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Optical Study of the Hydrates of Molecular Oxygen in Water[1]

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Molar light absorption coefficients, $\bar{\epsilon}$, at 2000 to 2150 Å. have been determined for molecular oxygen dissolved in water at 10 to 65°. The values of $\bar{\epsilon}$ have been found to increase with decrease in wave length and increase in temperature but to be independent of the concentration of the dissolved oxygen. The results have been explained in terms of the existence of two different hydrates of molecular oxygen in water. The hydrates appear to be present in nearly equal amounts at body temperature; their absorption spectra and thermodynamic constants have been evaluated and structures for them have been proposed. Liquid water has been found to absorb light at 2000 to 2300 Å. This light absorption has been found to increase also with decrease in wave length and increase in temperature but very much less than the light absorption of molecular oxygen in water.

Introduction

The recent discovery[2] at 25° that molecular oxygen dissolved in water absorbs light much more strongly than oxygen gas in the region of the spectrum between 2000 and 2500 Å. has led us to extend the measurements over the range 10 to 65° with the hope of learning more about the nature of molecular oxygen in water, the absorption coefficients of the oxygen species and the equilibrium constants of any reactions involving these species. The work at 25° has been confirmed in every respect and several new facts have been revealed. These facts bear upon the way in which molecular oxygen exists in aqueous systems both *in vitro* and *in vivo.*

Materials.—U. S. Navy Helium in cylinder W53, 1CC-3A2900, H-74678 was employed. Its purity was stated to be greater than 99.99%.

The carbon dioxide was from Dry Ice purchased from Pure Carbonic Inc.

The oxygen was purified Airco in cylinder 1CC-3AA-2015, X-42616.

The water was freshly distilled conductivity water saturated with nitrogen.

The glassware was either Pyrex or fused quartz. Before use, it was thoroughly cleaned and then soaked in distilled water at 100°.

The flexible tubing was of gum rubber.

Purification of Gases.—The gases were freed of suspended material and water-soluble impurities by passing each through a separate train consisting of a jar packed with cotton batting followed by a jar of conductivity water.

Solutions for optical density measurements were prepared by saturating water with the appropriate gas. This was done while the water was not less than two degrees below but never above the temperature at which the optical density of the solution was subsequently measured. The sum of the partial pressures of the gas and the water was always one atm.

Optical density measurements were made with a Cary recording spectrophotometer Model 11 MS; instrument number 69. The optical density and wave length scales of the instrument were calibrated in the manner described elsewhere.[3]

The air *vs.* air chart recordings of optical density, D, were the same with 0.02 unit in D for all cell compartment temperatures of 5 to 55°. At 65°, however, the corresponding values of D were higher than at lower temperatures by as much as 0.05 unit in D at 2000 Å. but by less at longer wave lengths.

In order to detect any impurities that might affect the results, chart recordings of optical densities were obtained at the same temperature in the following order for the stated materials in the light path in the upper cell compartment of the Cary: (1) air; (2) fused quartz absorption cell filled with conductivity water saturated with (a) either helium or carbon dioxide, (b) oxygen and (c) either helium or carbon dioxide that had replaced the oxygen; and (3) again only air. There was in every case only air in the lower cell compartment of the instrument. The optical densities of the solution described in 2c above were the same at 2000 to 8000 Å. as water which had never contained any molecular oxygen but had been saturated with carbon dioxide or helium which had replaced nitrogen.

Absorbance values, A, and molar extinction coefficients, ϵ, were determined as explained elsewhere.[4] $\epsilon cl = A =$

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[2] L. J. Heidt and L. Ekstrom, THIS JOURNAL, **79**, 1260 (1957).

[3] L. J. Heidt and D. E. Bosley, *J. Opt. Soc. Am.*, **43**, 760 (1953).

[4] L. J. Heidt and J. Berestecki, THIS JOURNAL, **77**, 2049 (1955).

TABLE I

MOLAR EXTINCTION COEFFICIENTS, $\bar{\epsilon}$, OF OXYGEN GAS DISSOLVED IN WATER AND PERTINENT INFORMATION

Absorbance values, A, are average values for the dissolved oxygen and are for a light path of 10 cm. in the solution. The reproducibility of the observed values of A was ± 0.02 in D or $\pm 4\%$ whichever was larger. The values of S_0 give gram moles of molecular oxygen per liter of water. Starred and unstarred values of S_0 are for $p_{\text{air}} + p_{\text{w}} = 1$ atm. and $p_{O_2} + p_{\text{w}} = 1$ atm., respectively, above the solution at the stated temperature.[6] p_{w} represents the vapor pressure of water. $\bar{\epsilon} = A/10S_0$. Temperatures are in degrees centigrade. The calculated values of A_1 and A_2 are based on the least squared and smoothed values respectively of ϵ' and ϵ'' in Table II.

