Carbohydrate Research, 34 (1974) 169–173

Note

A thermochemical approach to flame retardation for cellulosic materials

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(Received October 17th, 1973; accepted February 20th, 1974)

As combustion involves large amounts of heat, high temperatures, and change of state, thermochemical approaches may clarify our understanding of the mechanism of flaming of cotton fabrics and other cellulosic materials. This Note discusses dehydration processes of some related carbohydrates from the thermochemical standpoint.

Carbonization or charring of cellulosic materials appears to be the single most important reaction worth attention in the control of their combustion; it is, indeed, an index of the flame resistibility of the treated fabric. Moreover, a number of authors[1–3] appear to have concluded that simple dehydration of cellulose, $(C_6H_{10}O_5)_n$, is the main reaction leading to carbonization, but no clear statement on the role of the energy involved in the process is available. On the other hand, it is known that degradation reactions are highly influenced by the temperature, the period of heating, and the natural and "add-on" impurities[4–6]. From these studies, the loss in weight seems to correspond to 3–4 molecules of water per D-glucose residue. Thus, it is reasonable to suppose that dehydration is the major process that leads to char formation[3,7]. Less charring may result when certain regions or portions of cellulose volatilize completely. By catalyzing the process at lower temperatures, add-on materials enhance the chance of char formation over greater portions of the cellulose.

At higher temperatures, formation of 1,6-anhydro-β-D-glucopyranose ("levoglucosan") or tar is favored[8,9]. In addition, formation of other degradation products from cellulose and levoglucosan is possible. Some authors have found[9,10] that, at temperatures of 242° and higher, the degradation products of cellulose and levoglucosan are essentially identical.

The data on heats of combustion (ΔH_r°) that are available in the literature are given in Table I. It may be pointed out that the heat of combustion of various woods, such as birch, cherry, hickory, oak, pine, and poplar, based on reported data[17], is 773 ±10 kcal per 162 g (the equivalent weight of one D-glucose residue); this is significantly different from the value for pure cellulose, and may be attributable to the presence of lignin and other impurities which have high heats of combustion. The

TABLE I

THERMOCHEMICAL DATA[a]

Carbohydrate and formula	*Heat of combustion,* ΔH_c° *(kcal.mole^{-1})*	*Heat of formation,* ΔH_f° *(kcal.mole^{-1})*	*Free energy,* ΔG_f° *(kcal.mole^{-1})*	*Heat of dehydration,* ΔH_{deh}° *(kcal.mole^{-1})*	*Free energy of dehydration,* ΔG_{deh}° *(kcal.mole^{-1})*
D-Glucose, $C_6H_{12}O_6$	−673.0[11,12]	−303.8 −304.6[14]	−215.8[13] −217.6[14]	−106.6	−124.4
D-Fructose, $C_6H_{12}O_6$	−675.6[11]	−301.2		−109.2	
Sucrose, $C_{12}H_{22}O_{11}$	−1,349.6[11,12]	−535.8 −531.1[14]	−371.6[13] −369.2[14]	−216.6	−252.1
Cellobiose, $C_{12}H_{22}O_{11}$	−1,350.0[11,12]	−535.2 −529.4[14]		−217.2	
Levoglucosan, $C_6H_{10}O_5$	−678.0[12]	−230.4 −227.8[14]		−111.6	
Cellulose[b]	−650.0[c]	−258.4[c]		−83.6[c]	

[a] Similar data for these and other carbohydrates are given in refs. 11–16. [b] See ref. 17 for the heat of combustion of various woods. These are significantly higher than for pure cellulose, presumably owing to the presence of non-cellulosic impurities. [c] Calculated from data on combustion in ref. 18. See also, ref. 16.

way in which this difference affects the actual situation of the pyrolysis and combustion thereof will not be discussed here.

By using these combustion data and the standard heats of formation of carbon dioxide and water, the standard heats of formation (ΔH_f°) for the carbohydrates listed in Table I were computed. The free-energies of formation (ΔG_f°) for D-glucose and sucrose are given in the literature[13,14].

