Kinetics of the Aminolysis of Hydrogenated Tallow by Allylamine and Other Primary Amines in Methanol[1]

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Abstract

Kinetics of the aminolysis of hydrogenated tallow by allylamine in methanol solution under sodium methoxide catalysis was studied at several temperatures (60 to 90C) and catalyst concentrations. Under the experimental conditions the triglycerides were rapidly converted to the mixed methyl esters, which slowly reacted with the amine to produce the mixed amides. At constant catalyst concentration, disappearance of triglyceride was found to be first order in triglyceride and in amine. Because rate was found to be directly proportional to catalyst concentration, the experimental over-all rate was $-d[\text{Triglyceride}]/dt = k_3[\text{Triglyceride}]\,[\text{Amine}]\,[\text{RO}^-]$, and k_3 was 2.022 kg^2 mole^{-2} hr^{-1}. A mechanism proposed by Bunnett and Davis for ester aminolysis involving an ester-amine complex formed in a rapid pre-transition-state equilibrium is consistent with thermodynamic terms which reconcile a large negative entropy of activation (−44.17 cal deg^{-1} equivalent^{-1}) and relatively small energy of activation (11.60 kcal equivalent^{-1}). Relative rate constants at 70C under sodium-methoxide catalysis for the aminolysis of hydrogenated tallow by a variety of structurally different primary amines agreed, in general, with those found by others for the ethylene glycol-catalyzed reaction of methyl acetate with the same amines at 25C. However, monoethanolamine reacted nineteen times faster than predicted, which suggested a mechanism involving initial attack by the alkoxy anion of the ethanolamine in the rate determing step, followed by rapid, base-catalyzed, acyl acyl oxygen-to-nitrogen (O → N) migration. The velocity constants and thermodynamic constants reported enable prediction of the time required for specific yields under a variety of experimental conditions.

Introduction

NUMEROUS KINETIC INVESTIGATIONS have been made to elucidate the mechanism of ester aminolysis (1–10). These investigations have revealed the effect of structure on reactivity (4), have demonstrated the influence of solvents (3,4), including water (2,7–10) on rate, and have shown that the reaction is subject to both acid (2) and base catalysis (1,3, 5–10). Particularly noteworthy has been the strong accelerating influence of alkoxide catalysis (1,3,5,6) in nonaqueous systems. Acceleration of this normally slow reaction by alkoxide catalysis has been used successfully in preparative work (11) even with aromatic amines (12) and was found to be especially useful when volatile amines were reacted with fatty esters at room temperature (13). Alkoxide catalysis has been used extensively by the fat industry, since first introduced by Meade in 1949 (14) to accelerate the conversion of methyl esters and of triglycerides to mono- and diethanolamides in both batch (15–18) and continuous processes (19,20). Although these particular aminolyses are known to be fast, especially at high temperatures (20), their specific velocity constants have not been determined. In fact, no comprehensive study of the rate of conversion of triglycerides to amides in homogeneous solution under the influence of alkoxide catalysts has ever been made, although, under heterogeneous conditions and when excess amine was used, pure methyl stearate was rapidly converted, even at room temperature (13).

The purpose of this investigation was: (1) to determine conditions suitable for preparing mixed N-allylamides directly from hydrogenated tallow by a study of the reaction kinetics in methanol solution under sodium methoxide catalysis; (2) to relate rate quantitatively to both temperature and catalyst concentration in order to permit approximate predictions of rate over a variety of operating conditions; (3) to compare rate coefficients for N-allylamine aminolysis with those found for a variety of other primary amines in order to extend the general utility of the relationships determined for allylamine, and (4) to add, within the limits imposed by the experimental results, to the general knowledge concerning the mechanism of ester aminolysis and the influence of structure on rate.

Allylamine was selected as the primary amine to receive most attention in this investigation partly because of its intermediate position in a scale of primary amine reactivities toward both methyl acetate (21) and methyl stearate (13) and partly because of a recent observation (22,23) that pure N-allylstearamide can be converted to hard high-melting waxes by simple treatments with benzoyl peroxide at 90C. The wax application was also the reason for using fully hydrogenated tallow.

Methanol was chosen as the solvent to permit the use of sodium methoxide as catalyst and because both methanol and glycerol accelerate ester aminolysis (3, 24). The rate of the reverse reaction is too slow to seriously affect conversion to amide (5). It was expected that under the conditions selected, the difficultly soluble triglycerides would be rapidly converted to soluble mixed methyl esters (25) before the slower aminolysis reactions occurred. In confirmation, in this investigation the aminolyses of tallow and pure methyl stearate had equal rates under the same experimental conditions. Thus the kinetic constants reported here reflect the rate of attack on mixed methyl esters by selected primary amines, although they are reported in units of the respective triglycerides.

