Hydrogenation of Linolenate. XI. Nuclear Magnetic Resonance Investigation[1]

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Abstract

Nuclear magnetic resonance (NMR) spectra have been obtained during the hydrogenation of methyl linolenate with platinum, nickel and sulfur-poisoned-nickel catalysts and during the reduction of linolenic acid with hydrazine. Structural changes have been studied by "proton counting" techniques and include those for the total unsaturation (olefinic protons), 15,16-double bond (β-olefinic methyl protons), 1,4-pentadienes (di-α-olefinic methylene protons) and allylic methylene (α-olefinic methylene protons).

The number of olefinic protons is inversely related to the degree of saturation as determined by iodine value, GLC and hydrogen absorption. Amounts of double bonds in the 15,16-position and in the 1,4-pentadiene structures decrease linearly with increasing saturation, but the slopes of lines differ for specific catalysts. Sulfur-poisoned nickel has the most negative slope, followed by electrolytic nickel, and then platinum and hydrazine. Amounts of α-olefinic structures with increasing saturation are roughly constant for hydrazine and platinum during reduction with the first mole of hydrogen; they fall to zero at complete saturation. For the two nickel catalysts, the α-olefinic structures increase during absorption of the first mole and a half of hydrogen before dropping to zero. The possibility of substituting NMR measurements for iodine value, alkali-isomerization spectrophotometric determination and other structural analyses is discussed.

Introduction

THE PUBLISHED QUANTITATIVE analytical applications of high-resolution NMR spectroscopy to fats are contained in a paper by Johnson and Shoolery (4) who determined average mol wt and unsaturation of natural fats. More recently Glass and Dutton (3) described a procedure for determining 15,16-unsaturated C_{18} esters based on prior assignment of peaks by Storey (9). Other NMR analyses, potentially available but as yet untried, for structural analysis of hydrogenated fats include allylic methylenes and 1,4-pentadienes groups. Now NMR spectra have been obtained during the course of reduction of linolenate with platinum, nickel and sulfur-poisoned-nickel catalysts, and with hydrazine. The kinetic data resulting are interpreted in the light of previously established characteristics for metal catalysts and hydrazine.

Experimental

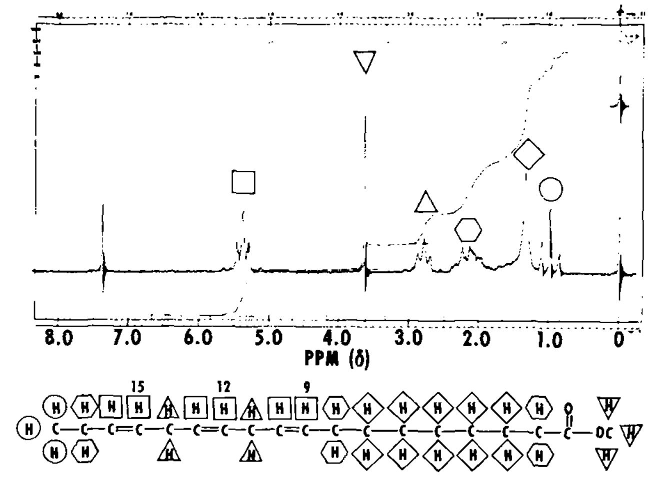
Procedures of hydrogenation, manometric manipulation and GLC are specifically described in reference 5 and of hydrazine reduction, in references 7 and 8. One-g samples of methyl linolenate (Hormel) were hydrogenated with a) 5% platinum-on-carbon, b) electrolytic nickel, and c) sulfur-poisoned-nickel catalysts. Hydrogenations with nickel catalysts were maintained at 140C, and the platinum was kept at 50C. The reaction mixture for each catalyst was sampled at approx 0.5-mole intervals of hydrogen uptake by inserting a syringe needle through a serum cap and withdrawing approx a 0.22-ml sample for GLC and NMR. Corrections in hydrogen uptake were made for the wt of withdrawn samples. Linolenic acid (3.7 g) was reduced with hydrazine at 50C (7,8); NMR and GLC samples were withdrawn at various time intervals of 0.25, 0.5, 1, 2, 4, 6.3, 12.5 and 15.5 hr. Samples were acidified with hydrochloric acid, and fatty acids were recovered from the mixtures by ether extraction. GLC analysis of the fatty acids was obtained on a 4-ft by ¼-in. glass column packed with 10% diethylene glycol succinate plus 1% H_3PO_4 on Chromosorb W and operated at 190C. Argon gas flow (23 ml/min) and a radium D ionization detector were employed.

