The Significance of the Activation Energy of Collision

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It is quite evident that our heat capacity results show no discontinuity in the neighborhood of 9.6° and no sign of a heat of transition. In our procedure the latter would naturally have been included in either the measurement corresponding to an average temperature of 7.4° or that for 11.6°, as the series of measurements left no temperature gaps between 0° and 26°. Therefore we can see no basis for the claim that pure nitrobenzene exists in two allotropic liquid forms.

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Acoustical measurements have established that the rate of vibrational energy exchange is in general strongly dependent on temperature.[1] In order to describe this the term "activation energy of collision" has been employed,[2] and this quantity appears to be of the order of one to three $h\nu$ where ν is the vibration frequency of the molecules in the experiments so far reported. I wish to report in this letter the preliminary result of a theoretical investigation which has attempted to give the "activation energy of collision" a more precise significance.

At first the excited and exciting molecules were considered held at a fixed distance, and then the relative kinetic energy was allowed to enter as a perturbation giving rise to an exchange of translational and vibrational energy. This led to two simultaneous differential equations for the eigenfunctions of the excited and the unexcited molecules. To solve these to a first approximation plane wave functions which vanished inside the kinetic theory diameter were introduced. This permitted a comparison between the outward flow of excited molecules with a normalized incoming wave of unexcited molecules. This gave for a collision energy E a probability for the exchange of a vibrational quantum proportional to $E^{1/2}(E-H\nu)^{5/2}$. This treatment differs from that given by Rice[3] in that the wave function of the internal coordinates includes as a parameter, a fixed value of the distance of separation due to the clamping of the molecules. It obviates as well the paradoxical approximation of adiabatic approach implied in an extension of the treatment of Kallman and London[2,4] to the conversion of translational into vibrational energy.

When integrated over all energies the temperature dependence of the yield is nearly proportional to the fourth power of the temperature times the usual factor $e^{-h\nu/kt}$. Expressed as an activation energy this is approximately $4kt$, which agrees well with the experimental values for carbon dioxide, carbon disulfide, etc. The second order effects such as the softening of the bonds at close approach, the effect of repulsion on the eigenfunctions previous to the point where they vanish, and the shielding by other atoms in polyatomic molecules would tend to increase this temperature dependence. The absolute magnitude of the yield was of the order of $10^{-4}-10^{-7}$ per collision depending upon the type of molecule. This is also in agreement with experiment.

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[1] Henry, Proc. Camb. Phil. Soc. 28, 249 (1932); Richards and Reid, Nature 130, 739 (1932); J. Chem. Phys. 2, 193, 206 (1934).

[2] Richards, J. Chem. Phys. 1, 874 (1933).

[3] Rice, J. Am. Chem. Soc. 54, 4559 (1932).

[4] Kallman and London, Zeits. f. physik. Chemie B2, 207 (1929).

Photo-Dissociation of the Vapors of Organo-Metallic Compounds

The photochemistry of the simplest organo-metallic compounds of the type MR_n (M = metal, R = CH_3, C_2H_5, C_6H_5) has not as yet received due attention. Only one observation may be cited, namely that of Berthelot and Gaudechon,[1] who found that liquid $Zn(C_2H_5)_2$ illuminated by a quartz mercury arc decomposes rapidly into ethane and zinc metal. We expect in fact that less energy is needed to disrupt the bond $M-C$ than the bond $C-C$; therefore photochemical reactions can be induced by smaller quanta such as those lying in the nearer ultraviolet.

A study of these compounds was therefore undertaken in this laboratory. Some of the results obtained are given here.

First, the absorption spectra of $Hg(CH_3)_2$, $Zn(CH_3)_2$ and $Pb(C_2H_5)_4$ were studied. These substances are very volatile. A structure in the absorption spectrum of $Hg(CH_3)_2$ could be detected only when this liquid was frozen down to $-150°C$. At room temperature the vapor pressure is so high that all the ultraviolet is completely absorbed.

The absorption spectrum of $Hg(CH_3)_2$ consists of a progression of diffuse bands in the region 2100–1970A. The spacing of these bands is equal to 350 cm^{-1} and represents presumably the vibration quantum of one of the valence modes of vibration of the mercury atom in the upper electronic state of the molecule. From the Raman spectrum the valence vibration frequencies of the Zn atom in the ground state of the $Zn(CH_3)_2$ molecule are known to be 506 and 617 cm^{-1}.[2] For $Hg(CH_3)_2$ no corresponding data are available, but the order of magnitude must be the same.

The electronic transition in the $Hg(CH_3)_2$ molecule is equal to 47,044 cm^{-1} or 5.8 e.v.

[1] Berthelot and Gaudechon, C. R. 156, 1245 (1913).

[2] S. Venkateswaran, Ind. J. Phys. 5, 145 (1930).

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:

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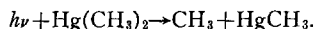
The curve of repulsion belongs presumably to the ground electronic state of the molecule and a large surplus of kinetic energy amounting to 50 kcal. is imparted to the products of photo-dissociation. The existence of such a curve explains also the diffuseness of the band spectrum.

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 illuminated 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:

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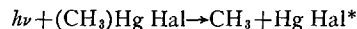
was ascertained.

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

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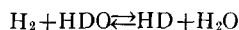
is given by

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

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

$$f_{H_2O} = \left(\exp + \frac{\zeta_{H_2O}}{kT} \right) \frac{(2\pi m k T)^{\frac{3}{2}}}{h^3} \frac{8\pi^2 (8\pi^3 ABC)^{\frac{1}{2}}}{2h^3}$$
$$\times (kT)^{\frac{3}{2}} \Pi_{i=k,l,m} \frac{1}{1 - \exp - \frac{h\nu i}{kT}}$$

$$f_{H_2} = \left(\exp + \frac{\zeta_{H_2}}{kT} \right) \frac{(2\pi m k T)^{\frac{3}{2}}}{h^3} \Sigma p \exp - \frac{E_{v,j}}{kT}.$$

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.*
$HDO + H_2 \rightleftarrows H_2O + HD$

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).