Procedure

Reactions were conducted in 25-ml flasks which were charged with hydrogenated tallow (about 1.2 eq/kg), a slight excess of amine (1.18 moles per equivalent of ester), freshly made 2 N sodium methoxide solution (13), and dry methanol, and then sealed and heated in a constant temperature bath. Reaction

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TABLE I

Second-Order Rate Constants and Reaction Concentrations for the Aminolysis of Hydrogenated Tallow in Methanol by Primary Amines

Expt. No.	Amine	Concentration, eq/kg[a]			Reaction temp, C	k_2	
		Tallow	Amine	Sodium methoxide		kg mole^{-1} hr^{-1} [b, f]	%
1	Allylamine	1.215	1.440	0.271	60	0.376	±2.01
2	Allylamine	1.215	1.440	0.271	70	0.514	±5.73
3	Allylamine	1.154[c]	1.424	0.257	70	0.582[c]	±4.79
4	Allylamine	1.215[c]	1.424	0.271	70	0.519	±3.15
5	Allylamine	1.231	1.231	0.271	70	0.544	±3.56
6	Allylamine	1.215	1.440	0.271	80	0.821	±7.87
7	Allylamine	1.215	1.440	0.271	90	1.307	±9.58
8	Allylamine	1.215	1.440	0	70	0.0085	±37.4
9	Allylamine	1.215	1.440	0	70	0.0534[d]	±9.16
10	Allylamine	1.217	1.443	0.122	70	0.229	±10.4
11	Allylamine	1.213	1.438	0.425	70	0.908	±3.49
12	Allylamine	1.211	1.435	0.605	70	1.120	±6.57
13	Allylamine	1.207	1.431	0.845	70	1.744	±6.73
14	Allylamine	1.202	1.425	1.202	70	3.149	±8.08
15	Allylamine	1.213[e]	1.438	0.271	70	0.168	±5.83
16	Monoethanolamine	1.215	1.440	0.271	70	19.905	±18.2
17	n-Butylamine	1.215	1.440	0.271	70	1.018	±33.4
18	iso-Butylamine	1.215	1.440	0.271	70	0.450	±9.50
19	Benzylamine	1.215	1.440	0.271	70	0.454	±11.1
20	sec-Butylamine	1.215	1.440	0.271	70	0.023	±28.6
21	tert-Butylamine	1.215	1.440	0.271	70	0.0019	

[a] Methanol concentration, 16.877 mole/kg.

[b] Rate constants, k_2 apply to the triglycerides; in terms of ester function these become (k_2/3) kg eq^{-1} hr-1.

[c] Hydrogenated soybean oil used in Experiment 3; both Experiments 3 and 4 carried to >90% disappearance of ester equivalents.

[d] In benzene.

[e] Pure methyl stearate was substituted for tallow.

[f] The slope and intercept of the plot of ln [amine]/[ester] versus time, hr, were determined by the method of least squares. Error in % was determined from the variance at 95% confidence limits. Average error at the intercept for the allylamine experiments was ±5.60%.

TABLE II

Representative Rate Determination in Methanol at 70C[a]

Time, hr	(a–x) eq/kg	(b–x) eq/kg	k_2 kg mole^{-1} hr^{-1}
0	1.215	1.440	
0.5	1.034	1.260	0.718
1.0	0.922	1.147	0.648
2.0	0.757	0.982	0.603
3.0	0.650	0.875	0.570
5.0	0.499	0.725	0.539
7.0	0.404	0.629	0.521
8.0	0.359	0.585	0.527
9.0	0.323	0.548	0.532
10.0	0.290	0.515	0.540
14.0	0.211	0.436	0.530
18.0	0.167	0.392	0.507
24.0	0.108	0.333	0.531
		Average	0.564

[a] Sodium methoxide concentration = 0.271 eq/kg. This is experiment 4 of Table I.

temperatures were between 70 and 90C to insure homogeneous conditions while avoiding high pressure. The flasks were withdrawn at predetermined intervals and chilled to stop the reaction. After hydrolysis to destroy soap and catalyst, the crude reaction product was isolated from a benzene solution by evaporation. To determine ester remaining, aliquots of the crude product were saponified by refluxing with 2 N alcoholic potassium hydroxide for 1 hr. Hydrolysis of N-allylstearamide was found to be negligibly slow under these conditions, like that of other simple amides (26).

Second-order rate constants were determined for each experiment using the relationship (27):

$$\ln B/A = k(B_0 - A_0)t + \ln B_0/A_0 \qquad [1]$$

where A_0 and B_0 were the initial concentrations, in equivalents per kilogram, of tallow ester and amine, respectively, and A and B were their concentrations at time t. A plot of ln B/A as a function of time yielded k ($B_0 - A_0$) as the slope and ln B_0/A_0 as the intercept. From the slope, the constant k_2 (kg. eq.$^{-1}$ hr^{-1}) was evaluated and converted to units of moles of triglycerides (kg. mole^{-1} hr.$^{-1}$) by multiplication by 3.

Slope and intercept were evaluated by the least squares procedure and per cent error was determined from 95% confidence limits after an analysis of variance. The ester remaining, A, at any time, t, was calculated from ester values.

Experimental Results. The velocity constants determined in this investigation are listed together with experiment numbers in Table I. Typical per cent conversions vs time curves and second-order function vs time curves are shown in Figures 1 and 2, respectively (Experiments 1,2,6,7). Approximate obedience to second-order kinetics was characteristics of all of the experiments listed in Table I even when individual experiments were carried to greater than 90% conversion. This is illustrated in Figure 3 which compares the results found for hydrogenated tallow (Experiment 4) and hydrogenated soybean oil (Experiment 3) toward allylamine. Since in both lines data points on the right side are in an experimentally insensitive region, it is not certain whether the differences in slope and rate constant are significant. When values of k_2 were calculated for each point of an experiment, some drift occurred, as shown in Table II for a typical experiment. The significance of this will be discussed in a later section.

