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The Kinetics of the Hydrogenation of Pure Fatty Esters. II. Mono-olefinic Systems: Cis-trans Isomerism

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THE FORMATION of *trans* isomers in the course of hydrogenation is considered a phenomenon of considerable importance to the commercial hardening of oils. It would seem desirable therefore, from a practical as well as from a theoretical standpoint, to obtain a satisfactory picture of the mechanism underlying *cis-trans* isomerism.

The contribution of Feuge *et al.* (2) toward a solution to this problem is important for several reasons, in particular, in supplying reliable data through the use of an infrared spectrophotometric method established by Swern and co-workers (4). These data show many points of similarity between the behavior of triolein and that of methyl oleate over a wide range of conditions. One of the salient features of the reaction, as revealed by this study, is the gradual evolution of the system toward a *cis-trans* equilibrium. Another feature is the necessity of the presence of hydrogen for the formation of *trans* isomers, in contrast with *cis-trans* isomerization reactions, such as those promoted by selenium. A possible explanation is that the adsorbed complex formed from hydrogen, nickel, and the unsaturated compound is the origin of both the saturated compound and the isomeric unsaturated form. It is probable that a certain proportion of the complex units, instead of being released from the catalyst in the form of saturated molecules, break down and revert to the constituents. Unsaturated constituents so released could be either *cis* or *trans* if the structure of the complex were such as to allow free rotation between the carbon atoms originally linked by a double bond. It is one of the purposes of the present article to show that the above postulate is consistent with hydrogenation data. For this purpose, data which Swicklik *et al.* tabulated in a recent article (3) will be used.

These authors have carried out experiments similar to those of Feuge *et al.* with a view to checking a postulated mechanism of the reaction. They concluded that a true first order model for the reactions involved was incompatible with the data. Good agreement was obtained when all rate constants were multiplied by the same function, $1 + \alpha t$, indicating, in their opinion, that the effectiveness of the catalyst increased with time. In their experiment No. 2, for example, the effectiveness of the catalyst would have increased four times by the end of the reaction. This would seem difficult to reconcile with the fact that the over-all hydrogenation rate was very constant throughout. It is another purpose of the present article to explain this and other puzzling facts, using to this end conclusions relative to zero order hydrogenation kinetics enunciated in Part I of the present series (5).

It is probable that a systematic study of the reaction by the method initiated by Feuge *et al.* will ultimately provide considerable help to the technologist by removing much empiricism from commercial hydrogenation practice. This would result from a comparison of reaction rate constants under various conditions. A simple method for the computation of these rate constants is given below.

Proposed Mechanism

Figure 1 describes the various phases of the reaction involving a system initially composed of a *cis* mono-olefinic ester, a nickel catalyst, and hydrogen. The temperature is assumed high enough to promote formation of *trans* isomers. Double bond shifts also occur, but adsorptive and reactional behaviors are assumed to be identical for all forms which are geometrical homologues. Thus $\bar{A}$ represents all the *cis* and $\bar{B}$ all the *trans* homologues.

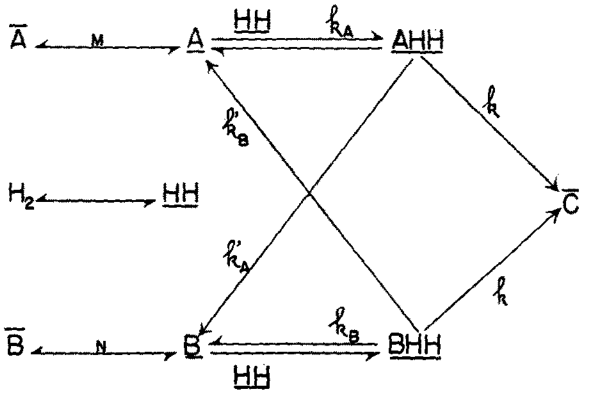

FIG. 1. Diagram describing a mechanism proposed for the hydrogenation of methyl oleate or triolein in the presence of a nickel catalyst.