°C.	$10^4 \times S_0$	λ, Å.	2000	2025	2050	2075	2100	2125	2150
10	16.77	A(obsd.)	0.708	0.518	0.376	0.285	0.217	0.173	0.141
		A_1(calcd.)	.699	.509	.366	.273	.199	.157	.123
		A_2(calcd.)	.730	.509	.366	.264	.195	.151	.123
		$\bar{\epsilon}$(obsd.)	42.2	30.9	22.4	17.0	12.9	10.3	8.43
24	12.49	A(obsd.)	0.558	0.409	0.296	0.218	0.162	0.127	0.098
		A_1(calcd.)	.565	.416	.303	.227	.171	.137	.107
		A_2(calcd.)	.585	.416	.303	.222	.166	.131	.107
		$\bar{\epsilon}$(obsd.)	44.7	32.7	23.7	17.4	13.0	10.2	7.81
25	2.36*	A(obsd.)	0.088	0.063	0.055	0.043	0.034	0.021	0.015
		A_1(calcd.)	.107	.079	.058	.043	.033	.026	.020
		A_2(calcd.)	.111	.079	.058	.042	.032	.025	.020
32	10.73	A(obsd.)	0.495	0.359	0.254	0.188	0.140	0.122	0.083
		A_1(calcd.)	.508	.376	.275	.207	.158	.128	.099
		A_2(calcd.)	.523	.376	.275	.203	.154	.122	.099
		$\bar{\epsilon}$(obsd.)	46.1	33.4	23.7	17.5	13.1	11.4	7.74
40	9.96	A(obsd.)	0.495	0.366	0.271	0.208	0.154	0.124	0.097
		A_1(calcd.)	.491	.365	.269	.203	.157	.128	.099
		A_2(calcd.)	.504	.365	.269	.200	.152	.121	.099
		$\bar{\epsilon}$(obsd.)	51.8	38.3	28.3	21.3	16.1	13.0	10.2
55	7.27	A(obsd.)	0.377	0.285	0.220	0.174	0.134	0.110	0.088
		A_1(calcd.)	.384	.287	.213	.162	.127	.104	.081
		A_2(calcd.)	.391	.287	.213	.160	.123	.099	.081
		$\bar{\epsilon}$(obsd.)	51.8	39.3	30.3	23.9	18.4	15.1	12.1
65	6.19	A(obsd.)	0.345	0.250	0.180	0.127	....	....	....
		A_1(calcd.)	.339	.254	.190	.144	....	....	....
		A^6(calcd.)	.344	.254	.190	.143	....	....	....
		$\bar{\epsilon}$(obsd.)	55.7	40.4	29.1	20.5	....	....	....

$\log_{10}(I_0/I)$ where c is in moles per liter, l is in cm. and $(1 - I/I_0)$ is the fraction of the light absorbed by the stated solute.

Results

Part I.—In the case of water saturated with helium at one atm. the values of $\Delta D = D_t - D_{10}$ were found to differ significantly from zero per 10° difference in temperature at 10 to 65° only in the region of the spectrum between 2000 and 2300 Å. and only when determined within 0.005 by evaluating ΔD for the same absorption cell and contents while kept in an atmosphere of helium and not removed from the cell compartment during the course of the measurements at the different temperatures. Suitable corrections always were made for any change in the recorded values of D for light passing through only air in both the upper and lower cell compartments of the Cary. At 2400 to 8000 Å. $D_{65} - D_{10}$ was negligible even for a light path of ten cm. in the solution.

The values of ΔD at 2000 to 2300 Å. obtained in the above way for water saturated with helium were found to be reversible with change in temperature and to increase with decrease in the wave length of the light.

At 2000, 2050, 2100 and 2150 Å. the values of $-\Delta D/\Delta(1/T)$ were found to be 90, 55, 37 and 16, respectively, in the ten cm. cell and of the same sign but very much smaller in the one cm. cell.

The windows of the one cm. and ten cm. absorption cells employed in these experiments were cut from the same original piece of fused quartz and were all 1 mm. thick, so the values of ΔD may be attributed only to the water. Helium does not absorb light at 2000 to 8000 Å. and is not very soluble in water. The weak light absorption by water at 2000 to 2300 Å. probably is due to a broadening to longer wave lengths of an electronic transition in the water molecule from the ground singlet state to the first excited singlet state. An electronic transition from the ground state of water to the triplet $^3B_1$ state, predicted many years ago by R. S. Mulliken,[5] is much less probable.

Part II.—In the case of water saturated with molecular oxygen the effects of changes in the temperature and partial pressure of the oxygen upon the values of A and $\bar{\epsilon}$ at 2000 to 2150 Å. for dissolved oxygen are presented in Table I. These effects were found to be reversible provided care was taken to keep the water saturated with the oxygen. At longer wave lengths up to about 2600 Å. the values of A for the dissolved oxygen were barely outside the limits of error and at wave lengths longer than 2600 Å. and up to at least 8000 Å. the values of A were negligible.

At 2000 to 2600 Å. the molar extinction coefficient, $\bar{\epsilon}$, of the molecular oxygen in all forms in the

[5] R. S. Mulliken, *J. Chem Phys.*, **1**, 502 (1933); **3**, 511 (1935).

water increased with decrease in the wave length of the light and with increase in the temperature of the solution. There is, however, no significant change in $\bar{\epsilon}$ when only the partial pressure of the gaseous oxygen in equilibrium with the solution is changed; this is shown by the results given in Table I at 25° where the partial pressure of the oxygen gas was increased from the value in air and water vapor to the value in pure oxygen and water vapor all at a total pressure of one atm.