Rate dependence on catalyst concentration is illustrated in Figure 4, where graphs of ln B/A vs time are compared at various catalyst levels. A plot

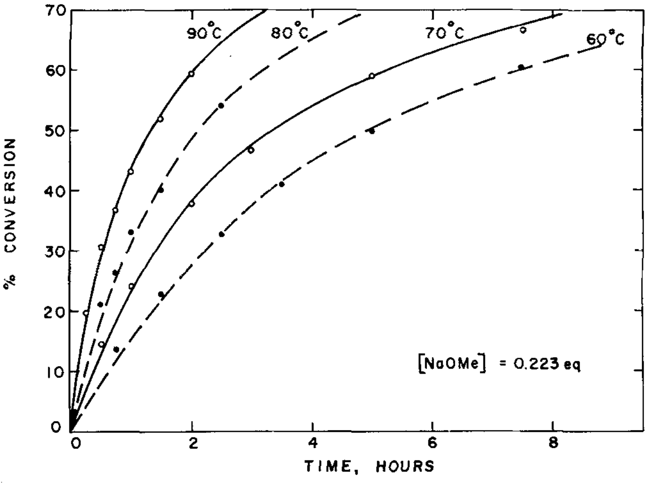


FIG. 1. Plot of per cent conversion vs. time for the aminolysis of tallow by allylamine in methanol at various temperatures, catalyzed by 0.223 eq. of sodium methoxide per ester equivalent.

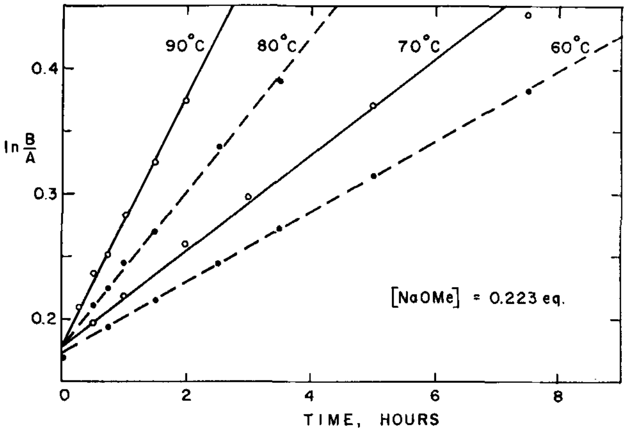


FIG. 2. Second-order plots of the aminolysis of hydrogenated tallow by allylamine in methanol, catalyzed by sodium methoxide, at various temperatures.

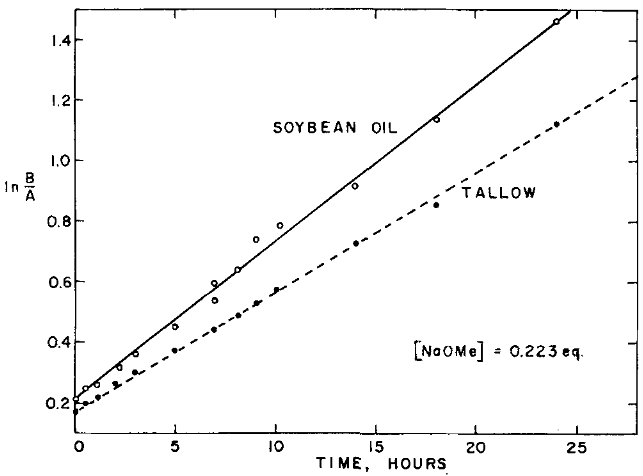


Fig. 3. Second-order plots of the aminolysis of hydrogenated tallow and soybean oil by allylamine at 70C to greater than 90% conversion.

of the second-order rate constants derived from these curves (Experiments 1,10–14) as a function of catalyst concentration, shown in Figure 5, established that rate was directly proportional to the concentration of sodium methoxide, as had been previously reported for the reaction of ethyl formate with n-butylamine (6). Therefore the reaction rate was found to be third-order overall, first order in ester; amine, and sodium methoxide respectively, as

$$-d[\text{Triglyceride}]/dt = k_3[\text{Triglyceride}][\text{Amine}][\text{Sodium Methoxide}] \qquad [2]$$

Thus, k_3 is the experimental third-order constant and has the numerical value 2.022 $kg^2\ mol^{-2}\ hr^{-1}$. Since the intercept of the plot in Figure 5 shows the possibility of a small residual second-order rate for the uncatalyzed reaction, the value of this intercept was determined as a separate experiment (Experiment 8).

