The Kinetics of the Catalytic-Transfer Hydrogenation of Edible Oils

Sir:

The very first paper published in the *Journal of the American Oil Chemists' Society* in the year 2000 and thus, as some people maintain, in the new century and millennium, is entitled: "A Second-Order Model for Catalytic-Transfer Hydrogenation of Edible Oils" (1). This paper reinterprets experimental data published earlier by Naglič *et al.* (2) by suggesting second-order kinetics instead of the first-order kinetics proposed originally. Now I am all in favor of reinterpreting experimental data, but I have read and studied this particular paper with growing dismay. In addition to some confusing typographical errors, the authors fail to take the relevant literature into account, they do not provide arguments for their approach, and finally, their findings and conclusions make no sense chemically.

With regard to the typographical errors the statement that "Corn oil has negligible amounts of linoleic acid while olive oil contains none," can be converted into truth by changing "linoleic acid" to "linolenic acid." Similarly, it is easy to assume that the statement, "The edible oils contain triglycerols . . ." should refer to triglycerides, but what is meant by the statement, "The diene (linolenic acid) concentration was found to be inversely proportional to the triene (linoleic acid) concentration for the edible oils considered in this study," is far from clear since it implies that oils containing no linolenic acid (such as olive oil, see above) have an infinite linoleic acid content. Similarly, the sentence, "The at concentration of *P* in terms of *A* is given in Tables 1–5," is far from clear.

In their paper, the authors refer to a review article by Bailey (3) possibly because Naglič *et al.* (2) also refer to this article, but they do not refer to one of his earlier and more relevant articles (4) in which the concept of the "common fatty acid pool" has been tentatively suggested. However, and without saying this explicitly, the authors base their approach upon this concept, despite the fact that subsequent authors have shown it to be invalid (5). Similarly, the authors, while using a palladium catalyst, do not take into account that an oleate shunt (direct reduction of linoleate to stearate) has been reported (6) for the palladium-catalyzed hydrogenation of methyl linoleate; this shunt also seriously affects the hydrogenation kinetics.

When introducing their approach, the authors (1) list two hypothetical reactions. In the first reaction, the formate ion reacts with water and metallic palladium to form palladium hydride (PdH_2) and a carbonate ion, and in the second reaction this hydride saturates a double bond. Then they state that, "this reaction cannot be treated as a first-order reaction." However, given the fixed amount of palladium present, and assuming the reaction forming the palladium hydride to be fast and to be going to almost completion, would lead to a near constant concentration of this hydride, and thus to a rate of reaction that is just first order in fatty acids and zero order in formate. It will also be first order in palladium, but the concentration of this catalyst was not varied (2), so this dependency did not become apparent.

When deriving the second-order kinetics, the authors introduce two variables; α and β, which they define as k_2/k_1 and k_3/k_1, respectively, whereby k_1, k_2, and k_3 refer to the rates of reaction of linolenic, linoleic, and oleic acid, respectively. This strikes me as illogical since the olive oil studied (2) does not contain any linolenic acid. Nevertheless, the authors report in Table 6 (1) a rate constant k_1 (linolenic acid) for olive oil, but do not report a value for k_3 (oleic acid) for this oil. On the other hand, Table 6 does not list any statistical "Fit indicators" for linolenic acid, whereas it lists those values for the other oils studied by Naglič *et al.* (2); typing errors again?

After having arrived at a reasonable fit between the experimental data of Naglič, *et al.* (2) and their own, second-order model prediction, the authors proceed to study the rate of the hydrogenation reaction as a function of time. Without explaining how, the authors then arrive at Figure 5 (1).

The rates of reaction shown in this figure do not steadily and monotonously decrease with time, but show "oscillations," which the authors explain by stating that for olive oil, "the initial rate of hydrogenation of linoleic acid is faster than oleic acid hydrogenation. And, as the total rate of hydrogenation is the sum of linoleic and oleic acid hydrogenation, the rate of hydrogenation is observed to increase initially." However, the figure showing the fatty acid profiles during hydrogenation of olive oil (1,2) indicates that the rate of formation of stearic acid (the rate at which oleic acid is hydrogenated) equals the rate at which linoleic acid is hydrogenated and causes the oleic acid profile to be horizontal during the early stages of the hydrogenation reaction. The explanation given by the authors (1) is therefore incorrect.

