (if I and I_0 are intensities at the middle of the line with and without absorber, α_0 follows from $I/I_0 = \exp(-l\alpha_0)$ where $l = 150$ cm). A simple integration yields the integral absorption coefficient

$$\int_0^\infty \alpha_\nu d\nu = \alpha_0 \times 0.103 \text{ (cm}^{-2}\text{)},$$

and thus the density of "dispersion electrons"

$$N_{\text{disp}} = \frac{mc^2}{\pi e^2} \int_0^\infty \alpha_\nu d\nu (\text{cm}^{-3})$$

(m = mass of electron, e = charge on electron in e.s.u., c = velocity of light).

The f value taken from the preceding paper gives the number of OH radicals that are able to absorb this individual line, since

$$N_{\text{line}} = N_{\text{disp}}/f.$$

These particular OH radicals, absorbing the line $Q_1(J)$, represent a certain percentage of all OH radicals, which is computed from the rotational distribution of OH at 300°K. (The detail of this lengthy computation was given in a preceding paper.) The total number of OH radicals N_{OH} thus determined is identical with the concentration taken by Frost and Oldenberg as "standard pressure."

IV. RESULTS

A. Concentration of OH

The lines $Q_1(1\frac{1}{2})$, $Q_1(5\frac{1}{2})$, $Q_1(6\frac{1}{2})$ were sufficiently isolated by the Hilger E1 spectrograph to produce clear interference fringes. The ratios (transmitted intensity I_t/incident intensity I_0) measured by photographic photometry, are given in Table I. The correction for lack of resolving power (see Section IIC) was applied (column 3) to the measurement given in column 2.

The best results were obtained from the line $Q_1(6\frac{1}{2})$ because it is singularly well isolated; moreover its absorption is weak enough so that it is in the range most favorable for measurement and computation. In utilizing the other lines for a check it turned out to be difficult to derive N_{OH} from their absorption ratios because, for the case of strong absorption, the correction for sector width leads to complicated formulae. Instead

---

[15] While Frost and Oldenberg determined the change of [OH] with time by snapshots of 8/90 sec., here the length of each snapshot was doubled in order to shorten the total time required for the exposure. Hence it must be taken into account that [OH] varies appreciably during each snapshot. The density of the photographic image is determined by the average intensity transmitted. The instantaneous value of the intensity transmitted is an exponential function of [OH]. Since the law of decay of relative concentrations of OH is known, the proper initial value of [OH], which leads to the average intensity acting on the photographic plate, could be derived. This correction for the sector width amounted to 25 percent.

such a check was more easily derived from the inverse calculation: Starting from the observed absorption for $Q_1(6\frac{1}{2})$ just mentioned and the theoretical relative intensities of the lines at 300°K the absorption of $Q_1(1\frac{1}{2})$ and $Q_1(5\frac{1}{2})$ was computed (column 5) and compared with the observed values (column 3). This check is as good as can be expected from the limitations offered by $Q_1(1\frac{1}{2})$ and $Q_1(5\frac{1}{2})$. For the final computation the value derived from $Q_1(6\frac{1}{2})$ was applied.

The result is a partial pressure of OH of 0.0035 mm. This is our value for the initial pressure in the experiment of Frost and Oldenberg (reference 1, Fig. 1, curve for H_2O). From their diagram, representing $1/[OH]$ as a function of time, it follows that their initial value of $1/[OH]$ equals 1.45×1/standard pressure. Hence their "standard pressure" was 0.0050 mm.[16]

As the sensitivity of the absorption method in the *furnace* experiment was estimated as 0.01 mm of OH, it was surprising that pressures so much smaller could easily be observed in the *discharge*. The sensitivity expressed as the lowest pressure of OH observable was much higher in the discharge than in the furnace for four reasons: (1) the discharge tube was longer than the furnace in the ratio 150/44; (2) at 300° a certain *density* of OH causes a smaller *pressure* than at 1473°C; (3) at 300°C the thermal distribution of rotation is restricted to a narrower range than at 1473°C; (4) because of the smaller broadening, the absorption is concentrated into narrower lines.[17]

B. Rate constants

In the work of Frost and Oldenberg, on the basis of *relative* determinations of OH, the rate constants could be given only in an arbitrary unit: The concentration of OH was measured in arbitrary "standard pressure units," while the concentration of H_2O or He was measured, of course, in mm. The absolute units of the rate constants at 300°C were computed on the basis of the calibration reported in the preceding section. Following Rodebush, the reaction $H+OH+M \rightarrow H_2O+M$ is assumed. The possibility of the reaction $OH+OH+M \rightarrow H_2O_2+M$ as an alternative, as suggested by Kondratjew, has been discussed in footnote 3. The results are as follows:

$$H+OH+H_2O \rightarrow H_2O+H_2O \qquad (1)$$

$$K(H_2O) = 1400 \text{ mm}^{-2} \text{ sec.}^{-1}$$

$$= 49 \times 10^{16} \text{ cc}^2 \text{ mole}^{-2} \text{ sec.}^{-1}.$$

$$H+OH+He \rightarrow H_2O+He \qquad (2)$$

$$K(He) = 600 \text{ mm}^{-2} \text{ sec.}^{-1}$$

$$= 21 \times 10^{16} \text{ cc}^2 \text{ mole}^{-2} \text{ sec.}^{-1}.$$

C. Sources of error

It is assumed that after interrupting the discharge at low pressure, broadening is due exclusively to the Doppler effect. The only other source of broadening that may be suspected is an unresolved hyperfine structure. No such structure, however, is to be expected theoretically, as was pointed out to us by Professor Van Vleck. The interaction between electronic angular momentum and nuclear spin, which is responsible for the hyperfine structure in the spectra of heavy elements, cannot have any effect because the O nucleus has no spin and the H nucleus has far too small a charge to cause so close an approach of the electron that an appreciable hyperfine structure could result.

An error may be due to the fact that these absolute values of concentration (Section IV, A) were measured with a different optical arrangement several months after the relative values had been obtained. The scattering of the relative values (Fig. 2, reference 1) indicates that the conditions in the discharge tube were not reproducible with great accuracy.

The uncertainty of the *f* value is another source of error. This is due mostly to the uncertainty in the energy of dissociation of the H_2O molecule. It is hoped that a higher accuracy may be ob-

---

[16] A far higher degree of dissociation of H_2O into $H+OH$, produced by an electric current, was reported by Rodebush and his collaborators (W. H. Rodebush, J. Phys. Chem. **41**, 283 (1937) and the reference in footnote 3). Their experiments differed from ours in the following respects: The pressures were lower and possibly the electrical energy higher. Furthermore, they applied a permanent current, while we measured the concentration after applying currents of such short duration ($1\frac{1}{2}$ periods of 60-cycle current) that, because of the long life of H and OH, the stationary concentration was not nearly reached.

[17] Reason (4) does not contradict the argument of Section II, B, which proves only that pressure broadening improves the observation of narrow absorption lines if a spectrograph of inadequate resolving power is applied.

tained by a more refined spectroscopic determination of this constant.

The errors in the photometric measurements remaining after the correction for resolving power has been applied may be assumed to be small compared with the two errors mentioned immediately above.

In order to ascertain the accuracy of our result a systematic investigation of the resolving power of our Fabry-Pérot spectrograph would be necessary. We estimate that the combined error in the concentration of OH so far as our measurements are concerned is not greater than 30 percent; the error in the rate constants is correspondingly higher.

It does not seem worth while to push the accuracy of the measurements reported here much higher for the reason that an incidental result of the spectra taken with the Fabry-Pérot plates is that the broadening of the OH lines by the electric current is very small. Because of this fact another method may be easier to apply; one may use as a background the OH lines themselves, excited with a weak current (or in fluorescence radiation) so that current broadening is negligible, measure the loss of *total* intensity of this light when passing through the absorbing gas, and finally compute the concentration from the system of formulae given by Ladenburg and Reiche[18] for the intensity of an emission line when passing through a gas in which a line of the same wave-length and broadening is absorbed. This would be technically the same method as reported by Avramenko and Kondratjew[7] although it would differ in the treatment of the broadening.

D. Discussion

In the reactions for which the rate constants are given in Section IV, B triple collisions are required for the combination of H and OH. How does the number of OH vanishing per sec. compare with the number of triple collisions per sec.? From the rate constant it follows that in the beginning of the reaction the rate of disappearance of OH is 5.8×10^{14} radicals per cc per sec. On the other hand, the number of triple collisions for the same moment is computed by Tolman's[19] formula with the gas kinetic data for H_2O applied to the H_2O molecule as well as to the OH radical (diameter $=2.6\times10^{-8}$ cm); the distance δ within which a pair $H+OH$ must be in order to be susceptible to a third body is assumed to be 3×10^{-8} cm. Thus the number of triple collisions per cc per sec. results as 0.42×10^{14}. This is smaller than the number of OH radicals disappearing per cc per sec. by the factor 14.

This, however, is not the first case in which this apparent discrepancy appears. Even larger excessive efficiencies for triple collisions were reported by Rabinowitch[20] for the combination of iodine atoms with C_6H_6 as third bodies. Such effects are still stronger among the more complicated molecules.[21] The explanation is that the gas kinetic treatment of triple collisions has been oversimplified in two respects. First, the gas kinetic cross section is taken from measurements of the viscosity of a gas; therefore it is derived from collisions in which an appreciable transfer of energy and momentum takes place; it may be that the cross section for collisions between free atoms and radicals leading to a reaction is larger. (For example, collision cross sections for the broadening of spectral lines are considerably larger.[22]) This unknown cross section is taken into account in Tolman's formula by the factor δ for which a rather large value (3×10^{-8}) was chosen. The second simplification of the gas kinetic treatment consists of representing the duration of a collision simply by the time required to pass a small distance of nearly diameter size. However, this treatment neglects the possibility that in a collision involving complex bodies the energy of combination may be taken up and distributed over several internal degrees of freedom. In such a case the collision partners may adhere until by a "beat" between the normal modes of vibration the energy is again localized in the coordinate corresponding to the separation of the two partners. This process has been treated on the basis of potential curves for

---

[18] R. Ladenburg and F. Reiche, Ann. d. Physik **42**, 181 (1913).

