Changes in Thermal and Optical Properties of Butteroil on Hydrogenation

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Abstract

The hydrogenation of butteroil was studied at varying conditions of temperature, hydrogen pressure and catalyst concentration. The calculation of reaction rates employing the first order rate equation yielded a single kinetic slope for hydrogenations performed at 60 psi (gauge), whereas a double slope was obtained at 15 psi (gauge). Near infrared spectral data of hydrogenated samples at 4600 cm^{-1} indicated good quantitative correlation with iodine values. Differential thermal analysis showed progressive disappearance of low-melting groups with concomitant appearance of high-melting groups as the hydrogenation time was progressively increased. Heats of melting, calculated from thermogram areas, showed a systematic increase as the amount of unsaturation was gradually reduced.

Introduction

The catalytic hydrogenation of oil and fat is now carried out industrially to modify the color, stability and plastic properties of naturally occurring lipids on a vast scale (1). Much of the work done reduces the unsaturation of vegetable oils to levels near those found in spreads and shortenings made from animal fats. In these operations reduction is seldom carried to the point where the iodine value (IV) of the product falls below 50.

Animal fats are rarely subjected to more than trace hydrogenation to achieve better shelf life and more desirable plastic properties. Therefore, when confronted with a request for samples of completely hydrogenated butteroil for test as an anti-blooming agent in chocolate candy manufacture (P. Keeney, personal communication, 1967), we found the literature sparse concerning procedures for the hydrogenation of butteroil. All available papers presented only trace hydrogenation studies (2,3).

This report describes the results of our studies of the catalytic hydrogenation of butteroil to near zero IV and some of the optical and thermal properties of the products so obtained.

Emphasis is placed on the quantitative aspects of the hydrogenation process as it was affected by changes in temperature, pressure and catalyst concentration. The numerical data obtained from IV and spectral determinations have been treated in a manner permitting the calculation of reaction rate constants. Additionally, use was made of qualitative and quantitative differential thermal analysis (DTA) to discern changes occurring in both melting characteristics and heats of melting of samples representing various levels of hydrogenation.

Experimental Procedures

Preparation of Butteroil

Fresh cream (obtained from mixed herd milk, Beltsville, Md.) was converted into butter. After heating the butter to 85 C, it was permitted to stratify before removing the aqueous layer. The butteroil was subsequently washed three times with hot water followed by the filtration of the oil through a glass-wool pad after each wash. Heating of the final filtered oil at 90 C under reduced pressure and with continuous nitrogen purging was performed to remove most of the residual water. The dried butteroil was stored at 4 C under a nitrogen atmosphere until used in the experimental work.

Hydrogenation Procedure

In all hydrogenation reactions a Raney nickel catalyst No. 28 obtained as a water slurry from the Raney Catalyst Co., Inc., Chattanooga, Tennessee, was used.

The butteroil-catalyst mixture was prepared for hydrogenation according to the following procedure: 22 g wet weight of catalyst was centrifuged at 2000 rpm for 15 min in an International centrifuge. The aqueous supernatant was decanted and the residue catalyst was transferred into a three-liter, three-necked distillation flask with 1 liter of melted butteroil. All of the remaining water in the mixture was removed by heating at 90 C and at 5 mm pressure (this required about 8 hr). The anhydrous mixture was stored at 10 C under a nitrogen atmosphere until used in subsequent hydrogenation work. For reaction runs requiring dilute catalyst concentrations, the above mixture was serially diluted with dry butteroil.

An exact measure of the amount of catalyst present in the above mixture was obtained gravimetrically as nickel oxide (NiO). A weighed aliquot of the catalyst-butteroil mixture was filtered through low ash filter paper. The filter paper with catalyst residue was placed into a weighed evaporating dish, ignited, and ashed for 16 hr at 600 C. Appropriate correction was made for the ash residue contributed by the filter paper.

