

Carbohydrate pyrolysis mechanisms from isotopic labeling Part 2. The pyrolysis of D-glucose: General disconnective analysis and the formation of C₁ and C₂ carbonyl compounds by electrocyclic fragmentation mechanisms

John B. Paine III*, Yezdi B. Pithawalla, John D. Naworal

Philip Morris USA Research Center, 4201 Commerce Road, Richmond, VA 23234, USA

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Abstract

The flash pyrolysis of D-glucose was investigated by the use of isotopic labeling with ¹³C, in conjunction with GC/MS. Co-pyrolysis of uniformly labeled and unlabeled D-glucose established the extent of unimolecular formation of each of the pyrolysis products. A complete set of singly labeled D-glucose isotopologs was used to determine the origin of specific carbons within each of the pyrolysis products. The Cyclic Grob 1,3-diol fragmentation and the tandem alkaline pinacol rearrangement/retro-aldol fragmentation (TAPRRAF) discovered from the pyrolysis of glycerin were applied to the analysis of pyrolytic fragmentation pathways for D-glucose. These mechanisms provide means of initial carbon–carbon bond breakage, and are consistent with the high proportion of carbon-unimolecularity observed for many of the volatile low-molecular weight products of the reaction. These and other reactions, including the retro-aldol fragmentation, carbonyl migration, dehydration, ene-reaction, retro-Claisen cleavage, hydrolysis, or alcoholysis were applied conceptually to the initial fragments resulting from either mechanism to ascertain the ultimate fate of the carbons of D-glucose. The “predicted” results were then compared with labeling patterns observed by experiment. The most promising rationalizations provided by this exercise are presented herein, for the formation of five C₁ and C₂ carbonyl-containing pyrolysis products: formaldehyde, formic acid, acetaldehyde, glycolaldehyde and acetic acid.

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1. Introduction

Carbohydrate pyrolysis is of central importance in the thermochemical conversion of biomass to sources of energy [1–3], the formation of flavors during the cooking of food [4], and in the formation of cigarette smoke constituents generated from carbohydrates in tobacco by the act of smoking [5,6]. Yet despite this importance, much of the detailed chemistry remains poorly understood, and the pathways of product formation of numerous pyrolysis products remain debatable [7]. For the first time, and to maximize the information available from the method, we have elected to probe carbohydrate pyrolysis chemistry by the flash pyrolysis of a *complete set* of

appropriately ¹³C-labeled D-glucose (**1**) (Fig. 1) samples. The resulting products were examined for identity, isotopic content and label location by means of gas chromatography/mass spectroscopy (GC/MS). This method allows a large number of products to be examined simultaneously using only a limited number of pyrolysis experiments. Flash pyrolysis is particularly appropriate for modeling the formation of tobacco smoke constituents, given the steep temperature gradients and short contact times inherent to a cigarette being puffed [8]. The use of labels was intended to determine the precise origin of the carbon atoms in the observed products from within the glucose molecule. Knowing this origin would simplify the determination of formation mechanisms. In particular, the use of labels was designed to probe the hypothesis that certain fragmentation mechanisms discovered in the course of glycerin pyrolysis [9] might have significant application to an understanding of carbohydrate pyrolysis in general.

* Corresponding author. Tel.: +1 804 335 2475.

E-mail address: John.B.Paine@pmusa.com (J.B. Paine III).