The influence of temperature upon the value of $\bar{\epsilon}$ at 2000 Å. is presented graphically in Fig. 1 where the values of $\bar{\epsilon}$ obtained at 10, 24, 32, 40, 55 and 65° are plotted as a function of a variable α which depends upon the temperature, but not upon the concentration of the molecular oxygen in water. The increase in $\bar{\epsilon}$ at 2000 Å. with increase in temperature is from about 42 at 10° to 55 at 65°; it is less at longer wave lengths.

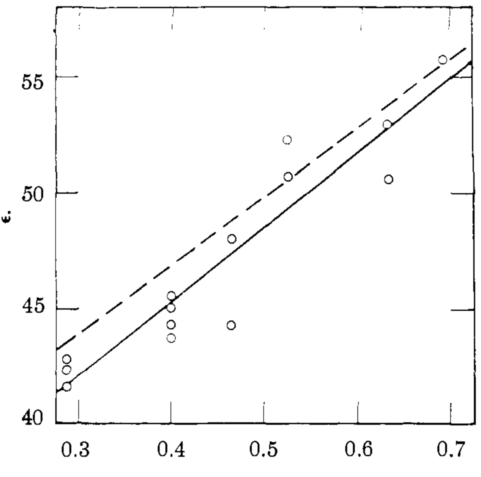

Fig. 1.—Molar extinction coefficients, $\bar{\epsilon}$, at 2000 Å. of oxygen gas dissolved in water at selected temperatures as a function of α, the fraction of $O_2\cdot aq$ in the form of the stronger light absorbing species O_2'. The points grouped vertically from left to right in the figure are at 10, 24, 32, 40, 55 and 65°, respectively. The solid line through the points is based on the method of least squares. The broken line is based on the smoothed values of ϵ' and ϵ'' taken from the lines in Fig. 4.

The values of the function α were obtained by considering simultaneously the influence of temperature upon $\bar{\epsilon}$ and upon the solubility of molecular oxygen in water.

The influence of temperature upon the solubility of oxygen in water is presented in Fig. 2 where we have plotted log K_0 *vs.* $1/T$. Here $K_0 = (O_2\cdot aq)/p_{O_2} = S_0$ equals moles molecular oxygen per liter of solution[6] when at equilibrium with a partial pressure of oxygen gas of one atm. above the solution.

It will be seen that the slope, σ_0, of the plot in Fig. 2 is positive and increases with increase in $1/T$; hence the amount of heat evolved per mole of oxygen dissolved in water increases with decrease in the temperature of the water. The change in enthalpy accompanying the formation of one mole of $O_2\cdot aq$ from $O_2(g)$ and water at a stated temperature is $\Delta H_0 = -2.3R\sigma_0$. The increase in ΔH_0 with increase in temperature is from −3.73 kcal. at 10° to −1.29 kcal. at 65°.

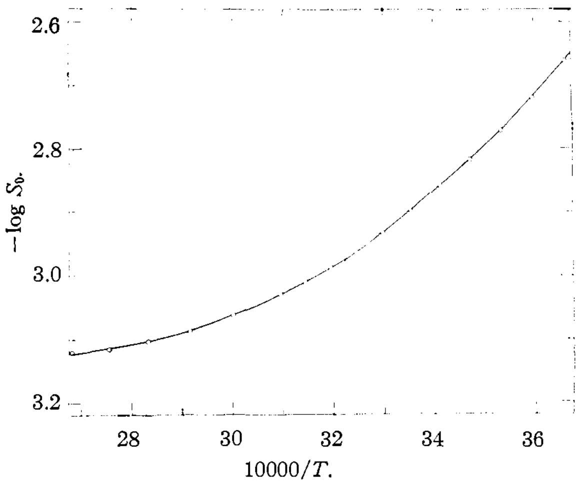

Fig. 2.—Solubility of oxygen gas in water at 0 to 100°. The values of log S_0 are for S_0 in moles of oxygen per liter of solution at equilibrium with a partial pressure of 1 atm. of oxygen gas above the solution.[6]

The changes in both $\bar{\epsilon}$ and ΔH_0 with change in temperature suggest the presence in the solution of at least two different hydrated species of molecular oxygen. We have designated the two species as O_2' and O_2''; these will surely exist in equilibrium with each other and will not necessarily have the same values of ϵ at all wave lengths.

The variation of $\bar{\epsilon}$ with temperature in terms of O_2' and O_2'' is given by the equation

$$\bar{\epsilon}(O_2\cdot aq) = \epsilon'\alpha(O_2\cdot aq) + (1 - \alpha)(O_2\cdot aq)$$

where α is the fraction of $(O_2\cdot aq)$ present as (O_2'), and ϵ' and ϵ'' are the molar light absorption coefficients of O_2' and O_2''. It follows that

$$\bar{\epsilon} = \epsilon'\alpha + \epsilon''(1 - \alpha) = \epsilon'' + \alpha(\epsilon' - \epsilon'')$$

Also

$$K^* = (O_2')/(O_2'') = \alpha(O_2\cdot aq)/(1 - \alpha)(O_2\cdot aq) = \alpha/(1 - \alpha)$$

so

$$\alpha = K^*/(1 + K^*)$$

and

$$\bar{\epsilon} = \epsilon'' + (\epsilon' - \epsilon'')K^*/(1 + K^*)$$

The last equation conforms to the dependence of $\bar{\epsilon}$ upon the temperature and to the independence of $\bar{\epsilon}$ upon the partial pressure of oxygen, since K^* would be expected to depend upon the temperature but not upon the equilibrium partial pressure of the oxygen.