The hydrogenation reactions were carried out on about 200 g of butteroil-catalyst mixtures. Reaction conditions examined included temperatures of 90, 105, 110 and 120 C, hydrogen pressures of 15 and 60 psig, and catalyst concentrations of 0.1% and 1%. All of the hydrogenations were conducted in the Parr Pressure Reaction Apparatus. Aliquot samples of about 20 g were removed during the hydrogenation sequence for analysis. The catalyst was removed from

TABLE I

Hydrogenation Conditions
Hydrogen Press., 60 Psig
Catalyst, 1% Raney Nickel

Time of hydrogenation min	Temperatures					
	120 C		105 C		90 C	
	IV	OD	IV	OD	IV	OD
0	34.8	.210	30.1	.182	34.8	.180
5	27.4	.165	26.8	.165	31.2	.170
10	17.4	.155	24.0	.155	29.1	.165
15	11.9	.130	21.2	.145	26.9	.160
25	4.2	.115	15.9	.115	23.2	.150
45	1.2	......	9.1	.092	15.7	.140
60			5.2	.080	12.0	.130
75			2.9	......	8.8	......

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[1] ARS, USDA.

TABLE II

Hydrogenation Conditions

Time of hydrogenation, min	Hydrogen press., 15 psig Temperature, 120 C Catalyst, 1% RN		Hydrogen press., 60 psig Temperature, 110 C Catalyst, 0.1% RN	
	IV	OD	IV	OD
0	34.8	.115	34.8	.182
10	27.8	.110		
15	24.7	.095	33.5	.175
25	20.9	.080		
35	15.0	.050		
45	8.7	.030	31.8	.165
55	4.2	.015		
65	2.0	.010		
75	1.8	.005		
90	1.7	......	29.4	.150
180			25.0	.135
300			18.2	....

the hydrogenated samples by filtration through Reeve Angel No. 812 fluted filter paper inserted in a heated funnel.

Methods of Analysis

The iodine absorption number was determined on all samples by the Hanus method of titration with sodium thiosulfate to a starch indicator end point (4).

Spectral examination of the hydrogenated samples was performed in the near and far infrared regions, as well as in the visible and ultraviolet regions. Only spectral data in the near infrared region at 4600 cm^{-1} could be quantitatively correlated with extent of hydrogenation; consequently, only this mode of spectrophotometric analysis was used in subsequent hydrogenation work. Instrumentation used to obtain the near infrared spectral data was the Perkin-Elmer 350 Double Beam Spectrophotometer. Quartz cuvettes with a 1 cm light path were used for sample and reference materials. All optical measurements were made at 60 C employing the most hydrogenated sample of the series as a reference material. In a search for other reference materials, Nujol was examined but was found inadequate. For studies in the near infrared and visible portions of the spectrum no dilution of the samples was necessary. For studies in ultraviolet and far infrared regions, the samples were diluted with solvents such as hexane or carbon tetrachloride.

TABLE III

Specific Reaction Rates of Hydrogenation of Butteroil

Temperature, C	Hydrogen pressure, psig	Catalyst, Raney nickel, %	Reaction rate k (sec^{-1})	
			OD data	IV data
90	60	1	2.74×10^{-4}	2.96×10^{-4}
105	60	1	5.0×10^{-4}	5.26×10^{-4}
120	60	1	1.34×10^{-3}	1.25×10^{-3}
110	60	0.1	2.68×10^{-5}	3.06×10^{-5}
120	15	1	1.12×10^{-3}	1.03×10^{-3}
			3.39×10^{-4}	3.51×10^{-4}

The thermal analysis determinations, performed on samples hydrogenated at 120 C, 60 psig and 1% catalyst, were made with a Du Pont differential thermal analyzer employing a plug-in calorimeter module according to the method previously reported (5). All samples analyzed by this technique were conditioned at 70 C for 30 min prior to their tempering at 20 C for about 70 hr. From their tempering temperature, the samples were program cooled at 5 C/min to −90 C. Their thermograms were recorded using a programmed heating rate of 5 C/min and a ΔT sensitivity of 0.2 C/in.

