Hydrogenation of Fats and Oils. Isomerization During Hydrogenation

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Abstract

This presentation includes a survey of the development of the presently accepted theory for the formation of isomers based on a half hydrogenation-dehydrogenation mechanism with atomic hydrogen, an appraisal of the relevant work of recent years for its significance when applied to the problem of isomerization, and certain experimental evidence from other fields of heterogeneous catalysis of interest in the hydrogenation of fats and oils. Effects of temperature, pressure, catalyst concentration, and degree of agitation used in commercial plants on the degree of isomerization are discussed. In addition the conditions necessary for the proper application of the term “selective” to a hydrogenation are examined. An interpretation of recent work to reduce isomerization while retaining selectivity by extending the normal range of the variables and by the use of solvents is covered. Selected works on catalysis from related fields are used to indicate possible modifications of the isomerization mechanism and, perhaps, to reveal fruitful avenues of research.

Introduction

Hydrogenation is the oldest and most important of the commercial processes used in the chemical modification of fats and oils. Sabatier in France as early as 1897 and Normann in Britain in 1903 were responsible for the basic development of the process as it is known today. By 1911, the first commercial product containing hydrogenated fat was on the market in this country. Today, the importance of the process is difficult to overemphasize. Currently, in excess of three billion pounds of vegetable oils are hydrogenated annually. The process has contributed more than any other technique to the great increase in the diversity of use of various fats and oils.

Discussion

Essentially the process involves bringing together an unsaturated fat or oil, a nickel catalyst, and hydrogen under such conditions that the hydrogen combines with the oil. The product is usually a semi-solid, or plastic fat. The original purpose of this process was to permit the use of cheaper vegetable oils in the place of more expensive animal shortenings. The first commercial products were crude and, sometimes, unsatisfactory. They consisted of blends of a solid (completely hydrogenated) fat with a liquid (refined and bleached) oil. It was not unusual for the consumer of the early products to find that the two phases had separated into their original unblended state. There was some “consumer resistance.” Gradual improvements in the process and the products led to today’s all-hydrogenated shortenings and related products, that are not only accepted, but are preferred by many consumers.

Yet, even today, hydrogenation must be regarded as an enigma of the fat and oil industry. Fundamentally, it is not well understood. Certain problems, which have plagued the industry from the beginning, are growing in importance. Much can be done toward modifying and improving the hydrogenation of vegetable oils. An increasingly recognized problem is that these hydrogenated oils differ chemically from natural oils to a large extent. An excellent review of the changes in the nutritive value of fats and oils after hydrogenation is available (10). Hydrogenated oils contain glycerides that may consist partially of positional and geometric isomers of normal linoleic acid. Hydrogenated oils may contain large amounts of positional and geometric isomers of oleic acid, cis-9-octadecenoic acid. It is generally agreed that glycerides of these isomers of oleic acid are utilized by the animal body as readily as are those of oleic acid itself, provided the fat product in which they occur does not have too high a melting point. Further work may be needed to assess fully the importance of isomeric products in human diets.

While no solution to the problem of eliminating the formation of geometrical or positional isomers during hydrogenation will be presented, it is hoped that various sections of this discussion will be of value to those interested in this field. The objectives of this paper will be to survey the development of the presently accepted theory for the formation of isomers, to appraise some of the more relevant work of recent years for its significance, to stress the paucity of the means of solution with the present theory, and to engender interest in more fruitful avenues of research by reviewing certain work from other fields of heterogeneous catalysis.

Development of Theory

The historical evolution of present-day theory of...
the hydrogenation of fats and oils, while interesting, is not necessary for an understanding of the subject. An orderly development of the process will be sufficient and is all that is intended. This development will necessarily be brief and may be said to be oversimplified. References are included for those who desire more information. What is true of the development of the theory may, in all probability, be scored against the interpretation put on some of the results and the choice of articles from related fields of catalysis.