Mechanism and Thermodynamics

Of several mechanisms proposed for the aminolysis of esters (1,5–7), the most plausible, especially as it applies to this work is the proposal of Bunnett and Davis (6) for the aminolysis of ethyl formate by n-butylamine in anhydrous solvents. Their mechanism, Equations 3 and 4, calls for an equilibrium between ester and amine rapidly established in a series of steps; reaction of complex I or II with a base B; and finally slow formation of a transition state and loss of alcohol to produce amide:

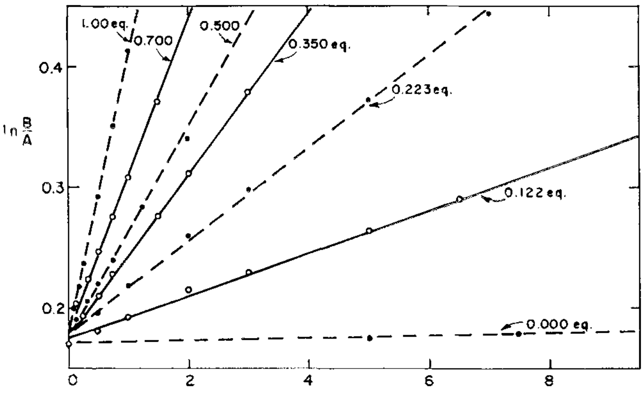


Fig. 4. Effect of sodium methoxide concentration on the aminolysis of hydrogenated tallow at 70C. Sodium methoxide varied from 0 to 1.0 eq. per equivalent of ester.

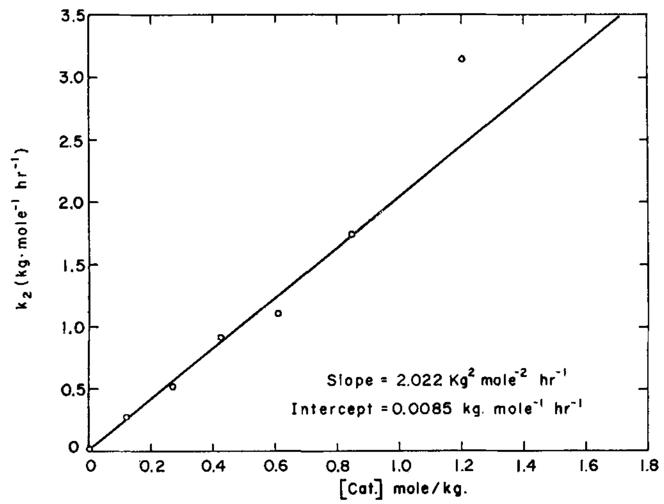
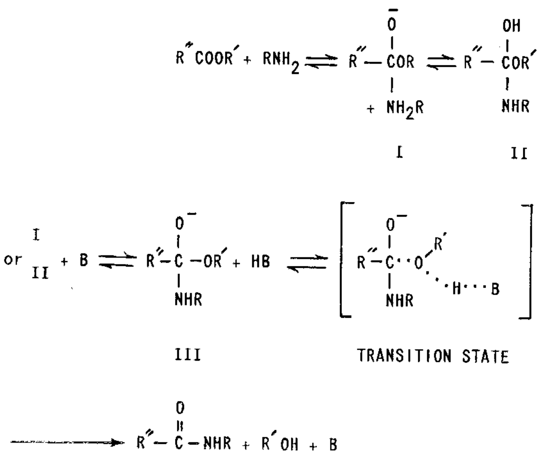


Fig. 5. Plot of rate constant k_2 vs. catalyst concentration. Evaluation of the third-order rate constant.



[3]

[4]

The disappearance of ester was given by Bunnett and Davis as

$$\text{Rate} = -d[\text{Ester}]/dt = k_{RO^-}[\text{Ester}][\text{Amine}][RO^-] + k_{RNH_2}[\text{Ester}][\text{Amine}]^2 \qquad [5]$$

The first term was thought to dominate in the presence of alkoxide catalysis, which was, of course, used in the present investigation.

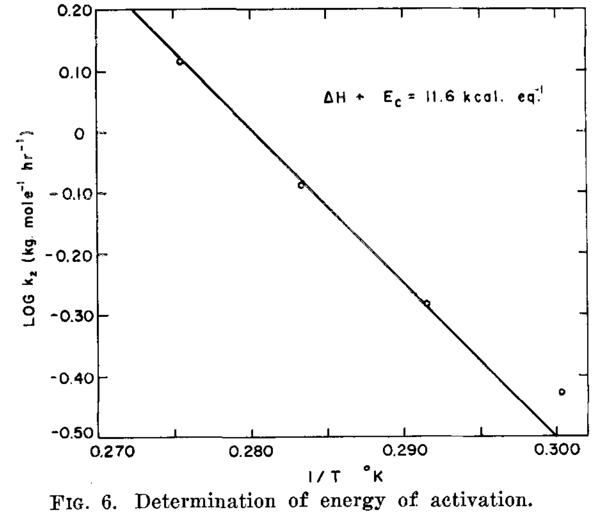


Fig. 6. Determination of energy of activation.