Figure 1 depicts the adsorptive equilibria between $\bar{A}$ and $\underline{A}$ and between $\bar{B}$ and $\underline{B}$; $\underline{A}$ and $\underline{B}$ are the respective adsorbed forms. It shows the reactions leading to the formation of complexes $\underline{AHH}$ and $\underline{BHH}$ from adsorbed hydrogen $\underline{HH}$ and, respectively, $\underline{A}$ and $\underline{B}$. A constant proportion k of complex $\underline{AHH}$ is shown to be released every minute, forming $\bar{C}$, the fully saturated compound. Another fraction k'_A breaks down, releasing $\underline{HH}$ and $\underline{B}$. Still another breaks down, reverting to its original constituents $\underline{A}$ and $\underline{HH}$; the reaction is one of the opposed reactions in the equilibrium between $\underline{A}$, $\underline{HH}$, and $\underline{AHH}$. Constant k_A is the equilibrium constant by Guldberg and Waage's principle for this reaction.

The fate of complex $\underline{BHH}$ parallels that of $\underline{AHH}$. The complexes are assumed to form concurrently to the opening of a double bond. During the short half life of the complex, free rotation along the residual carbon-carbon linkage would occur to a variable extent. Particularly large deviations from the original position would confer the isomerized status. Such "isomerized" complexes would yield the adsorbed isomerized form upon break-down.

The distinction between $\underline{AHH}$ and $\underline{BHH}$ is thus mainly of a statistical nature, and one would not expect properties, such as the stability of the complex-to-metal bond, to be different in either case. Hence it is assumed that the rate of release k is the same for both types. No assumption is made regarding the rates of break-down.

Basic Rate Equations

Let A, B, and C be the concentrations, expressed as percentages of total molar composition, for $\bar{A}$, $\bar{B}$, and $\bar{C}$, respectively. Because of the system of two consecutive equilibria between $\bar{A}$ and $\underline{AHH}$, losses of $\underline{AHH}$ because of either $\bar{C}$ or $\underline{B}$ formation must be compensated by losses of $\bar{A}$ from the medium. A steady state may be considered in such transfers since the quantities transferred per minute are so much larger than the quantities involved in the coverages of $\underline{A}$ and $\underline{AHH}$. Thus for all practical purposes the rate of loss of A is equal to the rate of loss of AHH due to both $\bar{C}$ and $\underline{B}$ formation. On the other hand, the rate of gain of concentration A through the series of transfers described by

$$\underline{BHH} \longrightarrow \underline{A} \longrightarrow \bar{A}$$

is equal to the rate at which $\underline{BHH}$ produces $\underline{A}$.

If $\underline{a}$ represents the total coverage for $\underline{AHH}$ and b the total coverage for $\underline{BHH}$, the over-all rate of change of concentration $\bar{A}$ is thus expressed by

$$dA/dt = -\underline{a}k - \underline{a}k'_A + \underline{b}k'_B \tag{1}$$

A similar reasoning leads to

$$dB/dt = -\underline{b}k - \underline{b}k'_B + \underline{a}k'_A \tag{2}$$

for the over-all rate of change of concentration B. The rate of change of concentration C is evidently

$$dC/dt = \underline{a}k + \underline{b}k \tag{3}$$

Expressions for Complex Coverages

It has been shown in Part I of this series of articles that two different cases may arise, depending on the abundance of hydrogen supplied. If the medium is kept saturated with hydrogen, the hydrogen coverage is large and the reactions leading to the formation of complexes do not compete. If the hydrogen supply is limited by diffusion, the hydrogen coverage falls to a very low level and the reactions leading to the complexes will compete for their share of hydrogen. In both cases the hydrogen coverage is a constant, and the coverages of adsorbed unsaturated species are proportional to the concentrations of these species in the medium. Thus coverages for $\underline{A}$ and $\underline{B}$ would be expressed by

$$\mu_A = PMA \tag{4}$$
$$\mu_B = PNB$$

where M and N are the respective adsorption equilibrium constants and P is a proportionality constant, depending on catalyst area and the extent of hydrogen coverage.

Let $\underline{h}$ be this coverage. The postulated mechanism has shown an equilibrium between $\underline{A}$, $\underline{HH}$, and $\underline{AHH}$. This is expressed by

$$\underline{a} = k_A \mu_A \underline{h} = k_A PMA\underline{h}$$

Similarly

$$\underline{b} = k_B \mu_B \underline{h} = k_B PNB\underline{h}$$

Let

$$k_A M = k_{03} \quad ; \quad k_B N = k_{02} \quad ; \quad P\underline{h} = S \tag{5}$$

The above expressions then become

$$\underline{a} = k_{03} AS \tag{6}$$
$$\underline{b} = k_{02} BS$$

These expressions are true only when there is no competition for adsorbed hydrogen (saturated medium).

