Reports

Effect of Fire-Extinguishing Agents on Combustion of Sucrose

Abstract. Although sucrose and cellulose are both carbohydrates of basically similar composition, the very materials which have been found to be most effective in preventing flaming combustion of cellulose are also effective in causing sugar cubes to support flame.

A common parlor trick, on the outcome of which many a free drink has been won, involves the ignition of a cube of table sugar. As many a loser of such a bet has discovered, a normally nonflammable sugar cube can readily be ignited by a match if it is just dipped into a little cigarette ash. This phenomenon was reported in the technical literature as far back as 1919 (*1*), and the mechanism of action of the cigarette ash, as well as the nature of its responsible components, has been the subject of speculation at intervals ever since.

The treatment of combustible materials to reduce their vulnerability to fire dates back to more than 400 years B.C. (*2*). Perhaps the first systematic investigation of the fireproofing of cellulosic material was conducted by Gay-Lussac (*3*) at the request of Louis XVIII of France. Since then, many empirical investigations have been undertaken, each using large numbers of chemicals, in a search for effective fire-fighting agents (*4*) or materials which may be used to impregnate wood (*5*) or fabrics (*6*) to increase their fire resistance.

The mechanism of action of fire-extinguishing agents has frequently been related to the well-known fire triangle (heat, fuel, oxygen). Thus fire may be

extinguished by cooling (for example, with water), or by isolating the fuel from oxygen (for example, by interposing a CO_2 blanket or by coating the fuel with a noncombustible, impervious layer). More recently, the effectiveness of some fire-extinguishing agents has been attributed to the breaking of the chain reactions occurring in the flame (*7*).

One other method by which chemicals may exert an effect on the combustion of solid fuels is by somehow altering the decomposition reactions (or rates of reaction) occurring in the solid. For such purposes, it is necessary to draw a distinction between flame-retardant effects and other decomposition effects, for example, glow retardance. Thus, the most highly recommended dry chemical for extinguishing fires (*8*), potassium bicarbonate, actually lowers the decomposition temperature of cellulose (*9*).

That good flame retardants may actually have a negative glow-retardant effect is illustrated in Fig. 1. For this demonstration, about 0.2 ml of 0.1*M* $KHCO_3$ solution was used to moisten a line down the side of a cellulose-extraction thimble, and the upper part of the thimble was ignited. The flames were then blown out, leaving a red glow around the entire periphery of the thimble, and the reaction was permitted to continue until no further smoke was observed. As may be seen, the glow in the untreated cellulose died out almost immediately, while the smoldering reaction continued down the entire length of the strip treated with $KHCO_3$. It appears that the roles of such salts as both flame-retarding and smoldering agents are expressions of the same reaction mechanism (*10*); this mechanism is generally accepted as a catalytic degradation of the cellulose molecule which produces large increases in the resulting char/tar ratio (*11*).

Since sucrose and cellulose are carbohydrates of basically similar composition, the catalytic action of salts which influence the oxidation of both materials should be similar. It was consequently quite surprising (to me, at least) to find that most of the reagents which have been found to have good

flame-retardant properties when applied to cellulosic materials are just the reagents which cause a sugar cube to support a flame.

To test the flame-supporting effectiveness of treated sugar cubes, each cube was dipped into the particular reagent so that 1 to 2 mg of reagent adhered to the cube. An attempt was then made to ignite the treated end of the cube with a match or a bunsen burner flame (identical results are obtained with both ignition procedures). Among the materials which had little or no effect on the combustibility of the sugar were the following: charcoal, sodium chloride, calcium carbonate, calcium oxide (dry), and sodium calcium borate (dry). On the other hand, flaming ignition of the sugar cube resulted after treatment with materials such as the following: calcium oxide (slurry), calcium hydroxide (dry), sodium calcium borate (slurry), potassium bicarbonate, sodium phosphate, monoammonium phosphate, ammonium chloride, ammonium bromide, sodium silicate, sodium tetraborate, carbon tetrachloride, and methylene chlorobromide.