The variation of ΔH_0 with temperature in terms of O_2' and O_2'' is given by the equation $\Delta H_0 = \alpha\Delta H' + (1 - \alpha)\Delta H''$ where ΔH_0, $\Delta H'$ and $\Delta H''$ are the heats of the reactions: $O_2(g) = O_2\cdot aq$; $O_2(g) = O_2'$ and $O_2(g) = O_2''$, respectively. In the case of the reaction $O_2'' = O_2'$, $\Delta H = \Delta H^* = \Delta H' - \Delta H''$ so $\Delta H_0 = \Delta H'' + \alpha\Delta H^*$.

We now have two independent equations in α or K^*: one equation in terms of the experimentally evaluated variable $\bar{\epsilon}$ and another equation in terms of the experimentally evaluated variable ΔH_0. This provides a way of evaluating K^* based on the simplest assumption that ϵ', ϵ'', $\Delta H''$ and ΔH^* are constants over the range 10 to 65°.

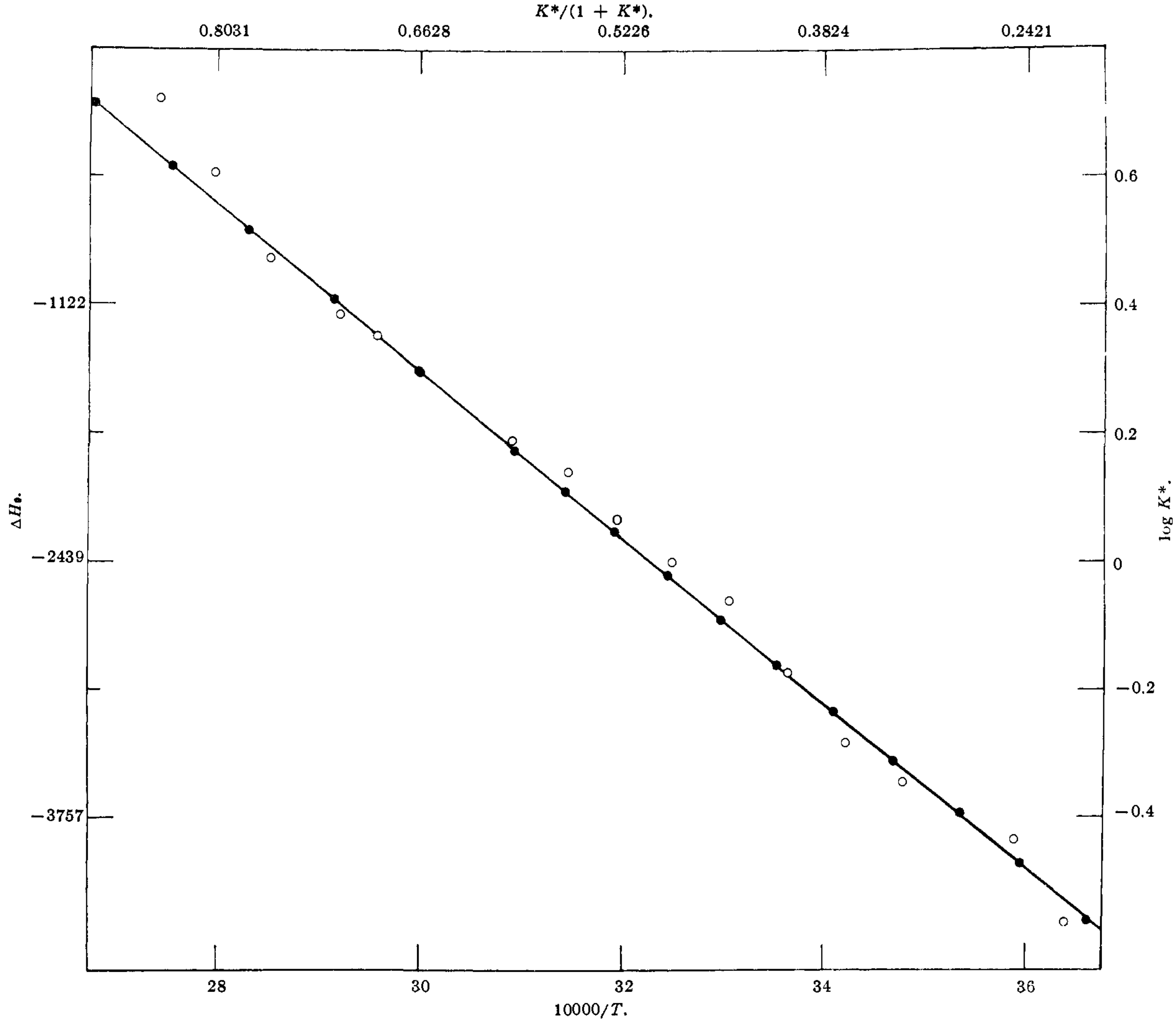

Fig. 3.—Variation of heat of solution of oxygen gas in water with change in temperature. Open circles represent ΔH_0 *vs.* $K^*/(1 + K^*)$. ΔH_0 is in small calories and $K^*/(1 + K^*) = \alpha$ equals the fraction of oxygen present as O_2'. Filled circles give our best estimate of the values of log K^* *vs.* $10000/T$ where K^* is the equilibrium constant of the reaction $O_2'' = O_2'$ and $T = 273 + °$.