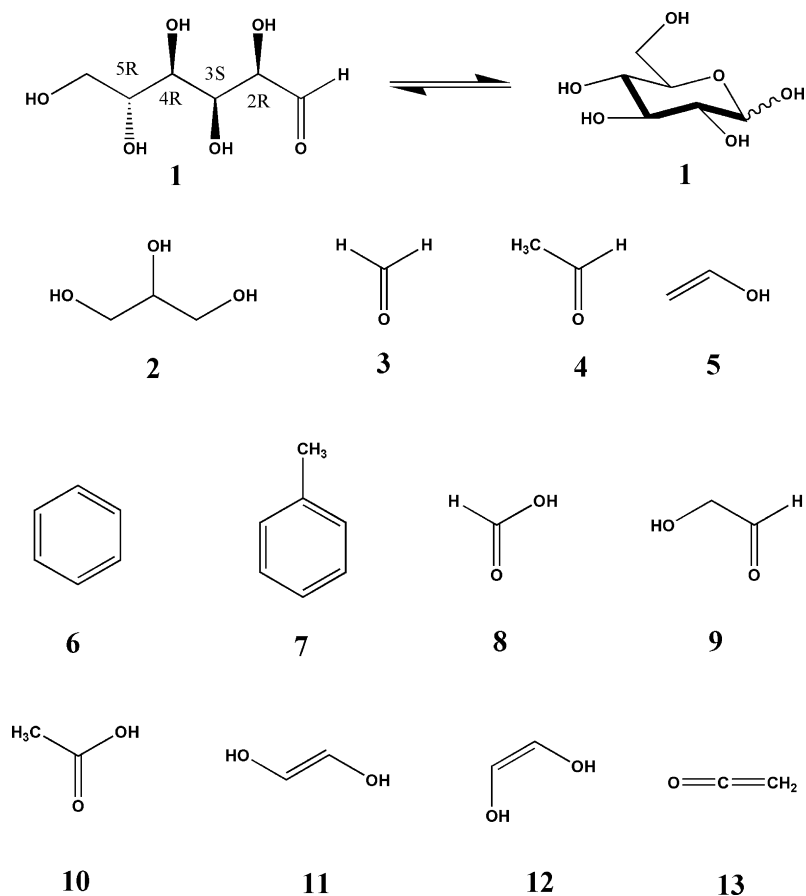


Fig. 1. D-Glucose (1), glycerin (2), and glucose pyrolysis products, including carbonyl-containing C₁ and C₂ products, and their precursors.

In the first paper in this series [9], isotopic labeling with ¹³C was applied to gain a clear picture of the detailed mechanisms (Scheme 1) by which glycerin (2) (Fig. 1) fragments by carbon–carbon bond breakage during pyrolysis. Glycerin had been chosen as a small-molecule model for the far more complex carbohydrate systems, which were to be further modeled by D-glucose (1). Glycerin was found to afford formaldehyde (3) and acetaldehyde (4) by at least two competing unimolecular pathways, differing in the orientation of acetaldehyde as contained within the glycerin precursor [9]. The two mechanisms, described in more detail below, were dubbed the “Cyclic Grob Fragmentation” [9,10], and the “Tandem Alkaline Pinacol Rearrangement/Retro Aldol Fragmentation” or “TAPRRAF” reaction (Scheme 1). Given that the two mechanisms (or mechanistic families) varied in proportion mostly between 1:3 and 3:1 ratios, depending upon the presence or nature of additives, the difference in energy barriers between the two competing mechanisms can only be on the order of several kcal/mol. The energetics of these processes have been calculated [11] and have been recently reported elsewhere [12], and fall near the range previously established by gas-phase kinetics [13]. Both mechanisms predicted that acetaldehyde would be initially produced in the form of its enol tautomer, ethenol (5), which has recently been reported for the first time as a constituent of flames [14,15]. Its invocation (along with other enols) into active participation in pyrolysis mechanisms is therefore justified.

Given the large number of 1,2,3-triol functionalities that exist among carbohydrates, and the circumstance that homologation exerts only a few kilocalories per mole of perturbation on a mechanism, it was clearly appropriate to extend these two mechanisms to an understanding of carbohydrate pyrolysis. This is the first in a series of papers that will focus on the pyrolysis of D-glucose (1). This paper will particularly focus on general considerations relating to the numerous modes of initial bond breakage provided by these mechanisms, and on the formation of C₁ and C₂ carbonyl-containing products. The C₃ and C₄ carbonyl-containing products will be discussed in Part 3 [16], and furans will be the subject of Part 4 [17]. These mechanisms provide low energy barrier means by which the carbon chain of carbohydrates initially breaks to form two carbon-containing fragments. Once the two fragments are formed, the increased restriction on degrees of freedom, relative to the precursor, makes further transformations more facile to unravel. We have examined conceptually the complete set of initial fragmentations, and followed these initial products to “predict” how they might deliver labels to prospective ultimate products. These predictions usually matched the dominant labeling patterns that were observed, and the prospective pathways are presented here or will be presented in later papers in this series. Minor labeling patterns were less readily found by this process.

D-Glucose (1) is the prototypical monosaccharide, and at the initiation of this work, was the only monosaccharide for which

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