On the Concentration of Deuterium by Electrolysis

D. H. Rank

---

be made up mainly by decreasing the strength of $C-C$, which denotes actually the difference between $C=C$ and $C-C$. The calculated heat of activation then will be somewhat lower, probably about 50 kcal. Sherman and Eyring,[3] using a more suitable value for $C=C$, previously calculated an activation energy of 51.5 kcal. for the hydrogenation of ethylene. Here again the reaction is approximately 30 kcal. exothermic. The theoretical activation energy for either 1–2 or 1–4 dehydrogenation is thus 80 kcal.; the experimental value in the former case is 70 kcal., and a similar figure seems reasonable for the 1–4 reaction.

There is also a second possible type of 1–4 dehydrogenation:[4]

$$CH_3CH_2CH_2CH_3 \longrightarrow H_2 + CH_2 : CH_2 + CH_2 : CH_2.$$
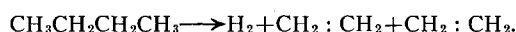
This type actually corresponds somewhat more closely to the six-electron model than does the production of butadiene from butylene. It is approximately 20 kcal. more endothermic, however, since it takes more energy to break $C-C$ than it does to reduce $C=C$ to $C-C$. The difference in activation energy will be considerably less than 20 kcal.; accurate predictions are impossible, but it appears worth while to look for this type of decomposition of hydrocarbons with a straight chain of at least four carbon atoms. By analogy with the 1–2 case, we shall expect to find 1–4 loss of methane, ethane, etc., and also, when the parent hydrocarbon is large enough.

The recent work of Frey and Hepp[5] may be interpreted as showing that this type of reaction occurs. For n-butane itself the evidence is somewhat conflicting; 1–4 dehydrogenation may constitute up to 5 percent of the primary reaction. For n-pentane the data may be interpreted as indicating the following primary products.

	Percent		Percent
$H_2 + C_5H_{10}$	5.2	$H_2 + C_2H_4 + C_3H_6$	18.5
$CH_4 + C_4H_8$	30.9	$CH_4 + C_2H_4 + C_2H_4$	12.2
$C_2H_6 + C_3H_6$	31.5		
$C_3H_8 + C_2H_4$	1.7		
	69.3		30.7

For n-hexane, 60 percent of the reaction seems to go by way of 1–4 unsaturation, and only 40 percent by 1–2. For 2-methylbutane and 2,3-dimethylbutane, 20 percent and 12 percent, respectively, of the total reaction involves 1–4 unsaturation. These results have been interpreted by Frey and Hepp, and by Rice,[6] in terms of Rice's free radical mechanism. A detailed analysis shows that the free radical theory and the present unsaturation theory predict the same products in approximately the same yields. For very long chains it would be necessary to postulate 1–6, 1–8, etc., unsaturation, with resulting scission into four, five, or more primary products, to match exactly the free radical predictions; there is no experimental evidence on this point. The free radical mechanism does predict a decrease in the mean molecular weight of the primary products as the pressure is lowered. On the unsaturation theory such a decrease should not occur in the region where the reaction rate is strictly first order. No existing data even approach being good enough to make this test.

There is little doubt that free radicals are formed from metal alkyls, and in a few other cases where there are unusually weak bonds, but it appears possible to give a nearly complete account of the decomposition reactions of organic chemistry in terms of 1–1, 1–2, and 1–4 unsaturation. It is hoped to discuss this subject in more detail later. For the present, it is sufficient to mention a few further examples of 1–4 unsaturation: the formation of ethylene and butadiene from cyclohexene, of carbon dioxide and allyl alcohol from glyceryl oxalate, and of methane, ethylene, and formaldehyde or hydrogen, ethylene, and acetaldehyde from ethyl ether. In this last case, the chief reaction is 1–2 splitting to ethane and acetaldehyde.

LOUIS S. KASSEL[7]

Physical Chemistry Section,
    Pittsburgh Experiment Station,
      U. S. Bureau of Mines,
        Pittsburgh, Pennsylvania,
          August 24, 1933.

[3] Sherman and Eyring, J. Am. Chem. Soc. **54**, 2561 (1932).

[4] Cf. Gault and Hessel, Ann. chim. [10] **2**, 376 (1924), who postulated a similar process to account for the production of hydrogen in the pyrolysis of hexadecane.

[5] Frey and Hepp, Ind. Eng. Chem. **25**, 441 (1933).

[6] F. O. Rice, J. Am. Chem. Soc. **55**, 3035 (1933).

[7] Associate physical chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

On the Concentration of Deuterium by Electrolysis

Bleakney and Gould[1] have raised the question as to the reason for the low concentration of deuterium in commercial electrolytic cells as is shown by the analysis of hydrogen obtainable commercially. They point out that this low concentration would imply that this tank hydrogen has all come from apparently new cells.

The specific gravity of water which was distilled from electrolyte which was kindly furnished by the Pittsburgh plant of the Burdett Hydrogen and Oxygen Company has been obtained. This water was carefully purified by distillation through a still which is used for the production of conductivity water, and then deaerated. The specific gravity was obtained by means of a buoyancy balance similar to that described by Lewis and Macdonald.[2] Six cells were sampled and the specific gravity obtained was 1.000013 compared to ordinary conductivity water at 18.2°C. The results on all samples agreed to about one part in a million.

The cells from which the electrolyte was taken had been in operation for about five years without the electrolyte having been renewed. A simple calculation showed that

[1] Walker Bleakney and Austin J. Gould, Phys. Rev. **44**, 268 (1933).

[2] G. N. Lewis and R. T. Macdonald, J. Chem. Phys. **1**, 341 (1933).

the amount of water electrolyzed during this period of operation was about 30 times the amount the cells contained. It would appear from this calculation that these cells had been in operation for a long enough period of time to have nearly reached their equilibrium concentration, this equilibrium concentration being given by the relation deduced by Lewis and Macdonald[2] as $1/\alpha$ times the concentration of the water added to the cells, where α is the separation factor. This separation factor α must be a function of the temperature at which the electrolysis is taking place, as is shown by the following calculation.

If we assume Dalton's law of partial pressures to apply, the fractional part of a mole of water vapor removed per mole of water electrolyzed will be $3P_W/2(P_A - P_W)$, which quantity we shall call ϵ. Where P_W is the partial pressure of water vapor at the temperature T, and P_A is the atmospheric pressure. Thus the amount of water removed from the cell will be $1 + \epsilon$ moles per mole electrolyzed. If δ_1 and δ_2 represent the amounts of H^1 and H^2 evolved per mole of hydrogen produced, and C_1 and C_2 are the respective concentrations of the two kinds of hydrogen in the electrolyte expressed as mole fractions, then $\delta_2 C_1/\delta_2 C_2 = \sigma$ is the true electrolytic separation factor. The hydrogen lost by vaporization of the water will be ϵ moles per mole electrolyzed. Thus the α of the Lewis and Macdonald[2] equation obviously becomes,

$$\alpha = (\delta_2 + \epsilon C_2)C_1/(\delta_1 + \epsilon C_1)C_2.$$

Assuming Bleakney and Gould's[1] value (1 part in 5000) for the abundance of deuterium in ordinary water, and using Lewis and Macdonald's[3] value for the density of pure deuterium oxide, the value of σ can be calculated if we further assumed that the electrolytic hydrogen analyzed by Bleakney and Gould[1] came from a typical old cell of the type which was referred to above. This calculation gives a value of 0.12 for σ which would agree fairly well with the provisional value of 0.10 given by Urey.[4] By taking this value (0.12) for σ and calculating α for this cell, ($T = 160°F$) the value of α obtained is 0.37. The experimental value of α for such a cell will be considerably higher than this calculated value, due to the fact that evaporation from the surface of the electrolyte, which will be considerable at this temperature, has not been taken into account in the calculation. Calculating for Lewis and Macdonald's[2] cells ($T = 35°C$) the value of α obtained is 0.16 which is in fair agreement with the experimental value of 0.20 when it is considered that the mechanical loss of water during the electrolysis is neglected, which loss would tend to increase the calculated value of α.

From the above considerations it would appear that commercial cells which are run hot in order to attain high power efficiency must necessarily have a low equilibrium concentration of deuterium, and also that the hydrogen produced by such cells will have a correspondingly low concentration of the heavier isotope.

The author is indebted to Dr. J. G. Aston of the Chemistry Department for the use of the thermostat and conductivity still which made the determinations of specific gravity possible.

D. H. RANK

Physics Laboratory,
    Pennsylvania State College,
        August 29, 1933.

[3] G. N. Lewis and R. T. Macdonald, J. Am. Chem. Soc. 55, 3057 (1933).

[4] H. C. Urey, Rev. Sci. Inst. 4, 425 (1933).

The Effect of Water Containing the Isotope of Hydrogen upon Fresh Water Organisms

Since the announcement by Washburn and Urey[1] that in electrolysis the residual water is enriched in heavy hydrogen, there has been a greatly increased interest in the separation and properties of isotopes. That the chemical reactivity of two isotopes with such different atomic weights would differ very considerably was of course clear, and the opinion that heavy water would have striking biological effects was generally held.

Lewis[2] has recently demonstrated that the seeds of tobacco will not germinate in pure H^2H^2O whereas seeds in ordinary distilled water sprouted within two days. We have recently performed a series of experiments to test the action of heavy water upon the vital activities of fresh water organisms. Our results are briefly summarized as follows:

(1) Water containing the isotope of hydrogen in high concentration (92 percent) was found to be toxic for the animals tested.

(a) Tadpoles of the green frog Rana clamitans died within an hour after being placed in the water. Control animals in 30 percent heavy water, and in ordinary distilled water, remained unaffected at the end of twenty-four hours.

(b) The common aquarium fish Lebistes reticulatus is killed by the water within an interval of two hours. Neither 30 percent heavy water, or distilled water exerted an effect over a twenty-four hour interval.

(c) Flatworms, planaria maculata are destroyed within three hours in the 92 percent heavy water, but were uninjured by the 30 percent heavy water over a period of three days.

(d) The protozoan, paramoecium caudatum is killed by the 92 percent heavy water within 48 hours. Water containing 15–20 percent of the heavy isotope of hydrogen did not affect the organisms during a three day interval. Paramoecium showed more resistance to the toxic action of the water than the highly organized animals studied.

H. S. TAYLOR
W. W. SWINGLE
H. EYRING
A. H. FROST

Chemical and Biological Laboratories,
    Princeton University,
        September 15, 1933.

[1] Washburn and Urey, Proc. Nat. Acad. Sci. 18, 496 (1932).

[2] G. N. Lewis, J. Am. Chem. Soc. 55, 3503 (1933).