Samples for NMR analysis were dissolved in carbon tetrachloride (20% W/V) containing a trace of tetramethylsilane as an internal reference. Catalysts when present were settled out. Spectra were obtained at a frequency of 60 mc/sec with a Varian A-60 NMR spectrometer. The number of protons involved in each structural group was estimated from areas under the appropriate NMR curves as measured by the automatic integrator except for the β-olefinic methyl protons; their determination is the subject of a prior communication (3).

Results and Discussion

Figure 1, the NMR spectrum for methyl linolenate, also presents the peak assignments and proton counts associated with the various structures of this ester.

Experimental data obtained during the reductions are shown in Figures 2–5. In these the number of double bonds/mole ester, calculated from GLC data,



Symbol	Structure	PPM δ	No. Protons
○	β - Olefinic methyl protons	0.97	3
⬡	α - Olefinic methylene protons*	2.25	6
△	Di -α- olefinic methylene protons	2.80	4
□	Olefinic protons	ca 5.38	6
▽	Methoxy protons	3.67	3
◇	Insulated methylene protons	1.33	10
			32

*Also includes methylene adjacent to carbonyl

FIG. 1. NMR spectrum, peak assignments and proton counts for methyl linolenate. Tetramethylsilane peak at 0 δ and benzene at 7.4 δ.

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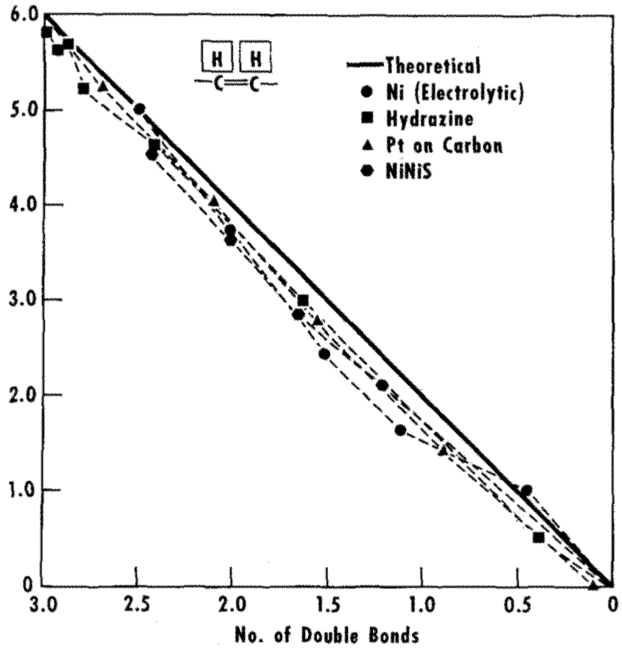

FIG. 2. Olefinic protons: NMR vs. GLC. Note, the solid symbols used to designate each catalyst have no relationship to similar open symbols in Figure 1.

is plotted on the abscissa and protons/mole of ester are plotted on the ordinate. A theoretical reduction, represented by a solid line in the figures, is that based upon hydrazine reduction (2,7). This reaction proceeds without isomerization and bond migration and is nearly nonselective with respect to attack on bonds at the 9-, 12- and 15-positions; e.g. hydrogenation rate constants are approx equal as shown in Figure 6.