Though the preparation of the oil, gas, and catalyst may affect the formation of isomers during hydrogenation, the details of their proper preparation are beyond the scope of this presentation. These details have been described by Bailey (6), who gives a thorough discussion of all phases of the hydrogenation process as it was understood prior to 1951. His discussion is valid today. However, the customary variables of the hydrogenation process and the usual ranges of these variables in commercial practice are basic to a discussion of isomer formation. Temperature, catalyst concentration, pressure, and degree of agitation are the customary variables. Today, as for many years past, temperatures range from 150 to 200°C; catalyst concentrations from 0.01 to 0.50%; pressures from slightly above atmospheric to about 100 psi. At least enough agitation is prescribed to uniformly and intimately mix the oil, catalyst, and gas. Generally, this is all the agitation that is supplied. Temperature and catalyst concentration are the more important variables because pressure and degree of agitation are dictated by the design of the equipment and are not easily changed.

The effects of the four variables have always been determined by measuring the physical and chemical properties of the products. Hydrogenation is usually continued until the lowest iodine value (I.V.) suitable to the desired physical consistency, or plastic range, of the product is obtained. Melting and congeal points along with other physical tests are used to gauge the consistency of the fat. After a consideration of the melting points of the component fatty acids and their triglycerides together with the required physical consistency and mothing qualities of the products, it is obvious that the hydrogenation of a linoleic to an oleic acid instead of an oleic to a stearic is required to achieve the desired physical characteristics in the products. Thus, the concept of a “selective” hydrogenation as being one in which the polyunsaturated component is preferentially hydrogenated to a monounsaturated component became accepted. The original formulation of this definition of selectivity is attributed to Richardson (23). Moore et al. (21) showed early that linoleic acid is hydrogenated much more readily than the oleic. Such acids are now known as the geometrical and positional isomers of oleic acid and, because of better analytical techniques, are known to be formed in greater quantities than originally suspected. However, processors learned by a proper adjustment of the variables, principally temperature and catalyst concentration, to maintain a careful balance between selectivity and isomer formation, thus preparing highly acceptable products with a wide range of physical properties. Generally, high selectivity is desired; only when a greater plastic range is wanted will the processor deliberately hydrogenate non-selectively and then only when preparing an unblended product. In spite of the success achieved, there was, and is, a desire to have more definite control over the process, to have some means of improving selectivity at will without the concomitant increase in isomer formation.

The formation of isomers as it is understood today will be clearer if one considers what effect changes in the variables have on the concentration, or availability, of hydrogen on the catalyst surface. A highly significant result is obtained by such a consideration. This result may be summarized as follows: any change that tends to decrease the availability of hydrogen at the catalyst surface tends to increase the selectivity. A few examples may help clarify this statement. Consider the effect of an increase in temperature. Because an increase in temperature increases the rate of reaction, hydrogen on the surface of the catalyst is consumed more rapidly; if all other factors, including rate of supply of hydrogen to the surface, remain constant, then the availability of hydrogen on the catalyst surface will decrease and the reaction will be more selective. Similarly, if more catalyst is added to the reaction, all other factors being constant, the supply of hydrogen to the catalyst as a whole decreases and the reaction becomes more selective. Increasing the pressure or the degree of agitation obviously makes more hydrogen available to the catalyst surface and the process becomes less selective. Through this idea of hydrogen availability on the catalyst surface it is possible to be more specific in a description of “selective” conditions: a run is considered to be more selective only if there is a comparative shortage of hydrogen at the catalyst surface. It should be emphasized that these considerations of selectivity are general and apply only under the normal commercial conditions described earlier.

Finally, all of the previous knowledge was augmented and synthesized into a theory to account for both selectivity and isomer formation during the hydrogenation of a variety of vegetable oils. A number of investigations, (2,4,9,11,14,27,28) have been concerned with this further development of theory. The principle has also been expanded to cover conjugated systems of double bonds (3,5). The theory is based on a half hydrogenation-dehydrogenation of the double bond with atomic hydrogen. The theory postulates that hydrogen gas is chemisorbed in the form of atomic hydrogen in and on the nickel catalyst. With large excesses of hydrogen, some molecular hydrogen may be present on the surface. The oil or fat is also adsorbed on the catalyst surface. The reaction takes place on or near certain “active centers” on the nickel and is visualized as consisting of the addition of one hydrogen atom to one of the carbons of the double bond to form a free radical. This free radical may then either react with another hydrogen atom to complete the reaction, or lose a hydrogen atom to the catalyst to reform the double bond. Seliec-