These results do not, of course, establish the mechanism of action of these reagents. It is felt that the negative results listed in the paragraph above show rather conclusively that the flame-supporting effect on sugar is chemical, rather than physical, in nature (thus, charcoal should be quite effective if the result were due to an increase in absorption of radiant energy). The effectiveness of the various chemical extinguish-
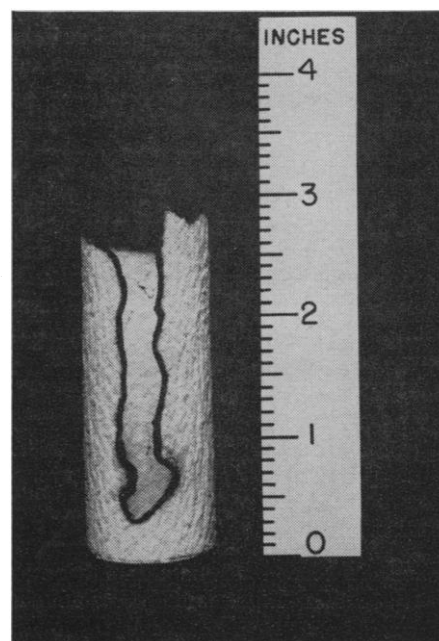

Fig. 1. Photograph of extraction thimble showing the result of glowing combustion down the line treated with potassium bicarbonate solution.

ing agents in fire fighting has been repeatedly demonstrated through the years and is beyond question. However, the exact nature of the chemical effect on the degradation of the solid (cellulose or sucrose) or on the reactions in the flame can remain the source of profitable speculation for some time to come.

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References and Notes

1. C. Thomae, Chem. Z. 43, 747 (1919).
2. References to the earliest recorded work on fireproofing may be found in J. E. Ramsbottom, The Fireproofing of Fabrics (H.M.S.O., London, 1947), and Rolf Schlegel, Untersuchungen ueber die Grundlagen des Feuerschutzes von Holz (Verlag Chemie, Berlin, 1934).
3. J. L. Gay-Lussac, Ann. chim. phys. 18, 211 (1821).
4. See, for exam → C. A. Thomas and C. A. Hochwalt, Ind. Eng. Chem. 20, 575 (1928); → H. D. Tyner, ibid. 33, 60 (1941).
5. G. M. Hunt, T. R. Truax, C. A. Harrison, Proc. Am. Wood-Preservers' Assoc. 28, 71 (1932).
6. R. W. Little, Ed., Flameproofing Textile Fabrics (Reinhold, New York, 1948).
7. A. B. Guise, Natl. Fire Protect. Assoc. Quart. 53, 330 (1960).
8. R. L. Tuve, ibid. 54, 158 (1960).
9. J. Taylor and F. Pollok, Fuel 28, 77 (1949).
10. J. E. Dolan, Chem. and Ind. (London) 1952, 368 (1952).
11. See, for exam → K. Tamaru, Bull. Chem. Soc. Japan 24, 164 (1951); R. C. Laible, Am. Dyestuff Reptr. 47, 173 (1958).

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Isotopic Variations in Meteoric Waters

Abstract. The relationship between deuterium and oxygen-18 concentrations in natural meteoric waters from many parts of the world has been determined with a mass spectrometer. The isotopic enrichments, relative to ocean water, display a linear correlation over the entire range for waters which have not undergone excessive evaporation.

Epstein and Mayeda (1) and Friedman (2) reported precise data for O^{18}/O^{16} and D/H ratios in nine nonmarine meteoric waters and found a rough linear correlation between the isotopic enrichments. In the course of research on isotopic variations in volcanic waters, I have analyzed mass spectrometrically some 400 samples of water from rivers, lakes, and precipitation in order to establish the exact nature of the isotopic relationship in meteoric waters. Gas samples were prepared by the standard CO_2-H_2O equilibration technique (1) and by reduction of H_2O to H_2 with uranium metal and analyzed on the McKinney-Nier type spectrometers used by the authors mentioned above as well as in my present laboratory.
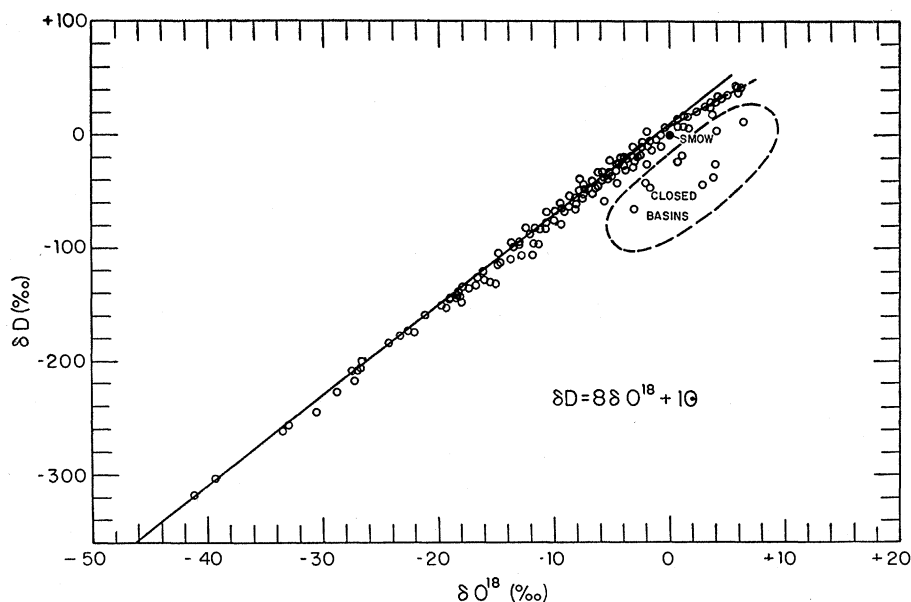

Fig. 1. Deuterium and oxygen-18 variations in rivers, lakes, rain, and snow, expressed as per millage enrichments relative to "standard mean ocean water" (SMOW). Points which fit the dashed line at upper end of the curve are rivers and lakes from East Africa.

The isotopic data for all samples analyzed for both isotopes (excluding detailed sets of data from Chicago and Steamboat Springs, Nev.) are shown in Fig. 1. About 40 percent of the samples are from North America, the rest being distributed all over the world. The data shown are per mil enrichments of the isotopic ratios D/H and O^{18}/O^{16} relative to a mean ocean water standard, that is,

$$\delta = [(R/R^\dagger) - 1]\,1000$$

where R is either isotopic ratio and $R^\dagger$ is the ratio in "standard mean ocean water" (SMOW) defined relative to the National Bureau of Standards isotopic water standard as described in a following report (3). The precision of the data is ±0.5 per mil, or ± 1 percent of δ, for D, and ± 0.1 per mil, or ± 0.5 percent of δ, for O^{18}, the larger error applying in each case and representing ±2 standard deviations.

The straight line in Fig. 1 represents the relationship

$$\delta D = 8\,\delta O^{18} + 10$$

(both δ values in per millage) and is seen to be an adequate fit to the data, except for waters from closed basins in which evaporation is a dominant factor governing the isotopic relationship. The samples which fit the dashed line at the high enrichment end of the curve represent rivers and lakes in East Africa. They fit a line with a slope of about 5, in contrast to the slope of 8 found for most of the data. Studies of evaporation in the laboratory, and in areas where seasonal data have been obtained, show that in free evaporation at ordinary temperatures the heavy isotope enrichment ratio $\delta D/\delta O^{18}$ consistently follows a slope of about 5 as observed in East African waters. Many of the points falling to the right of the line plotted in Fig. 1 have a similar slope of 5 when connected to points on the line which represent direct precipitation in the same area.

It can be shown (4) that for small enrichments the slopes in Fig. 1 are the ratios of the single-stage enrichments when the isotopic concentrations are governed by vaporization or precipitation under Rayleigh conditions at constant temperature. The isotopic vapor pressure data show that slopes of 8 and 5 correspond to Rayleigh processes at liquid-vapor equilibrium at temperatures of about −10°C and +100°C respectively. It seems, therefore, that atmospheric precipitation follows a Rayleigh process at liquid-vapor equilibrium, as first proposed by Kirshenbaum (5), but that the process of free evaporation at room temperature is governed by kinetic factors. The present studies have shown that this is so up to the boiling point, and that the disequilibrium occurs principally in the O^{18}/O^{16} separation (4). Some of the variability along the line in Fig. 1 is certainly due to evaporation effects as well as to variations in temperature of precipitation.

All points in Fig. 1 for δD and δO^{18} lighter than −160 and −22 per mil, respectively, represent snow and ice from the Arctic and Antarctic, while tropical samples show very small depletions relative to ocean water. This distribution is expected for an atmospheric Rayleigh process as vapor is removed from poleward moving tropospheric air. However, it is actually log (1 + δ)