Total unsaturation as determined by NMR (ordinate) and GLC (abscissa) is given in Figure 2. The number of olefinic protons is seen to be directly related to the degree of unsaturation as determined by GLC (correlation coefficient—0.992). Also, the number of olefinic protons is directly related to the degree of unsaturation as determined by hydrogen absorption (correlation coefficient—0.989). Statistical calculations indicate that the number of double bonds may be predicted from NMR data within a ±0.24 double bond unit if GLC measurements are used and within a ±0.30 unit if hydrogen absorption. Such a correlation was previously demonstrated by Johnson and Shoolery (4) with their more elaborate equipment that gave much higher precision.

β-Olefinic methyl protons as a function of degree of hydrogenation during the reductions are presented in Figure 3 (3). A solid straight line between 3 on the ordinate and O on the abscissa indicates the theoretical nonselective reduction of the 15,16-double bond, such as is approximated by hydrazine reduction (2,7). Reductions of linolenate with platinum catalyst and hydrazine most nearly approach this line; reductions with nickel catalyst closely follow. As previously shown by Scholfield and others (7) double bond migration and selectivity are negligible with hydrazine reduction and are less for platinum than for nickel (5, 6). Sulfur-poisoned nickel shows a much greater negative slope than the other three catalysts, thus indicating significant loss of 15,16-double bond. Selective reduction or, more likely, bond migration theories provide alternative explanations.

Di-α-olefinic methylene protons are represented by the "parabolic" curves in Figure 4. The calculation of nonselective reduction for hydrazine is represented by the solid line. Both hydrazine and platinum data approach this theoretical curve closely. The curves for nickel and sulfur-poisoned nickel fall off more sharply than those for platinum and hydrazine. Either selective reduction at the 12,13-double bond or a migration of double bonds to accomplish the same effect would seem to account for the steeper negative slope of nickel

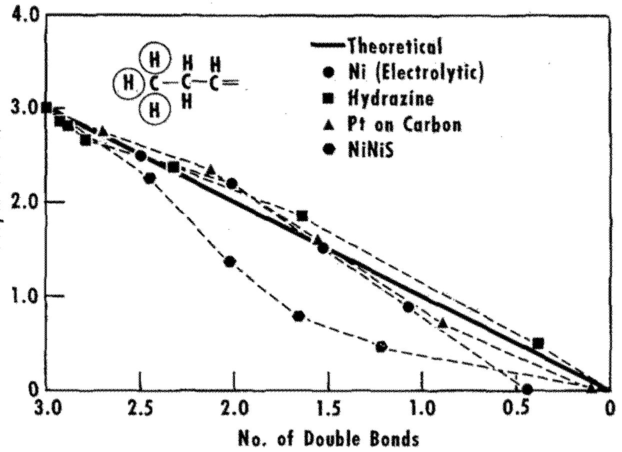

FIG. 3. β-Olefinic methyl protons as a function of catalyst and degree of hydrogenation.

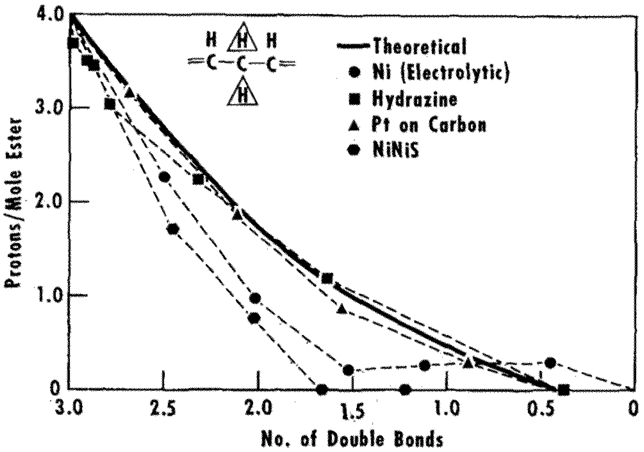

FIG. 4. Di-α-olefinic methylene protons as a function of catalyst and degree of hydrogenation.