In the second case, characterized by zero order kinetics, the over-all rate of hydrogenation is a constant. Let k_C be this constant.

Hence, from equation (3),

$$\underline{a} + \underline{b} = k_C/k \tag{7}$$

By analogy with homogeneous competitive reactions of the first order, $\underline{a}$ and $\underline{b}$ are proportional to their values when the reactions are not competing. Hence, from equations (6) and (7),

$$\underline{a} = k_C k_{03} A/(k_{03}A + k_{02}B)k$$
$$\underline{b} = k_C k_{02} B/(k_{03}A + k_{02}B)k$$

Introducing

$$k_C/(k_{03}A + k_{02}B) = e^{\alpha t} \tag{8}$$

these expressions become

$$\underline{a} = k_{03} A e^{\alpha t} k^{-1} \tag{9}$$
$$\underline{b} = k_{02} B e^{\alpha t} k^{-1}$$

Final Expressions of Rates and of System Composition

Considering the case when zero order conditions are established, the values for $\underline{a}$ and $\underline{b}$ given by equations (9) are substituted in equations 1, 2, and 3. Let

$$k'_A k_{03} k^{-1} = k_{01} \quad ; \quad k'_B k_{02} k^{-1} = k_{04} \tag{10}$$

These expressions then become:

$$dA/dt = -(k_{01}+k_{03})Ae^{\alpha t} + k_{04}Be^{\alpha t} \tag{11}$$

$$dB/dt = -(k_{02}+k_{04})Be^{\alpha t} + k_{01}Ae^{\alpha t} \tag{12}$$

$$dC/dt = k_{03}Ae^{\alpha t} + k_{02}Be^{\alpha t} = k_c \tag{13}$$

Let

$$e^{\alpha t}dt = d\theta$$

Then

$$\theta = (e^{\alpha t} - 1)\,\alpha^{-1} \tag{14}$$

The above system of differential equations then becomes identical in form to equations (12), (13), and (14) of Swicklik *et al.* The solution of these equations is thus

$$A = c_1e^{m_{01}\theta} + c_2e^{m_{02}\theta} \tag{15}$$

$$B = \frac{k_{01}c_1e^{m_{01}\theta}}{m_{01}+k_{02}+k_{04}} + \frac{k_{01}c_2e^{m_{02}\theta}}{m_{02}+k_{02}+k_{04}} \tag{16}$$

$$C = 100 - (A+B) \tag{17}$$

where θ has the value given by (14) and

$$m_{01} = (-b+\sqrt{b^2-4c})0.5 \tag{18}$$

$$m_{02} = -b - m_{01} \tag{19}$$

with

$$b = k_{01}+k_{02}+k_{03}+k_{04} \tag{20}$$

$$c = (k_{01}+k_{03})(k_{02}+k_{04}) - k_{01}k_{04} \tag{21}$$

Expressions for the composition, when the medium is saturated with hydrogen, are obtained by substituting θ by Skt in the above.

Determination of the Rate Constants

In the following demonstration the data tabulated by Swicklik *et al.*, corresponding to their experiment No. 2, a typical case of over-all zero order kinetics are used. Figure numbers cited refer to theirs also.

a) When $t = 0$,

$$A = 100 \quad ; \quad B = 0 \quad ; \quad e^{\alpha t} = 1$$

Introducing these values in equation (13),

$$dC/dt = 100\,k_{03} = k_c$$

Hence the value of k_{03} is found from the slope of the line obtained on plotting C *vs.* time. From Figure 3,

$$k_c = 0.69$$

Thus

$$k_{03} = 0.69 \times 10^{-2}$$

b) Introducing in equation (11): $t = 0$, $A = 100$, $B = 0$, $e^{at} = 1$

$$dA/dt_{t=0} = -(k_{01}+k_{03})10^2$$

The value of $dA/dt_{t=0}$ is found from the plot $\log_{10}A$ *vs.* time in Figure 1; the required value is that of the slope of the line, near the ordinate axis, multiplied by $\log_e 10 = 2.302$. Subtracting from the result the value of $100k_{03}$ yields $100k_{01}$. One finds