[19] R. C. Tolman, *Statistical Mechanics* (The Chemical Catalogue Co., 1927), p. 248.

[20] E. Rabinowitch, Trans. Faraday Soc. **33**, 283 (1937).

[21] See C. N. Hinshelwood, Trans. Faraday Soc. **34**, 105 (1938).

[22] See the recent review by P. Schulz, Physik. Zeits. **39**, 420 (1938).

a H atom colliding in some specified directions with a H_2 molecule.[23] A similar result—modified by the larger energy involved—is to be expected for the collision process H+OH; a longer mean life should follow for the collision OH+OH because of the larger number of degrees of freedom involved. In a computation in which the mean life of the collision complex is tentatively taken into account, Kondratjew derived a value as high as $k_{H_2O}=544$ mm^{-2} sec.$^{-1}$ which agrees, at least, in its order of magnitude with the experimental value.[24]

---

[23] H. Eyring, H. Gershinowitz and C. E. Sun, J. Chem. Phys. **3**, 790 (1935).

[24] An objection to the starting point of his computation is mentioned in Section I.

JULY, 1939 JOURNAL OF CHEMICAL PHYSICS VOLUME 7

Electrical Properties of Multilayers

R. W. Goranson and W. A. Zisman
Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C.

(Received March 14, 1939)

This paper presents certain results on the electrical properties of multilayers of stearic acid and various stearates plated on insulating materials. The experimental data lead to the conclusion that the electrical charges of these multilayers arise from the adsorption of ions from the substrate on the carboxyl groups of the floating stearate monolayer. With a calcium-bearing substrate, for example, the first stage in the process is a conversion of stearic acid to calcium stearate and this reaction is a function of the substrate pH and consequently of the degree of ionization of stearic acid. The next stage is represented by an adsorption of calcium ions on the carboxyl groups of the calcium stearate which are carried along with the monolayer in the plating process. The electric charges of X-multilayers thus arise from volume distributions of positive adsorbed ions. The positive ions adsorbed on the floating monolayer induce a cloud of negative ions in their neighborhood which, under certain conditions such as dependence on size and valency of the negative ions, may lead to electrically neutral and wetted films. With certain types of mixed films, i.e., where the percentage of stearic acid present is appreciable, the rate at which the plating process is carried out becomes an important factor in determining whether X- or Y-type films can be built up, and for these cases fast dipping and withdrawal speeds can neutralize an existing multilayer charge. In plating X-multilayers it has been observed that after about 500 layers have been deposited, and the electrostatic repulsive field of the multilayer has thus reached a certain value, the upper portion of the submerged probe has a silvery appearance which gradually moves down the probe with increasing number of dips, and film does not adhere to the multilayer over this portion. This electrostatic repulsive field thus sets a limit to the thickness of X-multilayers on insulators. Under certain conditions the outer layer of multilayers dipped in film-free solutions overturns and adsorbs ions from the solution, resulting, in some cases, in wetted films and, in others, in an electrical charging of the multilayers.

Introduction

If stearic acid is deposited on a clean water surface it spreads out on the surface; if now this film is compressed by a "two-dimensional" piston a packed monolayer of similarly oriented molecules is formed and has many two-dimensional analogs to three-dimensional states. The hydrocarbon chains project out of the water surface whereas the polar carboxyl groups, or heads, of these molecules remain in contact with the water.[1] If in addition a calcium (or barium) salt is dissolved in the water substrate a certain amount of the stearic acid will be converted to calcium (or barium) stearate,[2] the percentage of stearate in the stearate-stearic acid film increasing with increase in pH of the solution. For example, on a 10^{-4} molal salt solution, at pH 5.5 for calcium and 6.6 for barium, 50 percent conversion will occur; at pH 11, 100 percent conversion will occur for either salt.

It is found[3] that when certain polished surfaces, such as the surfaces of chromium or glass plates, are dipped down through the compressed floating stearate monolayer, a depressed meniscus occurs around the plate and, after the first dip, the two-

---

[1] I. Langmuir, J. Am. Chem. Soc. **39**, 1848 (1917).

[2] I. Langmuir and V. Schaefer, J. Am. Chem. Soc. **58**, 284 (1936).

[3] K. Blodgett, J. Am. Chem. Soc. **57**, 1007 (1935).