The Relative Reactivities of the Hydrogen Isotopes with Chlorine

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Phase Boundary Potentials of Monolayers of Long-Chain Fatty Acids

By means of the electrical method of measuring the phase boundary potentials (ΔV) of monolayers of long chain fatty acids described by Schulman and Rideal[1] we have investigated in some detail the behavior of the stable and metastable liquid expanded and the liquid condensed states of myristic acid. The experimental data reported by the above authors,[1] by Adam and Harding[2] and by Harkins and Fischer[3] are not in agreement and indeed doubt has been cast upon the existence of the metastable liquid expanded state and its transition into the liquid condensed state.

On compressing a liquid expanded film to areas between $40A^2$ and $20A^2$ per molecule a high phase boundary potential is observed which falls with time. The film is evidently metastable in respect to its contribution to the phase boundary potential. During this fall of ΔV the film is heterogeneous as can be readily verified by exploration of the surface. After waiting 4–5 hours when the molecular area is about $25A^2$ the film becomes homogeneous, but when the area is $38A^2$ it remains inhomogeneous. These experiments strongly support the micellar structure for the film as proposed by Langmuir.[4] This apparent change in the properties of the film appears to us to be most readily interpreted on the view that during the fall of potential

water is being squeezed out from between the chains themselves. This process of elimination of water can be accelerated by the addition of tannic acid to the underlying solution when equilibrium is found to be established in a much shorter period of time ($1\frac{1}{2}$ to 2 hours). Since the bulk solubility of the acid in the metastable liquid expanded state appears to be higher than that in the liquid condensed state and the solubility can be reduced both by saturation of a 0.01 N HCl substrate with myristic acid and also by the use of 0.1 N HCl as substrate we conclude that in addition to the hydrocarbon adhesion emphasized by Langmuir both the hydration of the chain and the properties of the polar head group are important fundamental factors for the existence of the film in these states.

N. W. H. ADDINK
ERIC K. RIDEAL

Laboratory of Colloid Science,
    Cambridge, England,
        February 5, 1934.

[1] Schulman and Rideal, Proc. Roy. Soc. **A130**, 259 (1930).
[2] Adam and Harding, Proc. Roy. Soc. **A138**, 411 (1932).
[3] Harkins and Fischer, J. Chem. Phys. **1**, 853 (1933).
[4] Langmuir, J. Chem. Phys. **1**, 756 (1933).

The Relative Reactivities of the Hydrogen Isotopes with Chlorine

It has been shown recently[1] that if mixtures of hydrogen, chlorine, and carbon monoxide are illuminated with light absorbed by the chlorine, the relative amounts of phosgene and hydrogen chloride formed are governed by the equation

$$(\Delta H_2 + \Delta CO)/\Delta H_2 = 1 + k(CO)/(H_2). \tag{1}$$

The left-hand member of this equation is equal to the reciprocal of the fraction of the chlorine which reacts with hydrogen; on the right-hand side the pressures of carbon monoxide and hydrogen in the reaction mixture are substituted. The constant, k, is the ratio of the specific rate constants of the reactions of the two gases with the active form of chlorine, and is equal to the reciprocal of the value of the ratio $(CO)/(H_2)$ for which the quantity $(\Delta H_2 + \Delta CO)/\Delta H_2$ is equal to two. This relationship offers a convenient method of comparing the relative reactivities of the two isotopes of hydrogen as the ratio of the values of k obtained by using ordinary hydrogen and the heavy hydrogen gives the ratio of the specific rate constants of these two isotopes for the particular reaction involved in this system. This method has the very great advantage that the results are not affected by inhibitors and therefore are more accurate than could be obtained by rate experiments.

The carbon monoxide and chlorine were prepared as in the previous work.[1] The heavy hydrogen was prepared from heavy water (obtained from Professor G. N. Lewis) by treatment with metallic sodium. This is the usual procedure followed in this laboratory and it has been found that all the hydrogen is liberated from the water if the

sodium is heated to approximately 300°C. The apparatus and experimental procedure were the same as previously described.[1]

The difference in the behavior of the two isotopes is quite marked. Whereas with ordinary hydrogen at 0°C it is necessary to have nearly four times as much carbon monoxide as hydrogen in order to have the chlorine divide equally between the two, with heavy hydrogen nearly four times as much hydrogen as carbon monoxide is needed. In Table I are given the values of $(CO)/(H_2)$ for which $(\Delta H_2 + \Delta CO)/\Delta H_2 = 2$. From Eq. (1) it is apparent that these are the values for the specific rate constants of the two hydrogen isotopes expressed in terms of the rate constant for the reaction of chlorine with carbon monoxide. In order to obtain as accurate values as possible from the data two graphs were made from each set of data, one being a plot of $(\Delta H_2 + \Delta CO)/\Delta H_2$ against $(CO)/(H_2)$, the other $(\Delta H_2 + \Delta CO)/\Delta CO$ against $(H_2)/(CO)$. The former emphasizes the errors in the measurement of ΔH_2 and the latter those for ΔCO. This method resulted in lowering the value 3.9 previously given for ordinary hydrogen at 0°C to 3.7 is given in the table. This change is within the limits of accuracy of the experiments which is about ten percent, because of errors in measuring the small changes.