$$k_{01} = 2.18 \times 10^{-2}$$

c) When B reaches its maximum (Figure 3), dB/dt is equal to zero. Equation (12) then yields, upon simplifying by $e^{at} \neq 0$, and rearranging:

$$k_{02}+k_{04} = k_{01}A/B$$

Introducing the values of B maximum and the corresponding value for A (respectively, 43 and 26) taken from Figure 3, and the value of k_{01},

$$k_{02}+k_{04} = 1.319 \times 10^{-2}$$

d) It will be shown that both m_{01} and m_{02} have negative values, m_{02} being much larger in absolute value than m_{01}. As a consequence the exponentials containing m_{02} become negligible when t is large. Equations (15) and (16) then reduce to

$$A = c_1e^{m_{01}\theta}$$

$$B = k_{01}c_1e^{m_{01}\theta}/(m_{01}+k_{02}+k_{04})$$

By dividing:

$$B/A = k_{01}/(m_{01}+k_{02}+k_{04}) \tag{22}$$

The slope of plot B *vs.* A should thus assume a constant value toward the end of the reaction. This is found indeed. The value of the slope (for points corresponding to the 90th, 105th, and 120th minutes) is 2.5.

Hence

$$k_{01}/(m_{01}+k_{02}+k_{04}) = 2.5$$

Introducing the values found for k_{01} and for $k_{02} + k_{04}$,

$$m_{01} = -0.477 \times 10^{-2}$$

e) Introducing in expression (18) the values of $k_{01} + k_{03}$, $k_{02} + k_{04}$, k_{01}, and m_{01},

$$-0.477 \times 10^{-2} = (-4.189 + \sqrt{2.89 + 8.72\,k_{04}}) \times 0.5 \times 10^{-2}$$

Hence

$$k_{04} = 0.97 \times 10^{-2}$$

Consequently, from the value of $k_{02} + k_{04}$,

$$k_{02} = 0.349 \times 10^{-2}$$

The above method of calculation applies when zero order kinetics are still maintained when B reaches its maximum. This is the case for experiment No. 3 of Swicklik *et al.* The constants have also been calculated for this experiment. They are listed in Table I along with the values obtained for experiment No. 2 and in each case the values obtained by Swicklik *et al.*

Comparison Between Theoretical and Experimental Values

The use of equations (15), (16), and (17) requires numerical values of m_{02}, c_1, c_2, θ, and a. They are obtained as follows:

TABLE I

Comparison Between the Numerical Values (x 10^2) of Rate Constants Computed by Swicklik *et al.* and Those Obtained by the Author from the Same Data [a]

	Swicklik *et al.*		Vandenheuvel	
Hydrogenation No...	2	3	2	3
k_{01}	2.4	9.1	2.18	9.44
k_{02}	0.6	2.5	0.349	1.86
k_{03}	0.5	3.7	0.69	3.86
k_{04}	1.0	3.5	0.97	4.37
k_{02}/k_{03}	1.2	0.67	0.505	0.485

[a] Taken from Swicklik *et al.* (3).

a) Introducing in (19) the values of k_{01}, k_{02}, k_{03}, k_{04}, and m_{01},

$$m_{02} = -3.712 \times 10^{-2}$$

b) It is found from (14) that $\theta = 0$ when $t = 0$. At the same time $A = 0$. Equation (15) yields

$$c_1 + c_2 = 100$$

Deriving (15), one obtains:

$$dA/d\theta = m_{01}c_1\, e^{m_{01}\theta} + m_{02}c_1\, e^{m_{02}\theta}$$

Substituting $d\theta$ by e^{at} dt, it value by definition, then assuming $t = 0$, which implies $\theta = 0$, and $e^{at} = 1$,

$$dA/dt_{t=0} = m_{01}c_1 + m_{02}c_2$$

It has been shown that

$$dA/dt_{t=0} = -(k_{01} + k_{03}) \times 10^2$$

Hence

$$m_{01}c_1 + m_{02}c_2 = -10^2(k_{01} + k_{03})$$

which can be solved with

$$c_1 + c_2 = 100$$

after introducing the values of m_{01}, m_{02}, k_{01}, and k_{03}, giving

$$c_1 = 25.8$$
$$c_2 = 74.2$$

c) From equation (8), replacing k_{02}, k_{03}, and k_C by their known values,

$$A + 0.505B = 100e^{-at}$$

Introducing corresponding experimental values of A, B, and t yields the following series of values for a

t	15	30	40	50	60	90	105	120
$a10^2$	1.67	1.73	1.73	1.63	1.65	1.62	1.69	1.86

Averaging the series,

$$a = 1.7 \times 10^{-2}$$

d) It is now possible to calculate values for θ from equation (14) and to replace all constants and parameters by numerical values in equations (15), (16), and (17). When the calculated values of A, B, and C are plotted against time, curves superimposable to the experimental ones but slightly displaced to the right are found. The shift corresponds to a time lag for the reaction of about 1 min.

Subtracting 1 min. from all values of time brings the calculated values in very good agreement with the experimental ones shown in Figure 2.

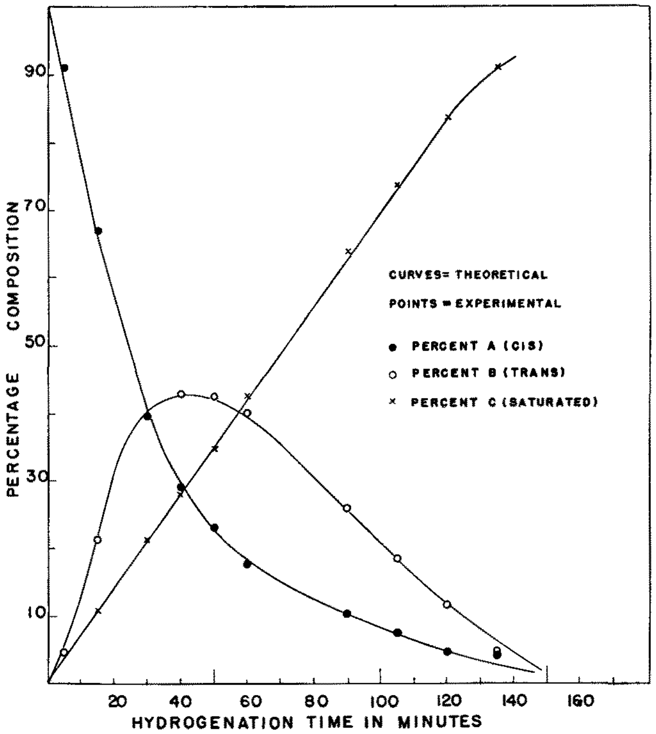

FIG. 2. Comparison of theory with experimental results obtained by Swicklik *et al.* for hydrogenation No. 2.

Discussion

Kineticists do not agree on the mechanism underlying the hydrogenation of the simplest olefin, *viz.*, ethylene. It would seem however that the associative theory is the more acceptable (1) and that hydrogenation is a two-step reaction involving a half-saturated stage. This concept was not used here because of the unnecessary complication it would introduce in the above demonstration. The changes it brings to the above scheme (Figure 1) amount to replacing $\underline{AHH}$ and $\underline{BHH}$, respectively, by $\underline{AH}$ and $\underline{BH}$, defined as the half-saturated complexes. The latter would substitute $\underline{AHH}$ and $\underline{BHH}$ in the breakdown reactions. Addition of a second hydrogen atom to $\underline{AH}$ and $\underline{BH}$ would constitute in each case an extra reaction step. Constant k would then be defined as the rate constant in both cases. The products of these extra steps, *viz.*, $\underline{AHH}$ and $\underline{BHH}$, would be considered as an adsorbed and undissociable saturated compound with properties identical in all respects. Since the saturated compound is very feebly adsorbed (5), its rate of release from the catalyst would be that at which $\underline{AHH}$ and $\underline{BHH}$ are formed. It can be seen how this scheme leads to the rate equations obtained in the previous one.

The introduction of function e^{at} in the rate equations was dictated by the necessity of obtaining relatively simple equations for the system composition and permitting the computation of rate constants to be made readily. Its choice is justified by the good correlation resulting from the calculation of a series of a values with exclusive use of the data. Since function e^{at} is a mathematical aid, a has no mechanistic significance.