Results and Discussion

The numerical data obtained from the hydrogenation work are presented in Tables I and II. Both iodine values and optical density values are given here in tabular form. As indicated earlier, the optical density values at 4600 cm^{-1} were concentration dependent and correlatable with iodine absorption numbers. A plot of iodine values versus optical density yielded a straight line which illustrated this concentration dependence.

An analysis of the experimental results assembled in Table I and part of Table II showed the hydrogenation of butteroil at 60 psig to be kinetically of the first order type. The reaction rate constants could be calculated for any time, t, from the following integrated form of the first order rate equation.

$$k = \frac{1}{t} \ln \frac{a}{a-x}$$

Instead of calculating individual k values at each time interval, a graphical method covering the whole reaction period was used. For this purpose, a rearranged version of the above equation was used.

$$t = \frac{\ln a}{k} - \frac{\ln (a-x)}{k} \quad (7)$$

The first term of the equation, a constant, can be eliminated and a plot of t against ln (a–x) should be linear in first order reactions with the slope of the straight line equal to −1/k. All of the hydrogenation reactions performed at 60 psig yielded data

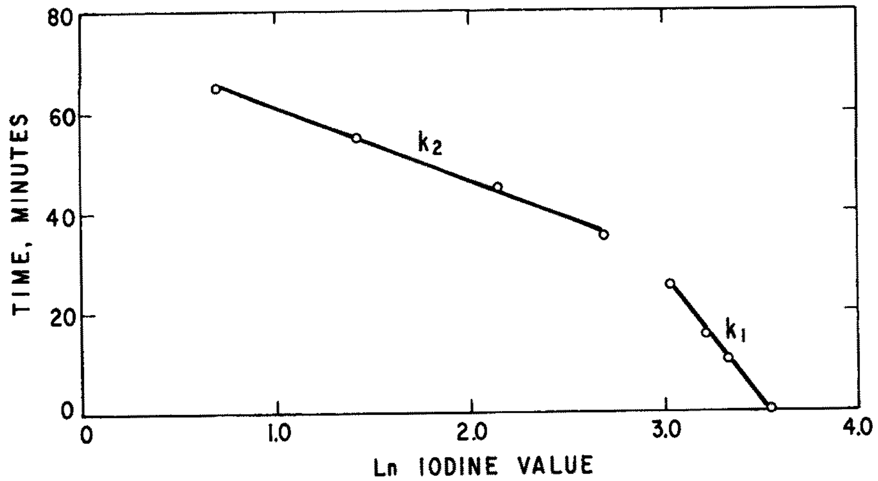

FIG. 1. Kinetic plot of butteroil hydrogenated at 15 psig.

that fit the above equation well and from which kinetic rate constants were calculated. The rate constants thus calculated are given in Table III. At hydrogenation pressures of 15 psig, however, a somewhat unexpected result was obtained when a plot of t against ln (a–x) was established. This is shown in Figure 1. Instead of a single slope similar to those obtained with the 60 psig data, there emerged what appeared to be two distinct slopes, indicating at least two different reaction rates. This possibly suggests a preferential or selective hydrogenation phenomenon not manifest at the higher pressure. An identical kinetic plot was obtained employing optical density values with good agreement in their reaction rate constants as shown in Table III.

Since optical density data were shown to be linearly related to iodine values, it was possible to employ these data in the calculation of reaction rate constants. These rate constants are shown in Table III and agree favorably with those obtained from iodine values. A previously defined kinetic equation was modified to yield the following form for optical density data:

$$k = \frac{1}{t} \ln \frac{E_o - E_{oo}}{E_t - E_{oo}}$$

The terms E_o and E_t correspond to the optical densities at 0 and t time respectively, whereas, E_{oo} is the optical density at 0 iodine value obtained by extrapolation from a plot of iodine value versus optical density. By using the graphical method with the above equation and plotting values of ln $E_o - E_{oo}/E_t - E_{oo}$ against corresponding values of t, the slope of a straight line corresponding to the reaction rate was obtained. The complete listing of reaction rate constants calculated from optical density data is given in Table III.