Applying the Arrhenius equation, we may write

$$k_2/k_1 = (s_1/s_2)e^{-(Q_1-Q_2)/RT}.$$

As we have the values of k_1/k_2 at two temperatures, we may

[1] Rollefson, J. Am. Chem. Soc. **56**, March (1934).

TABLE I.

Temperature	$\frac{H_2}{k_1}$	$\frac{H^2_2}{k_2}$	$\frac{k_1}{k_2}$
0°C	3.7	0.275	13.4
32°C	16.6	1.70	9.75

calculate $Q_1 - Q_2$ and s_1/s_2. The values obtained are $Q_1 - Q_2 = -1630$ cal. and $s_1/s_2 = 0.66$. If the two types of hydrogen molecules are assumed to have the same collision diameters and the same steric factors, s_1/s_2 should be $2^{\frac{1}{2}}$. The difference between this value and that calculated from
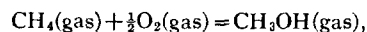
the data is not considered of any significance as an error of ten percent in one of the experimental ratios corresponds to a change in $Q_1 - Q_2$ of 540 calories and a change in s_1/s_2 of a factor of 2.7. We may conclude therefore that the molecules of heavy hydrogen are less reactive than those of ordinary hydrogen in the reaction to form hydrogen chloride due to the fact that the reaction involving the former has a slightly higher heat of activation.
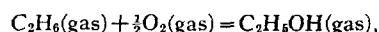
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February 8, 1934.

The Energies of the Atomic Linkages in Methane, Ethane, Methanol and Ethanol[1]

Data recently obtained in this laboratory on heats of combustion lead to the following values for the change in heat content associated with the addition of $\frac{1}{2}O_2$ to methane and ethane to form methanol and ethanol, respectively:

$$CH_4(gas) + \tfrac{1}{2}O_2(gas) = CH_3OH(gas),$$

$$\Delta H°_{298} = -30.24 \pm 0.09;$$

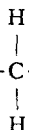$$C_2H_6(gas) + \tfrac{1}{2}O_2(gas) = C_2H_5OH(gas),$$

$$\Delta H°_{298} = -36.09 \pm 0.15;$$

kcal. per mole.

These data show that the energy of the process of

$$\text{breaking a } C-H \text{ bond in the molecule } R-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-H \text{ and in-}$$

serting an oxygen atom to form the molecule $R-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-O-H$
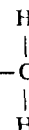
is appreciably affected by the nature of the substituent R; and that, contrary to what has been assumed by practically all investigators in this field, the energies of the atomic linkages in these and homologous compounds are quite significantly not additive.

In a subsequent paper which will appear in the *Bureau of Standards Journal of Research*, it will be shown that even in the normal paraffin hydrocarbons the energies of the atomic linkages are appreciably affected by the nature of the substituents, hydrogen atoms or alkyl groups.

FREDERICK D. ROSSINI

Bureau of Standards,
Washington, D. C.,
February 8, 1934.

[1] Publication approved by the Director of the Bureau of Standards, United States Department of Commerce.

Direct Experimental Measurement of Electron Affinities

The electron affinity of an electronegative gas, ΔE at 0°K of the reaction $X^- \rightarrow X + e^-$, may be readily calculated if the equilibrium constant of the above reaction can be measured. If the gas X_2 at low pressure is allowed to come in contact with a hot metallic surface (thermionic emitter), molecules X_2, atoms X, electrons e^-, and ions will leave the surface. If it is assumed that the relative amounts of the various molecular species leaving the surface are independent of the temperature of the molecules X_2 hitting the surface, that is if complete equilibrium on the surface exists, then the equilibrium pressures and the electron affinity may be simply calculated from the numbers of X^-, X, and e^- leaving the surface. In the case of iodine, calculations predict, and observations show,[1] that at above 1500°K the molecules are completely dissociated into atoms, and since a very small fraction of the atoms are converted into ions on a tungsten surface, the

number of atoms leaving the surface will be twice the number of impinging molecules. The necessary data for the calculations are then, the temperature of the surface, the pressure of the gas X_2 in the vessel, and the ratio of the currents carried by the ions and electrons.

By using, in a cylindrical arrangement, a tungsten filament (0.2 mm diam. 0 volts) a wire net grid (10 mm diam. about +10 volts) and a cylindrical plate collector (40 mm diam. about +15 volts) inside a solenoid producing a magnetic field parallel to the axis of the cylinder, the electron current from the filament can be completely deflected from reaching the plate at fair solenoid currents even in the presence of considerable gas pressure. (Magnetron set-up.) The heavy ions I$^-$ are unaffected by the magnetic field. The voltage necessary to obtain saturation

[1] Communication from Dr. Irving Langmuir.