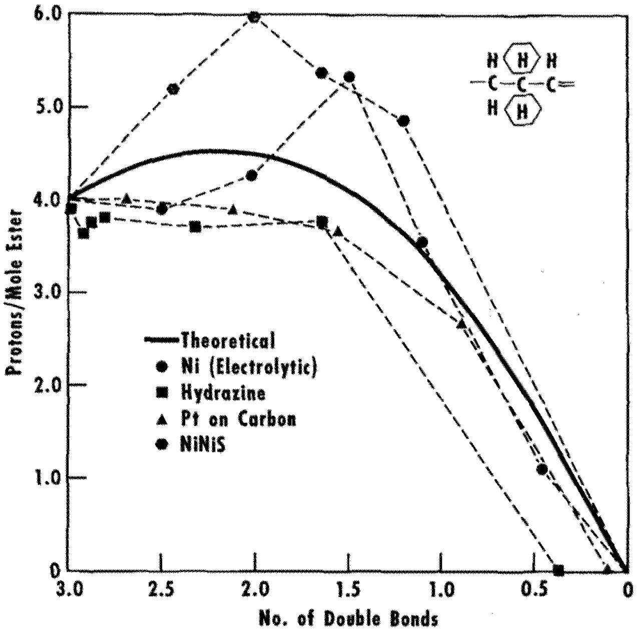

FIG. 5. α-Olefinic methylene protons as a function of catalyst and degree of hydrogenation.

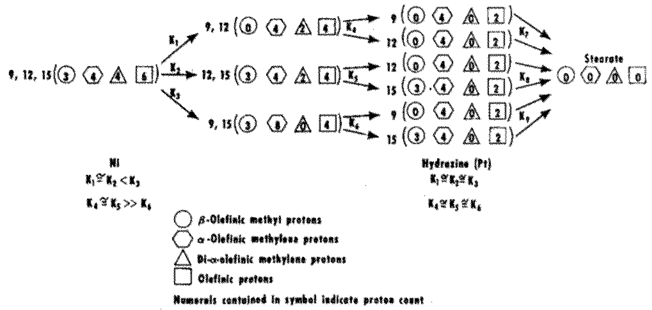

FIG. 6. Kinetic relations during reduction of linolenate and proton counts of intermediates.

and sulfur-poisoned nickel since these reactions reduce the number of di-α-olefinic methylene protons most rapidly.

α-Olefinic methylene protons as a function of hydrogenation is presented in Figure 5. In arriving at the proton counts for the α-olefinic methylene structures, corrections have been made for the methylene protons adjacent to the carbonyl group. These structures are roughly constant in amt for hydrazine and platinum during reduction with the first mole of hydrogen absorption; they fall off to zero at complete saturation.

The theoretical curve calculated for a nonselective hydrazine reduction (solid line) rises to a slight maximum due to the 9,15-diene isomer as statistically calculated. In Figures 1 and 6 the selective reduction of the 12,13-double bond yields 9,15-octadecadienoate with a proton count of 8 for the α-olefin structure compared to 4 for all the other isomers and isologs except stearate, which is 0. The discrepancy between the hydrazine data and the theoretical curve appears to be larger than experimental error and at present is unexplained.

Figure 5 also presents data for nickel and sulfur-poisoned nickel. Apparently the rise in proton count, approaching six, for these two catalysts at 1-mole hydrogen uptake is indicative of either a) the migration of bonds from the pentadiene structure or b) the selective hydrogenation of the 12,13-double bond and relative unreactivity of the resultant 9,15-isomer.