An examination of the reaction rate constants at 90, 105 and 120 C for hydrogenations performed at 60 psig and 1% catalyst showed them to satisfy the Arrhenius equation for obtaining the energy of activation. A plot of log k against the reciprocal of the absolute temperature, 1/T, gave a linear slope which is equal to $-E/2.303\,R$ and from which the energy of activation could be calculated. The energy of activation for the hydrogenation of butteroil at these conditions was 14.3 kcal.

A significant feature of the DTA profile of fats and oils is that the area under the curve is closely related to the solid content of the material. Any changes altering the original composition will produce concomitant changes in the profile. In a process such as the hydrogenation of butteroil, important changes should occur in the DTA profile reflecting composition changes resulting from the progressive reduction of unsaturation sites. Since the preponderance of the unsaturation resides in the low-melting portion of the fat, the most significant alterations would be expected to occur in the low temperature regions of the profile. That such an effect, i.e., a reduction in solid content at low temperatures with consequent increases in hydrogenation time, does take place is illustrated in Figures 2 and 3. Figure 2, sample A, which had been reduced by about 7 IV units, still retains the characteristic larger low melting peak of the original fat with a minimum at 18 C. As the butteroil samples are progressively hydrogenated, the low melting portion gradually diminishes as reflected in the DTA profiles B, C and D. Finally, when the butteroil has been reduced to an IV of 1.2, only a slight lower melting shoulder remains in

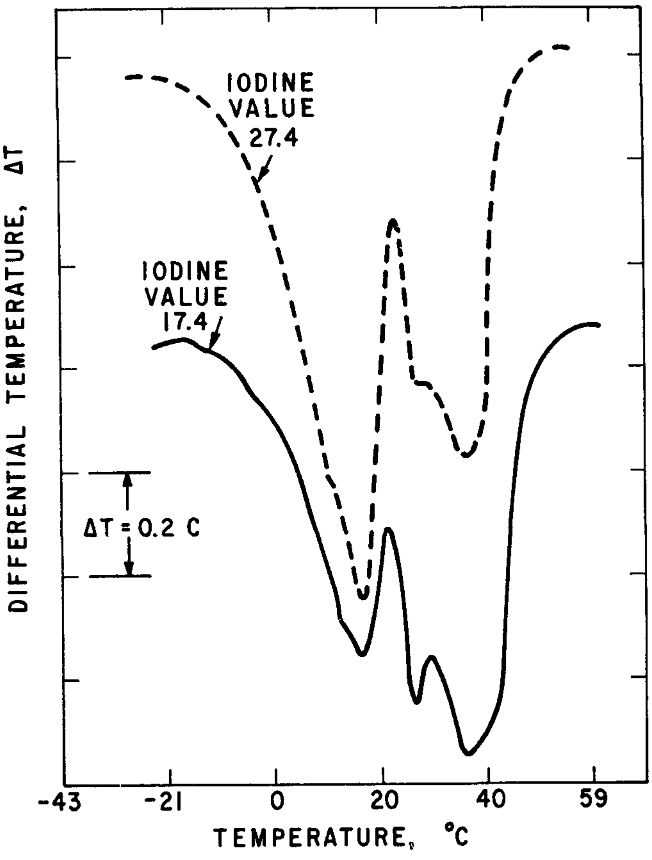

FIG. 2. DTA profiles of hydrogenated butteroil: IV 27.4 (Sample A); IV 17.4 (Sample B).