If the dehydration of D-glucose, sucrose, cellobiose, and levoglucosan under standard conditions is considered, the heats of dehydration are found to be, respectively, +3.6, +4.2, and +5.0 kcal per mole of the product formed. These low, endothermic values may not be significant at the combustion temperatures, but they show that these processes are not spontaneous. On the other hand, the dehydration of cellobiose to afford long chains, such as cellulose, according to the equation:

$$(n+1)\, C_{12}H_{22}O_{11} = C_6H_{11}O_6(C_6H_{10}O_5)_{2n}\text{–}C_6H_{11}O_5 + nH_2O,$$

is exothermic to the extent of 25 kcal per D-glucose residue formed. In reverse, the heat of hydrolysis of cellulose would be endothermic to various extents, depending upon the products formed.

If it is assumed that complete dehydration of these carbohydrates could take place to afford char in the graphitic state*, the heats of dehydration ($\Delta H_{\text{deh}}^\circ$) would be those included in the penultimate column of Table I; these values are exothermic. The free-energies of formation (ΔG_f°) for D-glucose and sucrose are negative, although the absolute values are lower than ΔH_f° because of the negative entropy of formation. The heats of formation (ΔH_f°) in the gaseous state should be less exothermic, because of the enhanced entropy. The heats of dehydration are largely negative, but, because the entropy of dehydration is positive, the free-energy of dehydration has a higher negative value. This fortunate circumstance favoring spontaneous dehydration is applicable to all carbohydrates (including cellulose).

On the other hand, depolymerization of cellulose to levoglucosan is an endothermic reaction to the extent of ~28 kcal (~117 kJ) per molar equivalent of D-glucose residue; this is readily deduced from the heats of formation given in Table I. This reaction is, therefore, more likely to occur at high than at low temperatures.

$$(C_6H_{10}O_5)_n = n\, C_6H_{10}O_5$$

At the lower temperatures, dehydration and exothermic reactions would predominate. At intermediate temperatures, the two kinds of reaction may compete. However, dehydration of nascent levoglucosan, an exothermic process, would be favored, as its heat of dehydration is large and exothermic. Thus, under an inert atmosphere and a pressure at which levoglucosan could volatilize, its dehydration might result in char formation. At low pressures in the absence of oxygen, various

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*This is the simplest assumption that may be made. The state of the pure carbon produced would not affect the argument, as the energy difference under standard conditions would be small compared to the energy changes involved.

organic products could result. Should an excess of oxygen be available under conditions of normal or low pressure, combustion of levoglucosan would be likely, and even were dehydration to occur in the vapor phase, dehydrated products might be oxidized before there was any chance of deposition of char. It may be concluded that, depending on the conditions, various reaction-paths may be followed in the degradation of levoglucosan[6-8,19]. Furthermore, catalysts may alter these reactions, either in or out of the original matrix.

The activation energy of carbonization of untreated cellulose is higher than that of treated samples. It has been suggested that the action of flame retardants involves a process of catalytic dehydration[2,3]. Whatever the mechanism of pyrolysis, it is important that, within the scope of the thermochemistry discussed here, flame retardants may change not only the extent but also the kind of reactions involved. Thus, whereas at the higher temperatures, free radicals may be formed by endothermic bond-scissions and dehydration, at lower temperatures, free radicals may mainly be generated by the process of dehydration[20]. The presence of flame retardants may consolidate the char by encouraging radical–radical reactions leading to the formation of C–C bonds.

It is possible that, prior to pyrolysis, flame retardants encourage the loss of free and absorbed water present in the accessible regions, and that part of the "water of constitution" (functional groups) is lost by ether formation or salt formation. Thus, by salt formation, 30 percent of the water-forming moiety may have been lost, provided that the flame retardant reacts with all of the hydroxyl groups. In reality, this may actually occur in the accessible regions.

On pyrolysis, the salts of cellulose may further disproportionate, with loss of water. In this way, a "blanket" of char (mixed with flame-retardant residue) would be provided for the compact, non-accessible, crystalline portion of the cellulose. This blanket of char and flame-retardant might further catalyze dehydration at relatively low temperatures. In addition, or alternatively, it might inhibit volatilization.

As water is lost at relatively low temperatures, and the concentration of free water is low, the side reactions are minimized; this allows a better chance for a thermodynamically favored dehydration process. No wonder that it has been suggested that small proportions of soluble salts may have accelerated the terrestrial formation of coal from wood long before high pressures and temperatures compacted it[21].

ACKNOWLEDGMENT

The author appreciates useful discussion with, and a review of the paper by, Mr. Jett C. Arthur, Jr., Southern Regional Research Center, USDA, New Orleans, Louisiana.

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