In support of the migration of bonds theory, we have shown previously (5,6) that platinum has low linolenate selectivity, low migration, and low *trans* isomerization characteristics for double bonds—nearly as low as that for hydrazine—whereas nickel has a much higher linolenate selectivity, greater bond migration and more *trans* isomerization. Linolenate selectivity, as previously defined, refers to the ratio of hydrogenation rate constants for linolenate and linoleate or the selectivity coefficient ($K = \frac{K_{Le}}{K_{Lo}}$) (2). Further, in unpublished work the sulfur-poisoned nickel showed high linolenate selectivity (3.0) and high *trans* (95%); in fact it had the highest selectivity ratio observed so far in this laboratory and the greatest activity in causing migration of bonds. These previously observed characteristics are in accord with observations made here of high α-olefinic methylene protons for the nickel, particularly for the sulfur-poisoned nickel catalyst.

To illustrate the effect of migration by one double bond in linolenate, Figure 7 was prepared. It shows the changes in proton count for β-olefinic methyls, α-olefinic methylenes, and di-α-olefinic methylenes for the resultant six isomers. For example, migration of the 15,16-double bond eliminates its corresponding signal. With no visible doublet between 1.45–1.88 ppm, probably no α-olefinic methyl protons are present and migration of double bonds to the 16,17-position must be small. With migration of the 9,10-, 12,13- or 15,16-double bonds the proton count for α-olefinic methylenes can range from 4–8 and di-α-olefinic methylenes from 0–2.

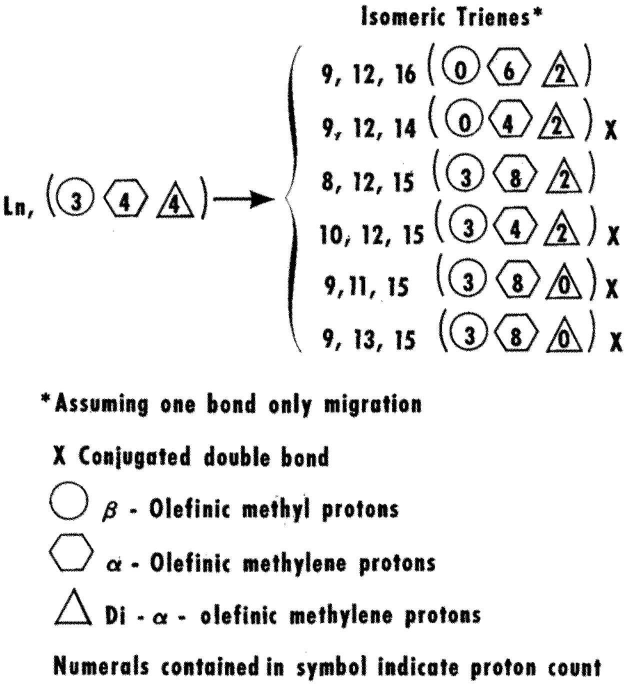

FIG. 7. Proton counts for linolenate isomers with one bond migration. (In addition, the 9,12,16-triene would show α-olefinic methyl protons.)

An alternative explanation to the bond migration hypothesis α for increase in α-olefinic methylene protons is the selective formation and low reduction rate of the 9,15-diene compared to the 9,12- and 12,15-isomers, hypothesis β. For hydrazine reduction, rates of formation of diene isomers k_1, k_2, k_3 are approx equal as are their reduction rates k_4, k_5, k_6 (8). For platinum and even more so for the nickel catalysts, the rate of formation of the 9,15- isomer (k_3) is greater than for the other two diene isomers; further, the rate of its reduction (k_6) is smaller than for the other isomers (k_4 and k_5) (1). Consequently, the 9,15-isomer accumulates in the reaction mixture for nickel catalysts and results in the observed increase of the α-olefinic methylene protons in the mixture.

It is tempting to postulate that hypotheis α, i.e., bond migration, explains the early rapid rise in α-olefinic methylene protons of Figure 5 for the sulfur-poisoned nickel catalyst and that hypothesis β, or selective formation and retarded reduction, explains the slower rise for the unpoisoned nickel catalyst.

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