It must be pointed out that $1 + at$, the function used by Swicklik *et al.* to "correct" their initial postulate of first order reactions, is an approximation of e^{at}. As shown by their equation (7), these authors saw it as a modification of the rate constant interpreted as an increase with time of catalyst effectiveness. The present treatment shows clearly that the presence of such a function in the rate equations is the normal consequence of competition between the reactions leading to the formation of complexes. It is not required when the reaction medium is saturated with hydrogen. Hence Swicklik *et al.* found $a = 0$ in their experiment No. 1.

Table I shows some inconsistencies in the numerical values obtained by these authors. Their k_{02}/k_{03} ratio in experiment No. 2 indicates a higher reactivity for *trans* in opposition with the accepted view that *cis* is more reactive. This ratio is also appreciably different from that corresponding to experiment No. 3, although experimental conditions differed only in the pressure used. Note that the k_{02}/k_{03} ratios by our values are about equal and acceptable under the above criterion. The value obtained by Swicklik *et al.* for k_{03}, experiment No. 2, is questionable since by making $t = 0$ in their equation (8) one obtains,

$$dC/dt = 100\, k_{03}$$

leading to our own value for this constant.

On the other hand, their statement expressing that k_{01}/k_{04} should equal the *trans-cis* equilibrium ratio appears unwarranted in view of equation (22). It can be demonstrated, through the use of this equation and of relation (18), that k_{01}/k_{04} will only equal the equilibrium ratio in the unlikely event that $k_{02} = k_{03}$.

From relations (5) and (10)

$$k'_A/k'_B = k_{01}k_{02}/k_{03}k_{04}$$

The value of this ratio is 1.135 for experiment No. 2 and 1.04 for experiment No. 3, by our values. The rates of break-down for the complexes are thus approximately equal.

The method proposed for the computation of the constants is undoubtedly less tedious and more expeditive than one by trial and error. The value of k_C, that of the *trans-cis* equilibrium ratio, and those of A and B when B is maximum, constitute the only data needed for its application. A relatively small time lag and zero order kinetic conditions are a prerequisite however. Fortunately this is the general case when conditions similar to those used in industrial practice are used.

It should be noted that equation (22) suggests the occurrence of the *cis-trans* equilibrium described by Feuge *et al.*

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Paper Chromatography of Phospholipides on Silicic Acid Impregnated Glass Fiber Filter Paper[1]

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As part of a program on the biosynthesis of the lipides, it was considered desirable to develop a paper chromatography method for resolving phospholipide mixtures and for testing the homogeneity of phospholipide preparations in general. Several methods involving conventional paper chromatography have been described (6, 7, 9). In addition, silicic acid-impregnated cellulose filter paper has been used (8). In most of the above procedures the chromatographed phospholipides were located on the chromatogram by means of functional groups in the phospholipide molecule e.g., amino-, quaternary ammonium-, and phosphate groups. Since the weight percentage of these groups in the phospholipid molecule is often relatively low, there would appear to be a good chance for overlooking phospholipide constituents present in relatively low concentrations in a given phospholipide preparation. Furthermore impurities not having one of the tested functional groups would pass unnoticed.

In an attempt to overcome these difficulties the technique of chromatography on glass paper impregnated with silicic acid (2, 3) has been investigated as a means for separating lysolecithin, sphingomyelin, lecithin, and phosphatidylethanolamine.

Experimental

Preparation of the Paper and Chromatographic Tank. Silicic acid glass fiber filter paper and the chromatographic tank were prepared essentially according to the method of Dieckert and Reiser (4). But, to insure adequate removal of HCl and KCl, the impregnated glass paper was washed six times with distilled water instead of four times, as reported earlier.

Method. Each phospholipide spotted on the chromatogram was applied in 10 μgm amounts as a 0.1% solution of the lipide. The chromatogram was routinely equilibrated for a period of 30 min. prior to the irrigation step. After equilibration the chromatogram was irrigated by the ascending technique. From 1 to 1½ hrs. were required for the solvent front to travel 10 to 12 in.

Solvent Systems. The five solvent systems investigated were 15, 25, 50, 70, and 90% (V/V) methanol in ethyl ether. A.C.S. grade solvents were used without further purification.

Spot Test Reagents. After development of the

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