TABLE III

Thermodynamic Constants for the Aminolysis of Hydrogenated Tallow by Allylamine

Constant	Value
$\Delta H + E_c$	11.60 kcal eq^{-1}
log sK_o $[RO^-]$	3.649
$RlnK_o + \Delta S^*$	-44.17 cal deg^{-1} eq^{-1} at 70C

TABLE IV

Calculated Reaction Times Required to Convert Hydrogenated Tallow to Mixed Allylamides at Different Temperatures and Amine-Ester Rations[a]

Variaion of temperature[b]			Variation of amine/ester ratio[d]		
Reaction temp °C	k_2 (kg $mole^{-1}$ hr^{-1} [c])	Time, hr, 90% Conv.	Amine/ Ester	Time, hr, 50% Conv.	Time, hr, 90% Conv.
60	0.309	37.9	1.18	3.77	22.8
70	0.514	22.8	1.5	2.76	13.3
80	0.832	14.1	2.0	1.95	7.2
90	1.276	9.2	3.0	1.23	4.7
100	2.021	5.8	4.0	0.89	3.3
125	5.430	2.2	6.0	0.58	2.1
150	13.032	0.90	8.0	0.33	1.5
175	28.447	0.41			
200	57.339	0.20			

[a] In methanol. Ester concentration 1.215 eq/kg; sodium methoxide, 0.223 eq per ester equivalent.

[b] At amine/ester ratio of 1.18.

[c] Calculated using absolute rate expression of Eyring and E_c and ΔS^* of Table III.

[d] At 70C.

Properly speaking, energy and entropy of activation are properties of the transition state. However, equilibria preceding the transition state will contribute to the numerical values of the thermodynamic constants as normally calculated, and it would be more correct in such cases to report the functions in a form that recognizes the equilibria. Appropriate expressions of the functions are developed in the following paragraphs, in which, unless specified, symbols have their conventional significance.

If K is the overall constant for the equilibria leading to II, and k_c is the rate constant for the reaction of alkoxide RO^- with a complex consisting of ester E and amine RNH_2, then

$$\text{Rate} = -d[E]/dt = Kk_c([E][RNH_2])\,[RO^-] \qquad [6]$$

In accordance with this scheme, the second-order rate constants of Table I are actually pseudo second-order and are equal to the product Kk_c $[RO^-]$. The quantity Kk_c is the slope of the plot given in Figure 5 and is the same as the experimental third-order constant previously mentioned, with the numerical value 2.022 kg^2 $mole^{-2}$ hr^{-1}, for the triglycerides.

Consideration of K as a function of temperature leads to

$$d\ \ln K/dT = \Delta H/RT^2 \qquad [8a]$$

or

$$K = K_o \exp\ (-\Delta H/RT) \qquad [8b]$$

Likewise the relation of k_c to temperature may be expressed (28) by the Eyring equation 9, in which E_c is the activation energy for formation of the transition state from the complex.

$$k_c = \frac{e\,kT}{h}\ e^{\Delta S^*/R}\ e^{-E_c/RT} \qquad [9]$$

But, since

$$s = \frac{e\,kT}{h}\ e^{\Delta S^*/R} \qquad [10]$$

multiplication of (9) by (8) and substitution of (10) give

$$Kk_c = sK_o e^{-(\Delta H + E_c)/RT} \qquad [11]$$

$$\log Kk_c = \frac{-(\Delta H + E_c)}{2.303R} \cdot \frac{1}{T} + \log sK_o \qquad [12]$$

$$\log k_2 = \log Kk_c[RO^-] = \frac{-(\Delta H + E_c)}{2.303R} \cdot \frac{1}{T} + \log sK_o[RO^-] \qquad [13]$$

It follows that a plot of log k_2 as a function of 1/T should be linear with a slope $-(\Delta H + E_c)/2.303R$ and an intercept log $sK_o[RO^-]$, in which *s* is the frequency factor of the Arrhenius Equation (28). Such a plot at 60, 70, 80, and 90C, based on Experiments 1,2,6,7, is shown in Figure 6. The numerical values of $(\Delta H + E_c)$ and log $sK_o[RO^-]$ were determined by the method of least squares. The 60C experiment was not used in the calculation.

To develop an entropy term recognizing the equilibrium, Equation 10 may be multiplied by K_o giving

$$e(kT/h)K_o \exp\ (\Delta S^*/R) = sK_o \qquad [14]$$

or

$$(R\ln K_o + \Delta S^*) = R(\ln sK_o - \ln kT/h - 1) \qquad [15]$$

To calculate the thermodynamic constants, the experimental third-order constant (Kk_c) of 2.022 kg^2 $mole^{-2}$ hr^{-1} was converted to units of equivalents and seconds, becoming 2.022/3(3600) kg^2 eq^{-2} sec^{-1}. Using equations 13 and 15, overall activation energy, the frequency-factor intercept, and the entropy term were evaluated as in Table III.

The low value of 11.6 kcal found for the activation term above indicates a much higher rate than was actually observed provided that the contribution of ΔH is small. The magnitude of the abnormal negative entropy term -44.1 cal deg^{-1} eq^{-1}, which greatly exceeds the value of -5 to -8 kcal deg^{-1} eq^{-1} usually associated with crowding in the transition state, suggests that pre-transition-state equilibria do occur in aminolysis. Because of the impossibility of separating the terms for equilibrium and rate, no definitive mechanistic conclusion can be reached, however. It is pertinent that the value of R ln $K_o + \Delta S_c^*$ for the uncatalyzed reaction, namely -55.05 cal deg^{-1} eq^{-1}, is similar to the value of -64 to -67 cal deg^{-1} eq^{-1} found by Day and co-workers (29) for the ammonolysis of various methyl esters.