The evaluation of K^* has been carried out by noting that under the above conditions the following plots are all linear: ε *vs.* $K^*/(1 + K^*)$, log K^* *vs.* $1/T$ and ΔH_0 *vs.* $K^*/(1 + K^*)$. Moreover, the slopes σ^* and ΔH^* of the last two plots are related by the equation $2.3R\ \sigma^* = -\Delta H^*$; hence the plot of log K^* *vs.* $1/T$ should coincide with the plot of $-\Delta H_0/2.3R$ *vs.* $K^*/(1 + K^*)$ when the proper values for K^* have been selected. R is the gas constant and $2.3 \log x = \ln x$. The results of this treatment of the data are shown in Figs. 1 and 3.

Let us first consider Fig. 3 which consists of plots of log K^* *vs.* $1/T$ and of ΔH_0 *vs.* $K^*/(1 + K^*) = \alpha$. The plots were made to coincide at 10 and 65° by finding values of K^* at those temperatures that satisfied the condition $2.3R\ (\log K^*_{10°} - \log K^*_{65°})\cdot(1/338 - 1/283) = (\Delta H_0 \text{ at } 10° - \Delta H_0 \text{ at } 65°)/(\alpha_{10°} - \alpha_{65°})$ and the condition that both plots should be linear at intermediate temperatures within the limits of error of ΔH_0. It was found that this could be done at 10 to 65° over a considerable range of K^* at any selected temperature but that the uncertainty in K^* was greatly reduced when the same conditions were extended to the values of ΔH_0 over the range 5 to 95° as is the case on Fig. 3. It will be seen that the deviations in ΔH_0 from the linear plot in Fig. 3 are larger at temperatures above 90°. This occurs because the values of ΔH_0 above 90° are not far from zero. All the points in Fig. 3 coincide with the straight line drawn among them within the limits of error in ΔH_0.

Let us now consider Fig. 1 which is a plot of ε at 2000 Å. *vs.* $K^*/(1 + K^*)$. The values of $K^*/(1 + K^*)$ at the stated temperatures are those calculated from the values of K^* obtained from Fig. 3. It will be seen in Fig. 1 that the points lie fairly well on the solid straight line which was obtained by the method of least squares. The fit of the points to this straight line and to the other straight line obtained as explained later is within the limits of error in ε and K^*. This can be seen in Table I by noting the agreement between the values of A(obsd.), A_1(calcd.) based on the solid line and

A_2(calcd.) based on the other line. The same situation exists up to 2150 Å.

The straight lines in Fig. 1 have slopes of $\epsilon' - \epsilon''$ and intercepts of $\bar{\epsilon} = \epsilon''$ and $\bar{\epsilon} = \epsilon'$ at values of α equal to 0 and 1, respectively. The values of ϵ'' and ϵ' obtained at 2000 to 2150 Å. are given in Table II. The absorption spectra of O_2' and O_2'' based on these values of ϵ' and ϵ'' are presented in Fig. 4. These absorption spectra appear to be the tail ends of spectra with peaks at shorter wave lengths. It is of interest to note that at 2000 to 2150 Å., both ϵ' and ϵ'' are much larger than ϵ for oxygen gas or pure water and that ϵ' is greater than ϵ''.

The thermodynamic constants of the hydrates, O_2' and O_2'', can be evaluated in the following way. In the first place our solutions of water saturated with oxygen are so dilute that the activity of the water and the activity coefficients of the oxygen species in the water are all very nearly unity when the standard state for the solvent is taken as pure water at 25° and 1 atm. and the reference state for the solute is taken as an infinitely dilute solution at 25° and 1 atm. It follows that the values of ΔF, ΔH and ΔS are the standard values when calculated from the above values of K and ΔH at 25° and 1 atm. The values of these thermodynamic constants[6] and pertinent information[7] are given in Table III where the species O_2' and O_2'' are assigned the formulas $O_2 \cdot H_2O \cdot aq$ and $O_2 \cdot 2H_2O \cdot aq$, respectively, for reasons given later in this article.

TABLE II

MOLAR EXTINCTION COEFFICIENTS, ϵ, OF HYDRATED MOLECULAR OXYGEN SPECIES IN WATER

The absorption of light by the dissolved oxygen decreased at longer wave lengths; it was negligible between 2500 and 8000 Å.

Species	λ, Å.	2000	2025	2050	2075	2100	2125	2150
O_2'	ϵ' (least sq.)	64.6	49.1	37.4	28.6	23.4	19.7	15.1
	ϵ' (smoothed)	64.6	49.1	37.4	28.6	22.5	18.4	15.1
O_2''	ϵ'' (least sq.)	32.4	22.8	15.5	11.3	7.2	5.2	4.2
	ϵ (smoothed)	35.0	22.8	15.5	10.5	7.2	5.2	4.2

TABLE III

THERMODYNAMIC CONSTANTS AT 25°

The values for the starred items are less precise than for the other items because they are based on values estimated for the first reaction as explained in the text.

Reactions or species	ΔF^0, kcal.	ΔH^0, kcal.	ΔS^0 or S^0, cal. °T^{-1} mole^{-1}	10^4K
*$O_2 \cdot 2H_2O \cdot aq = O_2 \cdot H_2O \cdot aq + H_2O(l)$	+0.222	+5.95	+19.21	6876
$O_2(g) = O_2 \cdot aq$	+3.95	−3.01	−23.3	12.63[6]
*$O_2(g) + H_2O(l) = O_2 \cdot H_2O \cdot aq$	+4.49	+0.51	−13.34	5.15
*$O_2(g) + 2H_2O(l) = O_2 \cdot 2H_2O \cdot aq$	+4.27	−5.44	−32.55	7.48
$O_2(g)$[7]	0	0	+49.00	
$H_2O(l)$[7]	−56.56	−68.37	+16.72	
$O_2 \cdot aq$	+3.95	−3.01	+25.7	
*$O_2 \cdot H_2O \cdot aq$	−52.07	−67.86	+52.38	
*$O_2 \cdot 2H_2O \cdot aq$	−108.85	−142.18	+49.89	

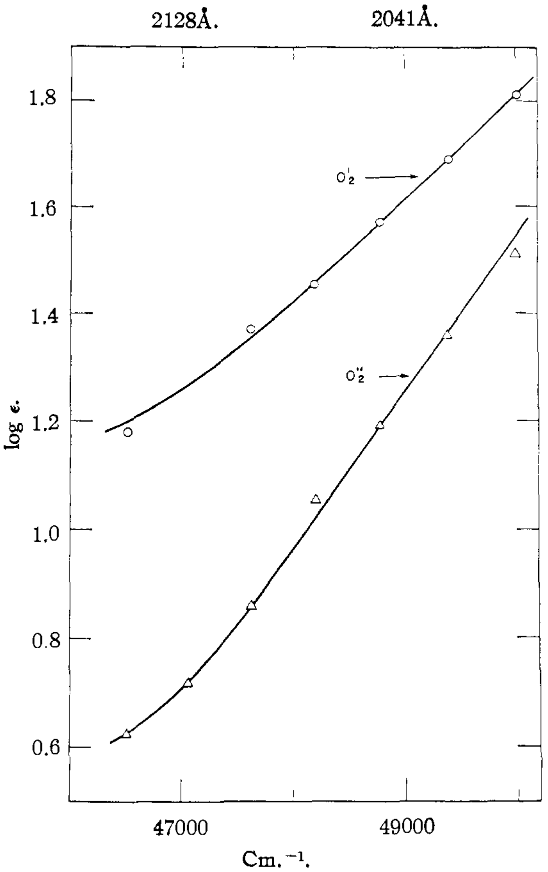

Fig. 4.—Absorption spectra of the hydrates of oxygen in water.

It is of interest to note that the value of K^* for the reaction $O_2'' = O_2'$ is about 0.7 at 25° and increases to unity between 37 and 38° so that both O_2' and O_2'' appear to be present in about equal amounts at body temperature. Also the change in ΔH_0 for the reaction $O_2(g) = O_2 \cdot aq$ is now explained as due entirely to a change in the ratio $(O_2')/(O_2'')$ with change in temperature.

The species O_2' and O_2'' have been assigned the stated formulas for two reasons. First, O_2' has been designated as the less hydrated species because $(O_2')/(O_2'')$ is increased as the temperature is increased. Second, the value of +19.2 e.u. for ΔS^0 for the reaction $O_2 \cdot 2H_2O \cdot aq = O_2 \cdot H_2O \cdot aq + H_2O(l)$ is about the same as the value of 16.5 e.u. for many reactions[8] in which one mole of water is freed from a hydrated species in water to become part of the liquid water acting as a solvent.

Discussion

Thus far no mention has been made of possible structures for the hydrates, $O_2 \cdot H_2O \cdot aq$ and $O_2 \cdot 2H_2O \cdot aq$. R. S. Muilliken has suggested in a private communication that one may be dealing here with electron donor–acceptor complexes with water acting as the electron donor.[9] The formulas of the

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(6) Values taken from "Handbook of Chemistry and Physics," 37th ed., Chemical Rubber Publishing Co., Cleveland, 1955–1956, pp. 1606–1607.

(7) F. Rossini and others, "Selected Values of Chemical Thermodynamic Properties," Circular of the National Bureau of Standards 500, U. S. Government Printing Office, Washington, D. C., 1952.

(8) (a) R. E. Powell, *J. Phys. Chem.*, **58**, 528 (1954); (b) R. J. P. Williams, *ibid.*, **58**, 121 (1954); (c) J. W. Cobble, *J. Chem. Phys.*, **21**, 1443, 1446 (1953).

(9) (a) R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952); (b) *J. Phys. Chem.*, **56**, 801 (1952); (c) *Rec. trav. chim.*, **75**, 845 (1956).

hydrates would then be written $H_2O{\cdot}O_2$ and $2H_2O{\cdot}O_2$ and the rather strong light absorption would be interpreted as the tail end of a charge transfer spectrum such as appears to be well established for a large number of cases with, for example, halogen molecules as acceptors.[10] Further, it has been found[11] that many organic donor molecules show similar behavior with oxygen, namely, new and enhanced light absorption at longer wave lengths than the absorption of the donor itself and that these results can be interpreted[11] in terms of donor-acceptor complexes with oxygen as the acceptor molecule.

An alternative explanation that we wish to offer explains also the variation in ϵ with temperature. This explanation is based on the different ways in which the hydrogen atom may act as a bridge between two other atoms.

The most common hydrogen bridge is the one existing in the dimer of acetic acid and between the oxygen atoms of water molecules.[12] In both cases the proton forms the bridge by being shared by four electrons, two attached to each of two electronegative oxygen atoms; also the proton is nearer one of the oxygen atoms than the other, the longer bond being called the "hydrogen bond" or "bridge hydrogen bond."

A second kind of hydrogen bridge is less common but, nevertheless, well recognized[13] as existing in diborane, B_2H_6. In this case there are two hydrogen bridges in the molecule and each appears to be a three center bond containing two electrons and a proton; here the proton in the bridge is equidistant from the two boron atoms.

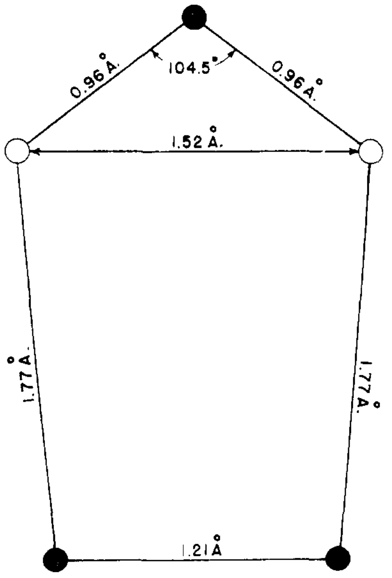

Fig. 5.—Proposed ring structure of the monohydrate of oxygen in water. The distances are between the nuclei of the atoms; filled and open circles represent the nuclei of oxygen and hydrogen, respectively. Other molecules of the solvent water are attached to the oxygen atoms in this structure by hydrogen bonds of the usual kind in water.

The existence of these two greatly different kinds of hydrogen bridges has suggested[2] the existence of a third kind of hydrogen bridge between the diradical form of molecular oxygen and water or paraffin hydrocarbons. In this bridge the proton would be shared by three electrons one of which comes from the diradical form of the oxygen molecule and the other two from the original electron pair bond O–H in the case of water and C–H in the case of a paraffin hydrocarbon. In this kind of bridge the proton would be nearer to the O or C atom, respectively, of its original electron pair bond than to the oxygen atom of molecular oxygen. The resulting structures would be a ring in the case of the 1:1 complex $O_2{\cdot}H_2O{\cdot}aq$ and a chain in the case of the 1:2 complex $O_2{\cdot}2H_2O{\cdot}aq$.

The formation of the ring structure would involve greater structural changes in molecular oxygen and liquid water than the formation of the chain structure and this is in accord with the fact, displayed in Fig. 4, that the absorption spectrum of O_2' differs more than that of O_2'' from the absorption spectra of molecular oxygen and water measured separately in the region of the spectrum between 2000 and 2300 Å.

In Fig. 5 we have presented a somewhat detailed picture of a tentative ring structure for the monohydrate, O_2'. The values assigned to the internuclear distances and bond angles are based on the structures of oxygen[14] and water[15] molecules as gases because the two hydrogen atoms of the water molecule would be drawn together in this structure by the smaller distance between the oxygen atoms in the oxygen molecule. The value of 1.77 Å. was chosen for the bridge hydrogen bond distance for the following reasons. In the case of the reaction $O_2(g) + 2H_2O(l) = O_2{\cdot}2H_2O{\cdot}aq$, two common type of bridge hydrogen bonds in water appear to be replaced by two of the proposed new type of bridge hydrogen bonds and the value of ΔH for the reaction is -5.44 kcal.; hence a value of $4.5 + 5.44/2$ or 7.2 kcal. per mole would be assigned to the energy of the proposed new type of hydrogen bond provided the sum of the values of ΔH is negligible for all other steps involved in dissolving molecular oxygen in water. The small difference between 4.5 and 7.2 kcal. per mole for the common and proposed types of bridge hydrogen bonds would result in an internuclear distance for the proposed bond that would be very little less than the value of 1.77 Å. for the bridge hydrogen bond distance in liquid water.[12]

It seems worthwhile to mention the possibility of a fourth kind of hydrogen bridge as existing between a halogen molecule and water or paraffin hydrocarbon. In cases of this kind, the proton would form the bridge by being shared by four electrons, two from one halogen atom on the

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[11] (a) D. F. Evans, *J. Chem. Soc.*, 345 (1953); (b) *J. Chem. Phys.*, **23**, 1424, 1426 (1955); (c) *J. Chem. Soc.*, 1351 (1957).