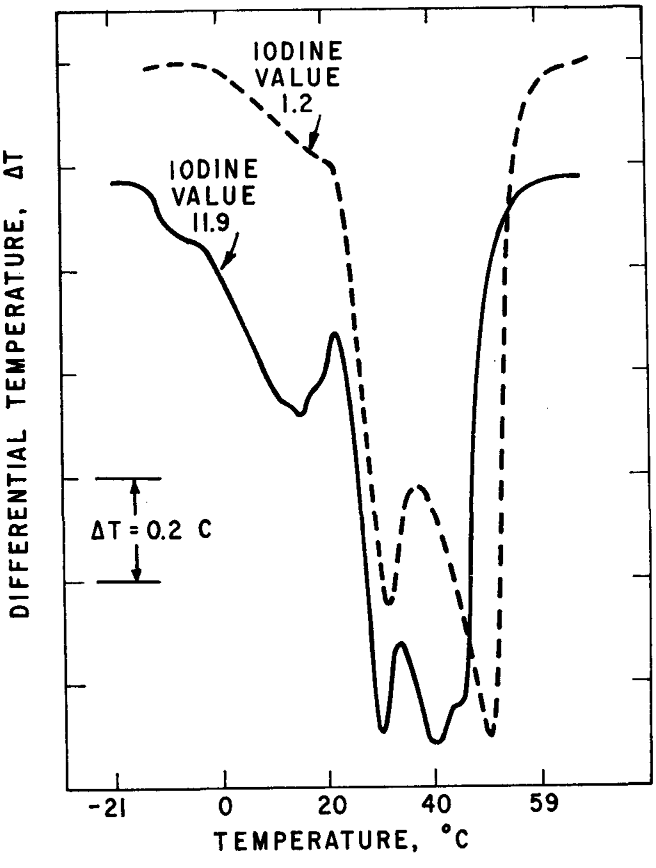

FIG. 3. DTA profiles of hydrogenated butteroil: IV 11.9 (Sample C); IV 1.2 (Sample D).

TABLE IV

Heats of Melting of Hydrogenated Butteroil[a]

IV[b]	Sample wt, mg	Heating rate, C/min	Heat of melting, cal/g
34.8	11.51	5	21.7
27.4	11.24	5	24.7
17.4	9.28	5	27.1
11.9	10.14	5	29.6
4.2	9.40	5	32.4
1.2	8.99	5	33.9

[a] All samples were tempered at 20 C for about 70 hr; samples cooled to −90 C at 5C/min.

[b] Samples hydrogenated at 120 C; 60 psig; 1% RN.

the DTA profile, indicating an almost total disappearance of the original low melting fraction.

A quantitative treatment of the DTA calorimetric profiles, with subsequent calculation of the heats of melting, was made on select hydrogenated samples. Results from these calculations are given in Table IV. A graphical representation of iodine value versus heat of melting yielded a linear plot indicating a good quantitative relationship that might be used analytically in future hydrogenation studies.

The catalyst concentrations used in the studies reported here would, in standard hydrogenation procedures, be regarded as somewhat high. This was realized at the outset of the work, but lower concentrations were generally avoided in the interest of rapid hydrogenation and lower temperatures. Higher than usual hydrogenation pressures were employed, but these were also used for the previously mentioned reasons.

Spectral examination of the samples was performed to determine if a quantitative relationship could be established that might be used in subsequent studies. That a quantitative relationship exists between near infrared data and iodine value has been aptly shown. However, in future studies aimed at employing near infrared data for sample analysis, it would be necessary to establish an adequate calibration plot. A satisfactory calibration plot would have to be obtained using a reference common to all hydrogenated samples. Such a reference standard might be a fully hydrogenated butteroil sample.

A very significant finding of the hydrogenation study was the appearance of a double kinetic slope for the butteroil hydrogenation at 15 psig. The double slope strongly suggests different unsaturated triglyceride groups responding differently to the absorption of hydrogen. If this different propensity towards reaction could be controlled by the hydrogen pressure, then possibly a true selective trace hydrogenation process could be developed. A highly controlled trace hydrogenation process might be expected to deactivate those sites most susceptible to oxygenation and consequently produce a butteroil with a significantly improved flavor stability.

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