The mechanism discussed in this paper is probably an over-simplification, as has been discussed by Bunnett and Davis (6) and Watanabe and DeFonso (5). The slight drifts found in the constants for individual points (Table II), which are similar to drifts found by others (1,5–7,9,24), suggest that a somewhat more complex situation prevails and that the over-all mechanism might well be a summation of several contributing mechanisms (6). In this work, the best, though not perfect, fit of the data was found by trial to be to the experimental second-order relationship of equation [1].

Calculation of Rate Under Various Conditions

In principle second-order rate constants may be computed for any temperature using the values of $(\Delta H + E_c)$ and log $sK_o[RO^-]$ given in Table III. Use of the thermodynamic data thus permits the estimation of rate constants at any temperature (up to decomposition) and, therefore, the time required to reach a chosen conversion at that temperature. Table IV lists data computed for several temperatures. Of course, such extrapolated results are only approximate, because of the error involved in the determina-

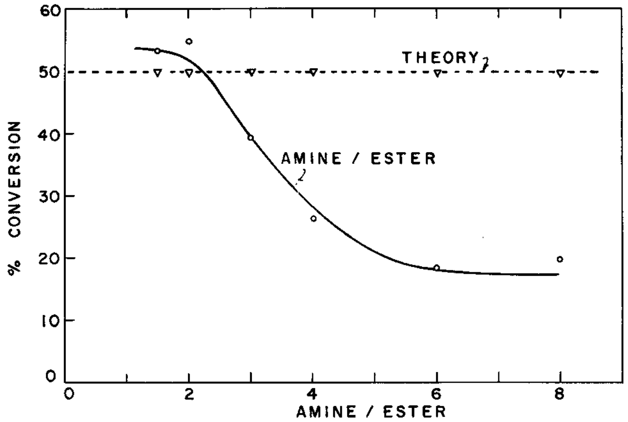


Fig. 7. Effect of variation in the ratio of amine to ester on the per cent conversion of experiments run to calculated half-times.

tion of activation energy and because the reverse reaction will probably become appreciable at high temperatures.

In a similar way, from the rate constants listed in Table I, the times necessary to reach a desired conversion at increasing amine-to-ester ratios might be estimated by use of an expression of the type below. Thus for a 90% conversion to amide

$$t_{90\%} = [\ln(B/A)_{90\%} - \ln B_o/A_o] \div k_2(B_o - A_o)/3 \quad [16]$$

In this expression $(B_o - A_o)$ may be varied and has the units assigned earlier. Reaction times calculated for 50 and 90% conversion are also listed in Table IV. To check the range of validity of such extrapolations, a series of experiments, at constant ester and sodium methoxide concentrations and increasing amine concentrations were run for the calculated half-times listed. As can be seen in Figure 7, beyond an amine/ester ratio of 2, the experimental conversions fell well below the calculated curve. Although qualitatively rates were higher at increasing amine/ester ratios, a quantitative proportionality failed as methanol experimentally was progressively replaced by amine. Thus rapid conversion of triglycerides to amide appears to be aided by a large initial ratio of methanol to ester. The decrease in methanol concentration resulting from increase in amine may either have altered relevant activity coefficients or it may have slowed the preliminary conversion of glycerides to methyl esters.

The effect of the use of two different solvents on rate in the absence of added catalyst was studied in the aminolysis of tallow by allylamine at 70C in solution in methanol (Experiment 8) and benzene (Experiment 9). It is assumed that, in the methanol experiment, transesterification precedes aminolysis. The 6.2-fold increase in rate of aminolysis in the benzene experiment is not well understood. Possibly glycerine is a more effective leaving group than methanol. However, solvation effects and competition by methanol could also contribute to the difference.

Relative Rates of Aminolysis

Second-order rate constants for the aminolysis of hydrogenated tallow by a series of primary amines are listed in Table I. Plots of ln B/A vs time, shown in Figure 8, illustrate the large effects on rate caused by structural features of different amines. Such sensitivity to structure indicates again that steric effects contribute to the entropy term, $R\ln K_o + \Delta S_c^*$ of

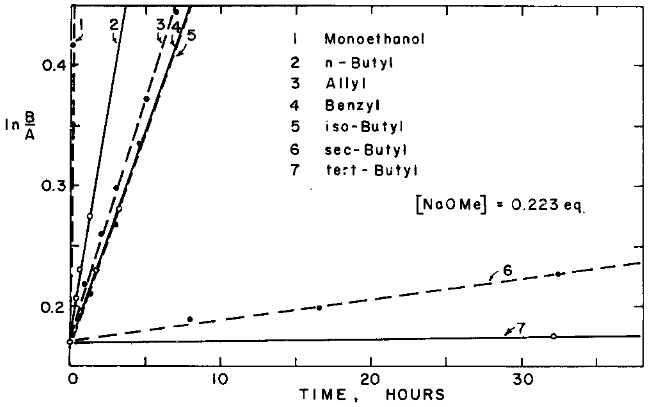
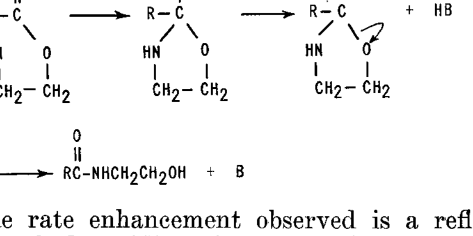


Fig. 8. Comparative aminolysis of hydrogenated tallow by several primary amines.