Moreover, it is chemically impossible for the a rate of hydrogenation to increase in the course of a "dead end" batch process. It may increase during the early stages if the catalyst has to be activated, but subsequently it can only decrease monotonously as and when the reactivity of the reaction mixture continuously decreases. Possibly, the authors based their derivation of their rate of reaction on the individual measurements by Naglič *et al.* (2) and, like all measurements, these measure-

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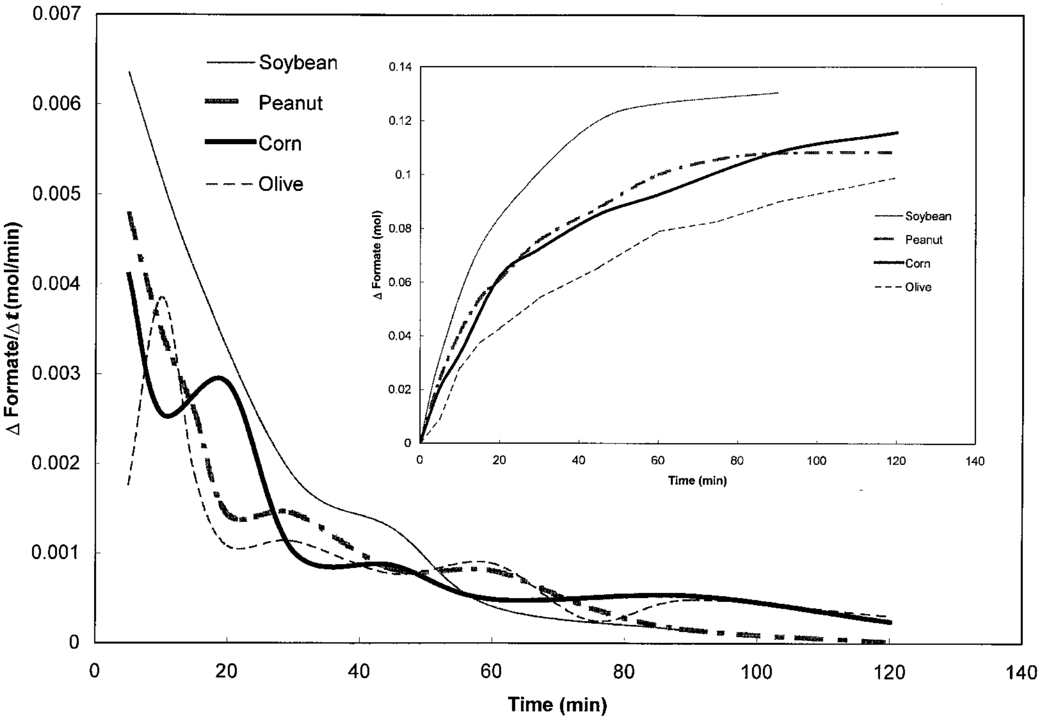

FIG. 5. Rate of formate ion consumption vs. time.

ments show analytical errors. In fact, the fatty acid profiles for olive oil (Fig. 1 in Ref. 2 and reproduced as Fig. 4 by the authors) show that the measurements at 5 min reaction time for stearic acid and oleic acid deviate quite strongly from the curve drawn through the experimental data. Similarly, the stearic acid contents at 20 and 45 min are below the curve whereas at 30 min the content is above the curve. Could this explain the maximum at 20 min, the dip at 30 min, and the peak at 45 min in the rate curve in the figure reproduced above?

Finally, frequency factors (*A*) and the activation energies (E_a) derived by the authors (1) merit some comment. Although they do not mention their data source, they probably obtained their data from a paper by Šmidovnik *et al.* (7) since these latter authors also used temperatures of 50, 65, and 80°C. As shown by Table 1, kinetic parameters arrived at by both sets of authors raise more questions than they answer.

In reaction kinetics, the frequency factor (*A*) indicates what fraction of the collisions between reagents having sufficient energy leads to a reaction. It is therefore governed by steric and directional requirements of the reaction. Since these requirements are fairly similar for linolenic, linoleic, and oleic acid reacting with palladium hydride, they will certainly not differ by a factor exceeding 1,000,000,000 as arrived at by the authors (1). Similarly, it does not make chemical sense to report an activation energy for the oleic acid hydrogenation that is an order of magnitude lower than the activation energy of the hydrogenation of linoleic acid. On chemical grounds, a slightly higher value would be far more likely.

In summary, I cannot but conclude that the manuscript submitted by Mondal and Lalvani (1) should have been rejected for publication.

TABLE 1.
Kinetic Parameters According to Different Authors[a]

	Šmidovnik *et al.* (7)		Mondal and Lalvani (1)	
	A (min^{-1})	E_a (kJ/mol)	A (mole% ·min)$^{-1}$	E_a (kJ/mol)
k_1 (linolenic acid)	7.64×10^5	49.3	1.51×10^3	44.88
k_2 (linoleic acid)	2.39×10^5	49.0	5.57×103	51.97
k_3 (oleic acid)	6.06×10^{12}	102.7	3.84×10^{-6}	5.12
A_2/A_3	3.94×10^{-8}		1.45×10^9	

[a] *A*, frequency factor; E_a, activation energies; k_1, linolenic; k_2, linoleic; k_3, oleic.

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