[12] (a) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, Chapter 9; (b) P. C. Cross, J. Burnham and P. A. Leighton, THIS JOURNAL, **59**, 1134 (1937).

[13] R. A. Ogg, Jr., *J. Chem. Phys.*, **22**, 1933 (1954).

[14] G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1950, p. 560.

[15] G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 489.

halogen molecule and two from the original electron pair bond, O–H in the case of water and C–H in the case of the paraffin hydrocarbon. In this kind of bridge the proton would be nearer to the O or C atom of its original electron pair bond than to the halogen atom of the halogen molecule. The resulting structures would be either rings or chains.

The enhanced absorption of light that has been found to take place when the halogen molecules Cl_2, Br_2 or I_2 are dissolved in water[10] or paraffin hydrocarbons[11] could be interpreted in terms of these structures as well as the electron donor-acceptor complexes previously postulated.[11] Our explanation suggests that in these solutions $\bar{\epsilon}$ for these halogens may also depend upon the temperature.

The halogen molecule, of course, also reacts with water to form significant amounts of the species $H^+ + X^- + HOX$ where X is Cl, Br or I. This fact and the absorption of light by HOX and X_3^- should not be overlooked in interpreting absorption spectra of water solutions of these halogens.[10]

The simultaneous existence of several different kinds of hydrogen bridges between certain solutes and solvents also is suggested. In the case of O_2 (or Cl_2, Br_2 or I_2) dissolved in an alcohol[16] there could form a 1:1 complex in the form of a ring consisting of one molecule of the solute and one molecule of the solvent. This complex would be made up of two different kinds of hydrogen bridges in the ring, one hydrogen bridge like that between O_2 (or Cl_2, Br_2 or I_2) and water and the other hydrogen bridge like that between O_2 (or Cl_2, Br_2 or I_2) and a paraffin hydrocarbon. Similarly there could form in these solutions a chain complex consisting of one molecule of the solute and two molecules of the solvent. In these solutions also $\bar{\epsilon}$ for the molecular form of the solute may, therefore, be found to depend upon the temperature.

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The Radiation Chemistry of Water Vapor. The Indirect Effect on Deuterium and the Exchange of D-Atoms with Water Molecules[1]

BY RICHARD F. FIRESTONE[2]

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An investigation of the tritium β-ray induced exchange between deuterium gas and water vapor containing tritium-water has been made in order to measure the radical-pair and water decomposition yields in irradiated water vapor. A value for the radical-pair yield of 11.7 ± 0.6 radical pairs/100 e.v. has been determined. The exchange takes place *via* a chain mechanism above 150°. Evidence for the chain-propagating step $D + HOH = H + DOH$ is presented. An apparent activation energy of 18 ± 1 kcal./mole is assigned to this reaction. Results from the radiolysis of pure water vapor indicate an upper limit of 0.02 for $G(H_2)$.

Introduction

Most of the known chemical effects of ionizing radiation on liquid water have been rationalized with free radical mechanisms and by considering the different track densities of densely and sparsely ionizing particles. Much attention has been directed toward measurement of the so-called molecular product and free-radical yields in water solutions.[3] The observed increase in the ratio of the former to the latter as heavier and more densely ionizing particles are employed has been partially explained by considering the initial spatial distribution of reactive intermediates (ions, free-radicals, excited molecules). In the case of light particles distances between "spurs," or regions of high local intermediate concentration scattered along the particle's trajectory, are large on the average, and escape from the "spur" effectively guarantees detection of an intermediate by reaction with an appropriate solute.[3] Thus, the free radical yield, or yield of intermediates free to react with solute molecules is relatively large in the case of γ-rays and energetic β-rays. On the other hand, intermediates formed in the much more closely spaced spurs of α-particle or nuclear recoil-ion tracks have a correspondingly lesser chance of escape and subsequent reaction with the solute. Consistent with this reasoning it is to be expected that a large decrease in density of the reaction medium should, by virtue of a resulting decrease in track densities and an increase in diffusion rates, promote an increase in the free radical yield at the expense of both the molecular product yield and of those fast track reactions, if any, which merely re-form water in denser media.

This investigation of the tritium β-ray induced decomposition of water vapor in samples 1000-fold less dense than liquid water demonstrates, as anticipated, that a much greater proportion of reactive species are free to react with "solute molecules" in the gas phase. In mixtures of tritium-water vapor at pressures of 1000 mm. and deuterium gas at mole fractions in the range 10^{-3} to 10^{-2}, the rate of hydrogen deuteride formation appears to be equal, below 150°, to the rate of formation of hydrogen atoms. The magnitude of G(HD) observed (11.7 ± 0.6 molecules/100 e.v.) indicates that the detectable water decomposition yield as well as the free radical yield is considerably greater in water vapor than in liquid water.

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] Morley Chemical Laboratory, Western Reserve University, Cleveland 6, Ohio.

[3] E. J. Hart, *Radiation Research*, **1**, 53 (1954).