Table III. Bulky amines are thought to crowd the transition state (21), and may also adversely displace a pretransition-state equilibrium. The relative rate constants found in this study at 70C were compared with relative constants determined by Day and coworkers (21) at 25C for the aminolysis of methyl acetate by the same amines in dioxane, catalyzed by ethylene glycol. Values reported in Table V for the isomeric butylamines are in good agreement. The moderate differences in passing to allylamine and benzylamine can be explained by assuming small differences in either energy or entropy of activation (or in both) for these systems. The large difference in the value found for monoethanolamine, however, suggests that, under sodium methoxide catalysis, a change in mechanism occurs.

The acyl moiety of ethanolamides is known to undergo rapid migration from the nitrogen atom to the oxygen atom under strong acid catalysis and from the oxygen atom to nitrogen under basic catalysis (30–32). These shifts, known, respectively, as (N → O) and (O → N) migrations, depend on the pH of the system. In this work it is believed that a rate-determining attack on ester by the alcohol portion of the amine, under the transesterification conditions prevailing, is followed by rapid rearrangement under basic catalysis as shown:



[17]

The rate enhancement observed is a reflection of the marked rapidity of transesterification under alkoxide catalysis (25). Additional enhancement can be expected because ethanolamine has been found to be twice as acidic as methanol in isopropyl alcohol solution (33). The value found for the velocity constant using diethanolamine (only approximate be-

TABLE V

Relative Reaction Velocities for Preparing Mixed Tallow Amides and Acetamides from Primary Amines

Amine	Relative k[a]	
	Mixed tallow amides[b]	Acetamides[c]
Monoethanolamine	19.55	1.09
n-Butylamine	(1.00)	(1.00)
Allylamine	0.505	0.195
Benzylamine	0.446	0.156
iso-Butylamine	0.442	0.411
sec-Butylamine	0.023	0.022
tert-Butylamine	0.002	Immeasurably slow

[a] Rate constants for n-butylamine taken as 1.00.
[b] This work, at 70C, using 0.223 eq sodium methoxide as catalyst.
[c] Reference (21), at 25C.

cause of experimental difficulties) was about one-half the value found using monoethanolamine. Steric and nucleophilic factors, the former very pronounced with secondary amines (13) could well account for a rate reduction of this order. However, the value of the rate constant, 8.34 kg mole^{-1} hr^{-1}, was still 8.2 times larger than the value found when n-butylamine was used, and hence a change in mechanism of the type described above is again supported. Strong rate enhancement by alkoxide catalysis helps explain the success of a low-residence-time continuous process for making diethanolamides (20).

Experimental

Amines and Methanol

The amines (Eastman, White Label) and methanol (anhydrous, A.C.S.) were stored over calcium hydride until reaction ceased and then distilled twice from fresh calcium hydride through a helix column.

Sodium Methoxide Solution

Two-molar solution was made by dissolving sodium, freshly cut and weighed under xylene, in the anhydrous methanol prepared as above, and the solution was titrated before use with 0.1N HCl.

Hydrogenated Tallow

Wilson-Martin Wilmar 1000 was used without purification. It had the following constants: mp 59.0–61.0C; saponification value 194.87; acid value 5.85; ester value 189.02. In Experiment 3, fully hydrogenated soybean oil was also used without further purification. It had the following constants: mp 67.0–68.5C; saponification value 189.22; acid value 13.53; ester value 175.69.

Kinetic Procedure

A typical experiment is described: Six oven-dried 25-ml Erlenmeyer flasks with necks about 24 cm long and 1 cm in diameter were each charged with 4.9576 g (0.0172 mole equivalents) of hydrogenated tallow, 1.1300 g (0.0198 mole equivalents; 1.18 mole ratio) of allylamine, 2.12 ml of the sodium methoxide solution and 7.49 ml of the anhydrous methanol. This volume of sodium methoxide solution included an amount exactly equivalent to the free acid present in the tallow. Thus the catalyst concentration in Table I is always based on effective catalyst.

The stoppered flasks, after cooling to −80C in dry ice, were flame sealed and, when warmed to room temperature, were immersed in a constant-temperature bath, controlled to ±0.1C. Zero time followed a 10-min experimentally established equilibrium time. Individual flasks were withdrawn at predetermined intervals, were quenched in ice water to stop the reaction, and the catalyst and amine destroyed with excess 10% aqueous hydrochloric acid. The reaction mixture was transferred with benzene and the acid to separatory funnels and warmed briefly to destroy residual amine and soap. The benzene layer was washed free of acid, dried and the crude reaction product isolated by evaporating the solvent in a draft of air. An ester value (0.2N KOH, 1 hr reflux) was used to determine the ester equivalents remaining. Hydrolysis of the amide was negligible under these conditions: samples containing 3 g of pure N-allylstearamide and pure N-n-butylstearamide, in quintuplicate gave the blank titration. This had been observed before (22). Rates of the base-catalyzed hydrolysis of amides in water-ethanol mixtures have been shown to diminish as ethanol concentration is increased, becoming very small in 95% ethanol (26). In a few early experiments nitrogen values checked well with those calculated from the amide present based on ester number. Crystallization of several crude reaction mixtures from acetone (10 ml/g) at 0C yielded mixed amides, mp 73–75C, in 85–90% conversions, based on the amount calculated to be present. Usually 6 experimental points (and sometimes 12, Experiments 3,4) were determined in each experiment; for some of the other amines only 4 or 5 were determined. The rate constant using tert-butylamine is based on a single point and the value of the intercept.

