The Exchange Reaction of Hydrogen and Deuterium Oxide

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Besides this band spectrum a continuous absorption down to 2800A is observed. The potential energy curve attained in the absorption act must be evidently a steep curve of repulsion. The photo-dissociation process produced is assumed to be:

$$h\nu + Hg(CH_3)_2 \rightarrow CH_3 + HgCH_3.$$
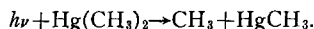
The curve of repulsion belongs presumably to the ground electronic state of the molecule and a large surplus of kinetic energy amounting to 50 kcal. is imparted to the products of photo-dissociation. The existence of such a curve explains also the diffuseness of the band spectrum.

To test definitely the possibility of a photo-dissociation process with the rupture of the bond $Hg-C$, the behavior of the compounds $(CH_3)HgI$ and $(CH_3)HgBr$ was studied. It was demonstrated previously that under the action of suitable light quanta the molecules $Hg(Hal)_2$ can be split up according to the scheme:

$$h\nu + Hal - Hg - Hal \rightarrow Hal + Hg\,Hal^*$$

where $Hg\,Hal^*$ is an excited molecule HgI or $Hg\,Br$ emitting its characteristic spectrum.[3] By analogy we expect this to be the case also for the methyl-halogen compounds of mercury.

In fact it was found that when diluted vapors of $(CH_3)HgI$ or $(CH_3)Hg\,Br$ are illiminated by short ultra-violet light, spectra belonging to excited Hg Hal molecules are emitted. From this and a detailed analysis of the experiments, the photo-dissociation:

$$h\nu + (CH_3)Hg\,Hal \rightarrow CH_3 + Hg\,Hal^*$$
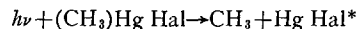
was ascertained.

The strength of the bond $Hg-C$ evaluated from these experiments is of the order of 60 kcal. per mole.

For $Zn(CH_3)_2$ and $Pb(C_2H_5)_4$ only a continuous absorption spectrum was observed.

The vapors of these latter substances are readily decomposed by ultraviolet light with the formation of metallic dust on the path of the light beam.

Further details and an analysis of the results obtained will be published soon elsewhere.

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[3] A. Terenin, Zeits. f. Physik **44**, 713 (1927).

The Exchange Reaction of Hydrogen and Deuterium Oxide

The exchange of deuterium between hydrogen and deuterium oxide molecules has been shown to take place at high temperatures.[1] There is now available sufficient spectroscopic data to calculate the equilibrium constant of the reaction.

The constant for

$$H_2 + HDO \rightleftharpoons HD + H_2O$$
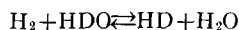
is given by

$$K = \frac{f_{H_2O}f_{HD}}{f_{HDO}f_{H_2}}$$

where the f quantities are the distribution functions for the several molecules. For water and hydrogen the functions are

$$f_{H_2O} = \left(\exp + \frac{\zeta_{H_2O}}{kT}\right) \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \frac{8\pi^2(8\pi^3 ABC)^{\frac{1}{2}}}{2h^3}$$

$$\times (kT)^{\frac{3}{2}} \Pi_{i=k,l,m} \frac{1}{1 - \exp - \dfrac{h\nu i}{kT}}.$$

$$f_{H_2} = \left(\exp + \frac{\zeta_{H_2}}{kT}\right) \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \Sigma p \exp - \frac{Ev, j}{kT}.$$

The function for HDO is similar to that for H_2O except that no symmetry correction is required and the statistical weight factor is 6 instead of 4. The function f_{HD} is similar to f_{H_2}, p being the weight factor. These more exact data for the H_2 and HD molecules are available from the work of Urey and Rittenberg.[2] Calculations were made for the additional temperatures necessary. The moments of inertia (ABC) and fundamental vibration frequencies for H_2O and HDO were obtained from Topley and Eyring.[3]

TABLE I. *Equilibrium constants for the reaction.*
$$HDO + H_2 \rightleftharpoons H_2O + HD$$

T	k	T	k
300	1.59	700	0.74
400	1.09	800	.68
500	0.93	900	.64
600	.81		

Here it is necessary to use the approximations for the vibrational energy. ζ is the energy of the molecule in its lowest state. The calculated values of the equilibrium constant are given in Table I. This temperature dependence of the equilibrium constant is almost entirely due to the effect of the temperature in the exponential term for the zero point energies.

Experiments were carried out in a Pyrex container of 1565 cc capacity and maintained at constant temperature by a sulfur vapor bath. The vessel containing one cc of liquid water with deuterium was filled with hydrogen to one atmosphere at room temperature. The rate of the reaction is illustrated in the following data.

Temp. = 495°C
time in hrs.   0   19⅓   46   86½
% D in water
sample   14.66   11.62   9.93   9.01
Temp. = 507°C
time in hrs.   0   2   4   8   22   44⅓   6 days
% D in water
sample   6.25   5.79   5.69   5.63   4.46   3.64   3.54

[1] Crist and Dalin, J. Chem. Phys. **1**, 677 (1934).
[2] Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933).
[3] Topley and Eyring, J. Chem. Phys. **2**, 217 (1934).

From these data the time required for equilibrium could be estimated. The measurements cannot be considered reliable for rate studies since the effect of a darkening of the vessel could not be determined. This study is now being continued in quartz apparatus. The analyses were made by means of the interferometer.[4]

TABLE II. *Equilibrium data for* $HDO + H_2 \rightleftharpoons H_2O + HD$.

No.	Temp. in °C	% HDO in water	% HD in hydrogen	k
1	526	12.88	9.46	0.71
2	526	6.74	4.56	.66
3	530	6.10	4.68	.76
4*	520	7.42	3.66	.48

* This is probably not at equilibrium due to a temperature fluctuation during the run.

The equilibria data are contained in Table II. In all but No. 1 the original mixture was HDO, $H_2O + H_2$ while in 1 the amounts of HDO and HD in the original mixture were the same. Thus the equilibrium was approached from both sides. The hydrogen sample was converted to water by passing over copper oxide and then analyzed.

According to the results of Table I the variations in k found here are to be ascribed to experimental error.

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            June 15, 1934.

[4] Crist, Murphy and Urey, J. Chem. Phys. **2**, 112 (1934).