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The Heats Of Hydrogenation Of Unsaturated Hydrocarbons

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Abstract

Recent precise experimental work on the heats of hydrogenation of hydrocarbon compounds containing one or more double bonds shows a variation from compound to compound which can be correlated with the structure of the molecule. For compounds containing one double bond or several non-conjugated bonds, the heat of hydrogenation per double bond is nearly constant. However, in compounds containing conjugated double bonds the average heat of hydrogenation per bond is less than in non-conjugated systems due to the interaction energy between the double bonds tending to stabilize the system. This effect is most pronounced in aromatice compounds. Although the hydrogenation of benzene to form cyclohexane (addition of three molecules of hydrogen per molecule of benzene) is an exothermic reaction, the hydrogenation of benzene to form cyclohexadiene -1,3 (addition of one hydrogen molecule per molecule of benzene) is an endothermic reaction. This signifies that the energy associated with the aromatic character of benzene is greater than the energy of hydrogenation of a double bond, so that the resultant of these two effects is an endothermic reaction.

TO a first approximation, the energy of a gaseous molecule containing electron-pair bonds may be considered to be the sum of the energies due to the various bonds. It therefore follows that the heat of hydrogenation of any unsaturated hydrocarbon (per mole of hydrogen) should be approximately constant, inasmuch as the hydrogenation involves in each case the formation of a carbon-carbon single bond and two carbon-hydrogen single bonds and the destruction of a carbon-carbon double bond (and a hydrogen-hydrogen single bond).

The recent accurate experimental work of Kistiakowsky and his co-workers* roughly substantiates the foregoing conclusions for unsaturated hydrocarbons not containing conjugated double bonds. For these latter systems, the heats of hydrogenation vary widely.

Table I shows some of the results of Kistiakowsky.

Table I. Heats of Hydrogenation

Compound	▲H at 83° C.
Ethylene	—32.8 kcal per mole
Propylene	—30.1
Butene-2 (cis)	—28.6
Butene-2 (trans)	—27.6
Trimethylethylene	—26.9
Tetramethylethylene	—26.6
Cyclohexene	—28.6
Cyclohexadiene 1, 3 (to form Cyclohexene)	—28.8
Benzene (to form Cyclohexadiene, 1, 3)	+5.6

In comparing the values for the series ethylene, propylene, butene-2 (*cis* and *trans*), trimethylethylene, and tetramethylethylene, the heats of hydrogenation are observed to decrease in the order given, corresponding to a decrease in affinity for hydrogen in the same order. In other words, the affinity of a carbon atom for hydrogen depends upon the number of hydrogens already attached to it. This conclusion is in accord with other known chemical properties of these compounds.

When we come to the aromatic hydrocarbons, we see that the addition of one mole of hydrogen is actually an endothermic reaction. The addition of another mole of hydrogen to the product of the first addition, cyclohexadiene — 1, 3, proceeds normally.

The free energy of the first reaction at 25° C. is calculated to be +13.6 kcal. whereas the free energy of the second reaction is —17.7 kcal. Thus, the equilibrium does not favor the addition of one mole of hydrogen to benzene. The equilibrium involving the simultaneous addition of three hydrogens to benzene favors the addition. However, this reaction is too difficult to occur kinetically. We therefore have a comprehensive understanding of the chemical behavior of aromatic compounds toward addition reactions.

If benzene could be simply regarded as cyclohexatriene with no interaction between the double bonds, the heat of hydrogenation to form cyclohexane should be just three times the heat of hydrogenation of cyclohexene to form cyclohexane. From Table I, this is 3 × -28.6=-85.8 kcal. The experimental value is -49.8 kcal. Hence benzene is more stable by an amount -49.8 -(-85.8)=36.0 kcal. than it would be if it were completely unsaturated in character (with no interaction between the double bonds). From the theoretical viewpoint, this extra stability of benzene (and other aromatic compounds) is shown to be a consequence of the fact that the normal state of the molecule is not that corresponding to either Kekulé structure but is a sort of combination of the two.

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* J. B. Conant and G. B. Kistiakowsky, Chem. Rev. 20, 181 (1937).