The velocity constant for the reaction of diethanolamine and hydrogenated tallow was determined, using a separate experiment for each increment on the time scale, by following the disappearance of amine to a methyl red endpoint after correction for the catalyst (5,21). Considerable scatter in the data points appeared at about 55% conversion. Because the rate constant found, 8.34 kg mole^{-1} hr^{-1}, was considered to be only approximately correct, it was not listed in Table I.

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A New Rapid Titration Method for Determining the Halogen Ratio of Wijs Solution and of Iodine Monochloride

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Abstract

The free iodine in Wijs solution is titrated directly, in strong hydrochloric acid solution, with standard potassium iodate solution. From this titration and the usual sodium thiosulfate titration for total halogen, the iodine/chlorine ratio is calculated. Results agree closely with those obtained by the longer chlorine-water method of Lopes. The halogen ratio of reagent grade iodine monochloride, a convenient material from which to prepare Wijs reagent directly, is also determined by the new titration method.

Introduction

THE PREPARATION OF WIJS solution is described in the AOAC Official Method Cd 1-25, April 1956, Iodine Value, Wijs Method. The solution is prepared by (a) chlorinating a 0.1 *N* iodine solution in glacial acetic acid, or (b) much more conveniently by adding iodine monochloride to glacial acetic acid. The ratio of iodine to chlorine in Wijs solution must be about 1.1. The determination of this halogen ratio involves two steps: 1) titration of total halogen with $Na_2S_2O_3$ solution; and 2) titration of total iodine by the method of Lopes (1). The second step is rather inconvenient because it involves preparing a saturated solution of chlorine in water, adding the Wijs solution, and boiling for 10 min. Up to now, no simple and rapid means has been available for checking the iodine/chlorine ratio of reagent grade iodine monochloride.

Experimental

In our laboratory, Wijs solution has always been prepared from iodine monochloride, by merely pipetting 5 ml into a liter of glacial acetic acid and mixing. For this method of preparation, it is essential that the ICl itself has the correct I/Cl ratio of about 1.1. Unfortunately, a recent lot of commercial ICl was received with an I/Cl ratio of less than one. It was necessary to grind iodine crystals, weigh out the required amount, and then dissolve them in the Wijs solution to boost the ratio to 1.1.

This necessitated running a number of total iodine determinations by the somewhat tedious chlorine water procedure of Lopes. A more rapid and direct method for titrating the free iodine is described by Kolthoff and Belcher (2). In strong HCl solution, the following reaction with KIO_3 takes place.

$$2I + KIO_3 + 6HCl \longrightarrow KCl + 5ICl + 3H_2O$$

The Wijs solution is added to a mixture of 1:1 HCl and CCl_4 in a flask and shaken, whereby the free iodine present is extracted into the CCl_4 layer, coloring it violet. The mixture is then titrated with 0.04 *N* KIO_3 solution, to a colorless end point, as a measure of the free iodine.

As a confirmatory test, the foregoing KIO_3 method was first applied to a mixture of acetic acid, 1:1 HCl, and CCl_4 containing a known amount of free iodine. Excellent results were obtained using 10-ml and 15-ml portions of iodine solution. Using 10-ml portions of one iodine solution, the amount of iodine present was 0.1218 g and the amounts found by titration with 0.0642 *N* KIO_3 were 0.1217 g and 0.1220 g. Using 15-ml portions of another iodine solution, the amount of iodine present was 0.1938 g and the amounts found by titration with 0.03962 *N* KIO_3 were 0.1936 g and 0.1940 g.

The iodine/chlorine ratio was then determined on a Wijs solution using both the method of Lopes and the KIO_3 procedure: the I/Cl ratio by the Lopes method was 1.10 and 1.12; by the KIO_3 method, it was 1.11 and 1.11. Both methods give the same answer.

The detailed new procedure for determining the iodine/chlorine ratio of Wijs solution, and also of reagent grade iodine monochloride, is described in the next section.

Determination of Halogen Ratio of Wijs Solution

Reagents

1) Potassium iodate solution, 0.04 *N*. Dry ACS reagent grade KIO_3 for one hour at 110C. Weigh 2.1402 g of the dried salt, dissolve in water, dilute to one liter in a volumetric flask, and mix.

2) Hydrochloric acid, 1:1. Dilute 37% HCl with an equal volume of water.

3) Potassium iodide solution, 15%. Dissolve 150 g in distilled water and make up to a liter.

Procedure

Measure 50 ml of 1:1 HCl and 50 ml of CCl_4 into a 500-ml iodine flask. By means of a pipet, transfer 25.00 ml of the Wijs solution to the flask, and shake. Titrate the free iodine in the violet-colored CCl_4 layer with the KIO_3 solution to a colorless end point using vigorous shaking.

On a second 25.00 ml portion of the Wijs solution, determine the total halogen by adding 150 ml of water, 15 ml of 15% KI solution, and titrating with standard $Na_2S_2O_3$ solution to a starch end point.

Calculate the I/Cl ratio as follows: