Catalytic Effects in the Ammonolysis of Vegetable Oils[1]

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ABSTRACT

Catalysts for the ammonolysis of soybean oil are, in order of decreasing overall effectiveness, ammonium acetate, sodium methoxide, 9-aminononanoic acid, sodium soyate, ammonium nitrate, alanine, sodium acetate and glycerol. At 125 C, a reaction time of 1 hr and a 30:1 mole ratio of ammonia to ester, ammonium acetate achieved ammonolysis in 16%, 61% and 84% conversions at the respective concentrations of 0.0, 0.1 and 1.0 mole per mole ester groups. Conversion was 98% complete in 4 hr with 1.0 mole. The ammonolysis generally exhibited the expected first order kinetics up to about 80% reaction.

INTRODUCTION

Higher fatty amides are useful industrial chemicals as well as intermediates for several laboratory processes, for example, the synthesis of nylon-9 (1). Commercially, fatty amides are made by reaction between fatty acids and excess ammonia at 150-300 C and 1 atm (2); reaction time is typically 10 hr at 150-200 C (3). High temperatures and long reaction times significantly dehydrate the amides to nitriles. For example, reaction of stearic acid and ammonia at 300 C produces stearonitrile (4).

Alkyl esters, including triglycerides, of fatty acids are also suitable starting materials for amide preparations by reaction with excess anhydrous ammonia under autogenous pressure. Temperatures needed are lower than with fatty acids; although slow ammonolysis occurs even at 25 C (2), temperatures above 150 C are required for practical reaction rates (5). Nitrile formation begins about 175 C (6), becomes significant above 190 C and causes discoloration and lower amide yield (5). A 1.5% conversion of stearamide to stearonitrile occurs in 7 hr at 190 C (7).

A catalyst is necessary to give practical rates for ester ammonolysis at temperatures well below the amide dehydration point and to permit operation below the critical temperature of ammonia (133 C). Ammonium salts are reported to be catalysts in anhydrous ammonia (2,7-9) but not in methanol solution (10). The rate of ammonolysis of seed oils in excess anhydrous ammonia was doubled at 165 C by adding 17% NH_4Cl; in 2 hr, the reaction with soybean oil was 32% complete and with olive oil, 55% complete (8). Other inorganic ammonium salts (11), ammonium benzoate (11) and about 5% of the ammonium salt of the corresponding free fatty acid (7) have served as catalysts. The relative activity of four ammonium salts as catalysts for the ammonolysis of ethyl benzoate in anhydrous ammonia was in the order (11) of benzoate> chloride>bromide>perchlorate, the reverse of their relative degree of ionization in water.

The effectiveness of strong bases as catalysts is unclear. Although a Russian patent (12) ascribes activity to metal amides, their high base strength causes extensive proton abstraction at the α-carbon and little ammonolysis in liquid ammonia (13,14). Alkoxides have been used as ammonolysis catalysts in lower alcohols (10) and as aminolysis catalysts (15,16). Hydroxyl compounds, particularly glycols (17), as well as acetonitrile (18) and neutral salts (19), also promote ammonolysis.

Our study was undertaken to develop a practical method for rapid ammonolysis of vegetable oils under mild conditions. A variety of known and new catalysts and reaction conditions were compared at 100-150 C; excess anhydrous ammonia was the solvent.

EXPERIMENTAL PROCEDURES

Materials

Crude soybean oil (A.E. Staley Mfg. Co.) contained 0.43% free fatty acid. Alkali-refined soybean oil (Archer Daniels Midland Co.) had 0.03% free fatty acid. USP olive oil (Mario's Food Products, Detroit, Mich.) had an iodine value of 83 and $n_D^{30} = 1.4647$. Methyl oleate from Applied Science Laboratories contained 99% monoene (95% Δ^9). All catalysts were commercial reagent grade materials used as supplied unless noted otherwise in Table I. Moisture sensitive catalysts were handled in a dry atmosphere.

Ammonolysis Procedure

Catalyst was placed in the autoclave (Table I, footnote a), which was flushed with dry N_2 and kept under N_2 thereafter; the lower half was cooled in dry ice for 1 hr. With H_2O-absorbing catalysts (Runs 3, 4, 16, 18 and 19, Table I), the autoclave was first dried at 150 C and cooled under dry N_2 before charging. The ester was then charged, the head secured to the autoclave and the entire autoclave cooled in dry ice for 1 to 1 1/2 hr. Commercial 99.99% pure anhydrous NH_3 was condensed to ±3 ml of the desired volume into a graduated cold trap that had been oven dried at 125 C and cooled under dry N_2. The NH_3 was then transferred to the open autoclave under N_2. The autoclave was sealed and heated to the desired operating temperature within 30-50 min, the exact period depending upon the autoclave and temperature. At the end of the reaction, NH_3 was slowly vented through an appropriate manifold system. With rocker bombs, which were first cooled to dry ice temperature, the NH_3 was allowed to evaporate from the opened bomb as it warmed to room temperature. There was no problem with foaming during the NH_3 boil-off except in Runs 18 and 19 with CH_3ONa.

For the rate studies (Table I, Runs 1-20), samples were obtained by means of a 1.2 mm bore tube extending to the bottom of the autoclave; the line was flushed with 2-3 ml reaction mixture before collecting each 0.5-1.5 ml sample.

Some stress corrosion caused by the anhydrous NH_3 vapor occurred at the top of the solenoid housing of the 0.5 liter stainless steel (type 316) autoclave; pitted fissures were observed.

Amide Purification

The crude ammonolysis product was freed of glycerol and catalyst by washing in the molten state five to seven times with 5-6 vol hot H_2O, or by dissolving in 3-4 vol hot acetone and adding to 4-5 solution vol H_2O at 0 C, filtering the precipitated solids and washing the solids with 1-2 vol H_2O. Certain runs required that these procedures be modified. The amides from Runs 3 and 17 were separated from catalyst by dissolving in CH_2Cl_2, filtering or centrifuging and finally evaporating the solvent before H_2O-washing. The basic catalyst in Runs 18 and 19 was neutralized by addition of a slight excess of HCOOH or NH_4Cl solution before work-up; severe emulsion problems

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TABLE I

Ammonolysis of Fatty Esters

		Charge[b,c]				Reaction conditions[d]			Per cent ammonolysis[e]			
				Catalyst					Graphs			
Run number	Reactor[a]	Ester wt, g	NH_3, moles RCOO-	Identity	Moles/ RCOO-	Temperature C	Time, hr	Maximum pressure, psig	1 hr	4 hr	Final product	First order k at 50% reaction (hr^{-1})
1[f]	M	RS, 79	30	0	0	150	6.0	2100	19 (2.4)	70 (3.0)	89	0.28
2	M	RS, 79	30	0	0	125	5.0	1250	16 (3.7)	60 (3.6)	74	0.22
3	M	RS, 79	30	-COOH resin[g]	0.10	125	6.0	1400	3 (2.4)	31 (3.0)	53	0.12
4	M	RS, 79	30	Glycerol[h]	0.50	125	7.0	1300	16 (2.5)	68 (3.3)	91	0.25
5	M	RS, 79	30	NH_4NO_3	0.10	125	6.5	1350	35 (2.7)	86 (4.4)	96	0.51
6	M	RS, 79	30	NH_4OAc	0.10	125	5.8	1375	61 (3.0)	89 (4.6)	96	0.92
7[i]	M	RS, 79	30	NH_4OAc	0.20	125	6.0	1125	65 (4.2)	95 (4.6)	96	1.11
8[i]	M	RS, 79	30	NH_4OAc	0.20	125	7.0	1300	66 (3.3)	95 (5.0)	98	1.51
9	M	RS, 79	30	ex HOAc[j]	0.20	125	6.0	1300	73 (2.6)	93 (4.2)	98	1.39
10	M	RS, 79	30	NH_4OAc	0.50	125	5.8	1325	75 (3.2)	96 (4.5)	96	1.65
11	M	RS, 79	30	NH_4OAc	1.00	125	5.8	1200	84 (4.7)	98 (6.8)	98	1.92
12	M	RS, 198	3	NH_4OAc	0.14	125	6.1	400	10 (3.6)	66 (3.7)	91	0.24
13	M	RS, 79	30	NH_4OAc	0.20	100	4.7	810	32 (3.4)	84 (4.7)	91	0.45
14	M	RS, 79	30	$CH_3CH(NH_2)COOH$	0.10	125	5.5	1310	32 (3.2)	84 (4.7)	97	0.41
15	M	RS, 79	30	$H_2N(CH_2)_8COOH$[k]	0.10	125	5.8	1225	49 (2.4)	60 (3.9)	92	0.65
16	M	RS, 80	30	NaOAc[l]	0.20	125	6.0	1425	19 (2.5)	72 (3.7)	94	0.28
17	M	RS, 63	37	Na soyate[m]	0.25	125	6.0	1500	46 (2.4)	82 (4.1)	86	0.57
18	M	RS, 79	30	$NaOCH_3$	0.20	125	6.0	1325	61 (3.5)	85 (4.4)	---	1.00
19	M	RS, 79	30	$NaOCH_3$[n]	0.20	125	5.0	1210	80 (6.0)	80 (5.8)	79	3.65
20	M	CS, 79	30	0	0	125		1225	18 (3.7)	58 (4.1)	65	0.21
21	R	CS, 44	30	0	0	72	0.5	400	---	---	---	
						125	4.0	1200	---	---	84	
22	R	CS, 44	30	NH_4OAc	0.20	125	4.0	1200	---	---	91	
23	R	CS, 44	30	NH_4OAc	1.00	125	4.0	1200	---	---	93	
24	L	CS, 200	24	NH_4OAc	0.90	75	0.5	400	---	---	---	
						125	3.8	1210	---	---	98	
25	L	OL, 100	68	NH_4OAc	0.90	60	0.2	290	---	---	---	
						100	1.0	775	---	---	---	
						125	4.8	1250	---	---	98	
26	L	MO, 50	52	NH_4OAc	1.10	90	1.0	730	---	---	---	
						125	3.0	1225	---	---	86	

TABLE I (Continued)

[a] All reactors were stainless steel, type 316. M, 0.5 liter Magne-dash autoclave made by Autoclave Engineers (610 ml total free space, 5.3 cm bore) having a plunger agitator with two discs of 2.1 cm diameter 7.8 cm apart and a 3.8 cm travel at 1-1.5 cycles/sec; R, 330 ml rocker; L, 1 liter Magne-dash. Total volume in lines and gauges was 10-20 ml.

[b] RS, alkali-refined soybean oil; CS, crude filtered soybean oil; OL, pure edible olive oil, MO, 99% methyl oleate.

[c] Ammonia and catalyst both expressed as moles per mole ester groups (fatty acyl radicals). Catalysts: -COOH resin, polymethacrylic acid-type ion exchange resin, expressed as equivalents COOH/mole RCOO-; NH_4NO_3, ammonium nitrate; NH_4OAc or NaOAc, ammonium or sodium acetate; Na soyate, sodium soap made from RS; $NaOCH_3$, sodium methoxide.

[d] Time periods shown are those at the indicated operating temperatures, after heat-up periods (30-50 min at the start, 10-20 min between stages). The pressure dropped gradually during each run typically 75-150 psi.

[e] Based upon the percentage N on the dried water-washed product by the micro-Kjeldahl method vs theory (soybean amides 5.06% N, olive 5.08, oleamide 5.20). The values for 1 and 4 hr represent averaging of data from arithmetic (e.g., Fig. 1), probability (e.g., Fig. 3) and arcsin plots; 95% confidence limits (L_{95}) are indicated in parentheses.

[f] Another run under these nominal conditions, but with the temperature increasing from about 140 to about 165 C, gave 24% reaction in 1 hr, 92% in 4 hr and 93% in the final product after 6 hr.

[g] Amberlite CG-50 (100-200 mesh) was vacuum-dried at 100-125 C/0.1 mm for 7 hr.

[h] Anhydrous vacuum-distilled (0.1 mm) laboratory reagent grade, center cut, n_D^{25} = 1.4725.

[i] Runs 7 and 8 were nominal replicates.

[j] The NH_4OAc catalyst for Run 9 was made in situ from reagent grade glacial acetic acid.

[k] A research product (mp 192-194 C) prepared in this laboratory from soybean oil (19).

[l] Commercial anhydrous powder was gently fused until bubbling ceased (5 min) and cooled under dry N_2.

[m] The 81.2 g RS + Na soyate charge was derived from 79.0 g RS (0.2717 mole RCOO-), 2.14 g NaOH (0.0534 mole) and 21.8 g H_2O; stirred 1.3 hr at 90 C under N_2; dried at 38-62 C/10-0.02 mm for 8 hr in a rotary evaporator.

[n] The $NaOCH_3$-RS mixture was preheated briefly to 150 C before cooling, charging the NH_3 and proceeding with ammonolysis as usual.

were nevertheless encountered, and extensive centrifugation was required. Cooling the hot mixture of H_2O and crude product in ice to solidify the amides simplified removal of the aqueous phase.

After glycerol and catalyst were removed, the amide products were prepared for N analysis by vacuum drying at 30-40 C at 0.2 mm of Hg for 20-24 hr or above the melting point at 80-90 C at 0.1 mm for 1-4 hr for 50-80 g samples or 5-10 min for 0.1-0.3 g samples.

Several experiments were carried out to confirm the absence of any undesirable effect on the product amides by the purification procedures. Hydrolysis of soybean amides in H_2O at about 90 C was not detectable in 3 hr. Loss of intermediate soybean monoglyceride was negligible; less than 2% loss occurred when a synthetic mixture containing 7 parts commercial monoglycerides and 10 parts soybean amides was carried through the standard sequence.

The amides hold 2-3% H_2O that can be removed by melting in vacuo at 80-100 C/0.05 mm for 5-10 min. This H_2O is regained by long exposure to saturated air at 30 C.

Kinetic Studies

The extent of reaction was based on the N content of the dried H_2O-washed product as determined by the Kjeldahl method. The percentage ammonolysis was calculated, as for example with soybean amides, by the equation 100 x % N/5.06, where 5.06 is the theoretical N content. Plots are given in Figure 1 for the extent of reaction vs time at the operating temperature for representative runs. The points on Figure 1 are each based on 1-8 N analyses, and the curve positioning was weighted proportionately.

Soybean Amides

The precipitated product of Run 24 was a light yellow-tan waxy solid (192 g); it had an mp 55-74 C on a hot stage, differential thermal analysis (DTA) peak at 71 C, IV 132 and 5.08% N (theory, 5.06%). The amide was readily recrystallized by dissolving in 1.4 vol hot acetone, diluting with 1 vol methanol and cooling to -22 C to give a 71.5% recovery of off-white granules, mp 62-77 C, IV 118. Dilution of the filtrate with 0.5 vol H_2O precipitated the more unsaturated amides as 22.1 g wax, mp 35-67 C, IV 160.

The DTA melting peak was not significantly affected by product purity above 90% or by sample pretreatment. The peak occurred at 70 ± 2 C, a range within the limits of reproducibility of the instrument.

The solubilities (g/100 g solvent) of soybean amides (Run 24 product, mp 55-74 C) in lower alcohols at 10, 20 and 30 C, respectively, were: CH_3OH, 3.7, 10.8, 51.6; C_2H_5OH, 5.6, 16.7, 44.5; n-C_3H_7OH, 8.5, 17.7, 54.3 (6.4 at 0, 118.5 at 35 C) and n-C_4H_9OH, 5.0, 21.2, 51.0. These solubilities are much greater than those of the two pure saturated components, palmitamide and stearamide (6).

The oxidizability of soybean amides was measured by bubbling air through a 1.3 cm (diameter) by 2 cm (depth) molten samples at 90-95 C for 12 hr; the net weight gain and N loss in the dark brown product indicated an oxygen uptake of 0.6 g atom/mole amides and an amide vaporization loss of 2.9%.

Soybean amides exhibited metal-suspending and corrosion-inhibiting properties. A mixture of 0.70 g soybean amides, 0.32 g soybean oil, 0.16 g precipitated Cu powder and 2 ml H_2O was heated to 85 C in a 1.3 x 12 cm test tube and shaken for 2 min. The Cu became suspended in a stable emulsion that showed no separation at 85 C for 10 min or at 25 C for one week. Similar tests with 0.34 g amides plus 0.73 g soybean oil, or 0.77 g oil alone or 0.62 g amides alone showed little or no suspending action. The rusting of a common 0.2 x 3.7 cm iron nail was completely prevented for at least three days when fully immersed at 25 C in H_2O that had previously been saturated with soybean amides; controls with H_2O alone or soybean oil-saturated H_2O rusted within 3 hr. Nails in contact with filter paper wetted with a 0.1% solution of soybean amides in 1:1 H_2O/C_2H_5OH showed no rust in a closed chamber in 20 hr; rust appeared on a control with this solvent alone within 3 hr.

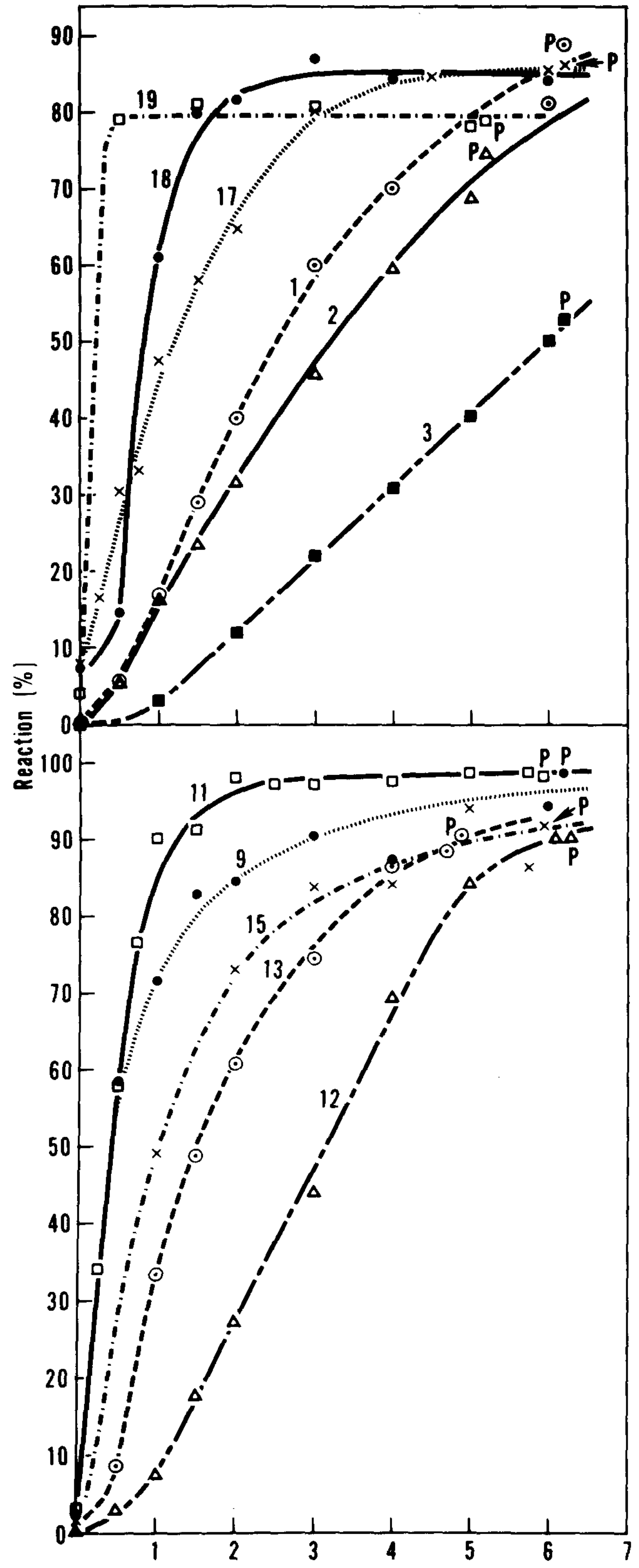


FIG. 1. Ammonolysis of soybean oil at 100-150 C in excess anhydrous NH_3 as the solvent (30:1 NH_3/RCOO- ratio, except No. 12 at 3:1). Curve labels correspond to run numbers in Table I, where the temperatures and catalysts are also listed. Points labeled P represent the final isolated reaction product.

Olive Amides

The crude, washed product (95 g, mp 72-74 C, 4.96% N) from Run 25 was recrystallized once each from hexane and acetone (350 ml each, cooled to 0 C) to give a 91% overall yield of white solid, mp 73-75.5 C [lit. mp 73-74 C (5)], DTA 76.5 C, IV 83 and 5.08% N (theory, 5.08%). Evaporation of solvent from the hexane filtrate left 2.8 g brown paste, mp to 48 C, IV 136.

Oleamide

The washed product (48 g, mp 55-71 C, 4.49% N) from Run 26 was recrystallized from 245 ml benzene at 0 C. The filter cake was rinsed with 100 ml benzene at 5 C to give 31.8 g white microflakes, mp 70-74.5 C [lit. mp 69-72 C (7), 75-76 C (21)], 4.94% N (theory, 4.98%). The solubilities of crude oleamide (g/100 g solvent, mp 55-71 C) in two alcohols at 0, 10, 20 and 30 C, respectively, were: CH_3OH, 2.7, 6.4, 24.3, 60.5; and n-C_3H_7OH, 5.0, 9.5, 23.8, 77.4.

Recovery of Glycerol

Removal of ammonium acetate from glycerol was tried by distillation and ion exchange methods. Distillation gave the most complete removal. Crude glycerol (3.95% N, equivalent to 21.7% ammonium acetate) left after evaporating H_2O from part of the melt-washing filtrate of Run 9 was flash distilled through an unpacked 0.9 x 6.5 cm column at 0.04 mm. Most of the NH_4OAc sublimed over in the foreshot. The main glycerol fractions (60% of the charge) had 0.06-0.10% N (0.33-0.55% NH_4OAc), 38.5% C, 9.3% H (theory, 39.1% C, 8.8% H) and n_D^{22} = 1.4735.

Removal of NH_4^+ was only 80% complete when another portion of the melt-washing filtrate from Run 9 (containing glycerol and 5 mEq NH_4OAc) was passed through a 2.5 cm (diameter) by 14.3 cm (depth) bed of 100-200 mesh polymethacrylic acid-type ion exchange resin (70 ml, 250 mEq nominal exchange capacity) at 2-2.5 ml/min. A mixed bed deionizing resin (100 ml of "Amberlite" MB-1) removed 59% of NH_4^+ at a flow rate of 9 ml/min from a 10% aliquot of the wash filtrate from Run 10.

RESULTS AND DISCUSSION

The relative effectiveness of the ammonolysis catalysts compared in Runs 1-19 is in the order: $NH_4OAc > CH_3ONa > H_2N(CH_2)_8COOH >$ Na soyate $> NH_4NO_3 >$ alanine $>$ NaOAc $>$ glycerol, based upon the extent of reaction after 1 hr at 125 C (from graphs like Fig. 1) and interpolation of data for nonequivalent catalyst levels. The advantages of NH_4OAc as a catalyst include its low cost, low corrosiveness (vs. NH_4Cl), high efficiency on both a molar and weight basis, high solubility in the reaction mixture, ease of removal from the amides by H_2O extraction, high volatility (permitting separation from the byproduct glycerol), the comparable ease of removing its H_2O soluble dehydration product ($AcNH_2$) and the absence of double bond migration. A strong base ($NaOCH_3$, Run 18) conjugated 96% of the diene in 6 hr at 125 C.

Under our conditions of using a large excess of NH_3 (30:1 NH_3/RCOO-mole ratio), the ammonolysis of soybean oil (and presumably other fatty esters) exhibits in part the expected first order kinetics with respect to soybean oil (SBO). However, plotting log $\{100/(100\text{-}\%\ \text{reaction})\}$, mathematically equivalent to the standard first order graph of log $\{[SBO]_0/([SBO]_0\text{-}[SBO]_t)\}$, vs. reaction time generally did not give the expected straight line relationship over the entire 0-100% reaction range (Fig. 2). Most curves were relatively linear up to about 80% reaction, in contrast to the reported full range linearity of the acid-catalyzed hydrolysis of fats with a slight excess of H_2O (22). Some change in order during ammonolysis has also been observed with methyl phenylacetate; the reaction was initially first order in the ester and 3/2 order in NH_3 (10). The points on most of the nonlinear curves are within 95% confidence limits (23) of a linear relationship; these limits are indicated in the caption for Figure 2. The confidence limits (L_{95}) were calculated from the standard deviation (s) with the formula, $L_{95} = \pm 2s\sqrt{\bar{n}}$, where $\bar{n}$ is the average number of N analyses used to determine each point in the plot. A statistical analysis of data on 174 N analyses was used to calculate s, which varied from 0.11% in the 0-2.5% N region up to 0.23 at 4.2-5.1% N, with a mean of 0.19 (±3.75% reaction). A novel feature of Run 12, with a reduced NH_3/RCOO ratio of 3:1, is the overall linearity of the curve, but with two different slopes, suggesting a significant change in the character of the system at about 10% reaction.

The first order rate constant, $k = (1/t)\ln[100/(100 - \%\ \text{reaction})]$, was calculated for each of the 20 rate study runs at 50% reaction. These constants, listed in Table I, were obtained from the best fit straight line through data points on the first order graph (e.g., Fig. 2) in the region of 20-70% reaction. The effectiveness of the catalysts indicated by these constants is in the same order as determined after a 1 hr reaction from curves like Figure 1. One ammonolysis with $NaOCH_3$ (Run 19) that used a nonstandard procedure—preheating the soybean oil and $NaOCH_3$ briefly to 150 C before cooling and addition of the NH_3—gave the fastest reaction, $k = 3.65\ hr^{-1}$. An $NaOCH_3$-catalyzed run carried out in the standard manner (Run 18) gave a slightly lower rate than the same level of NH_4OAc (Runs 7-9). There is some overlap of the 95% confidence limits on the graphs for these two catalysts, however.

Other data transformations that yielded a greater number of linear relationships between degree of reaction and time are the graphs of log time vs percentage reaction on a probability scale (Fig. 3) (24) and the arcsin transformation (23). Both have the effect of linearizing this type of data by expanding the degree of reaction scale at each end of the graph and compressing it in the central, steepest sections. The indicated 95% confidence limits in Table I were determined as described above, except that only those points fixing the position of the curves in the 1 and 4 hr region of plots like Figure 1 were used in the calculations.

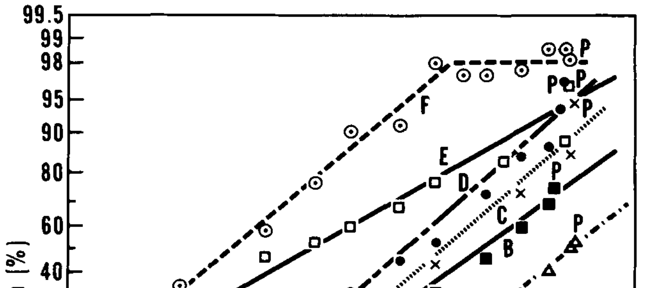


FIG. 3. Probability plots for representative soybean oil ammonolyses at 30:1 NH_3/RCOO- and 125 C; catalyst levels and L_{95} per Figure 2: (A) 0.1 equiv. RCOOH ion exchange resin, Run 3; (B) no catalyst, Run 2; (C) 0.2 NaOAc, Run 16; (D) 0.1 $CH_3CH(NH_2)COOH$, Run 14; (E) 0.1 NH_4OAc, Run 6, L_{95} 4.3; and (F) 1.0 NH_4OAc, Run 11.

Certain ammonolyses leveled off at a degree of reaction short of 100%, notably the CH_3ONa-catalyzed Runs 18 and 19 (Fig. 1); the "unreacted" soybean oil had evidently been converted to inert Na soaps (10). Their presence was evidenced during product work-up in the facile formation of stable aqueous emulsions and the presence of CH_2Cl_2-insoluble fatty materials. The apparent leveling of the high rate 1 mole NH_4OAc-catalyzed Run 11 at 98-99% reaction

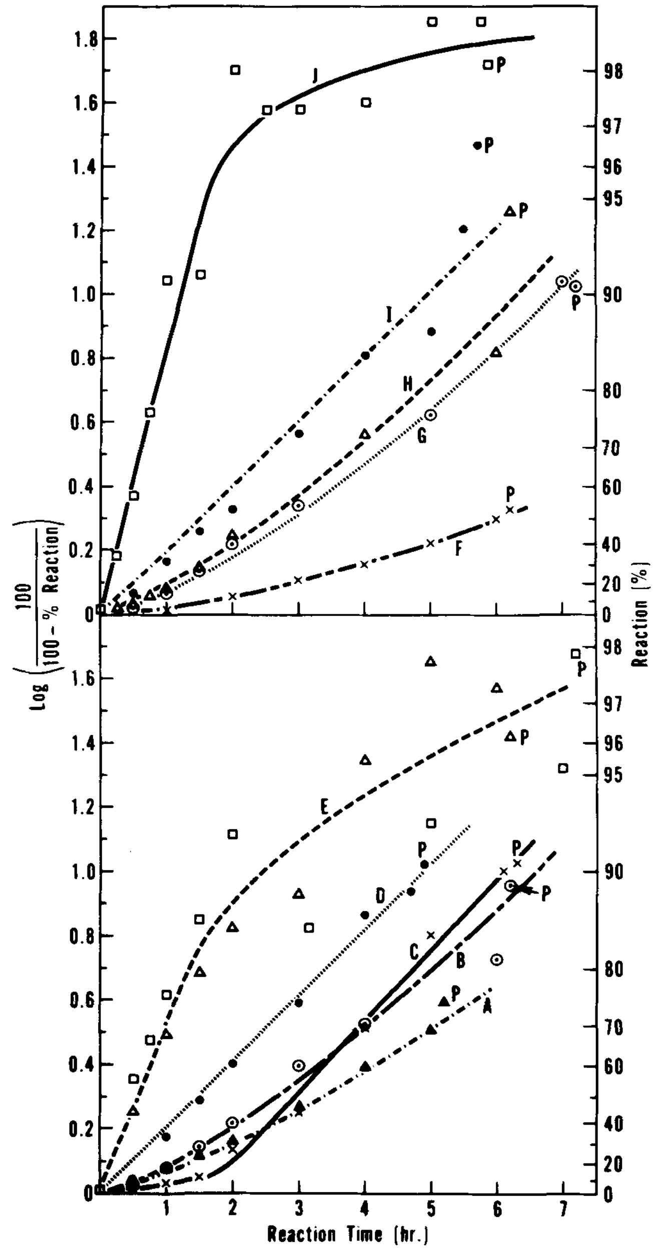
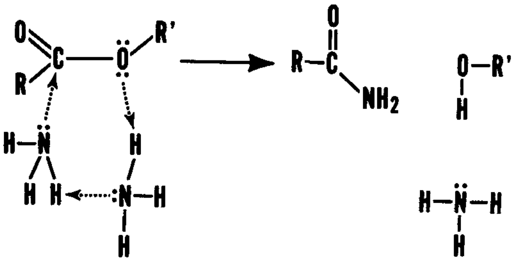


FIG. 2. First order plots of soybean oil ammonolysis at 125 C and 30:1 NH_3/RCOO- (unless indicated otherwise), without a catalyst (A and B) or with indicated catalyst levels per mole ester groups; L_{95} = the 95% confidence limits, expressed as ±X% reaction, based upon s = 3.75 (see text): (A) no catalyst, 125 C, Run 2, L_{95} 5.7: (B) no catalyst, 150 C, Run 1, L_{95} 4.2; (C) 0.14 NH_4OAc, 3:1 NH_3/RCOO-, Run 12, L_{95} 5.3; (D) 0.2 NH_4OAc, 100 C, Run 13, L_{95} 4.9; (E) 0.2 NH_4OAc, average of Runs 7 (△) and 8 (□), L_{95} 3.7; (F) 0.1 equiv. RCOOH ion exchange resin, Run 3, L_{95} 4.8; (G) 0.5 glycerol, Run 4, L_{95} 5.0; (H) 0.2 NaOAc, Run 16, L_{95} 3.9; (I) 0.1 $CH_3CH(NH_2)COOH$, Run 14, L_{95} 4.9; and (J) 1.0 NH_4OAc, Run 11, L_{95} 5.0.

(Fig. 1) may reflect either the slight reversibility of ammonolysis (10,13,25) or simply the rather wide 95% confidence limits on the data in that region. The linearity of the graph of per cent reaction vs. time for soybean oil ammonolysis in the presence of a carboxylic acid ion exchange resin (Fig. 1, Run 3) suggests a diffusion-controlled process, perhaps because the oil was largely adsorbed on the resin surface. The predominant linearity for ammonolysis in a lower level of NH_3 (3:1 NH_3/RCOO ratio, Fig. 1, Run 12) is surprising because the proportion of NH_3 calculated to be in the liquid phase was about 75%. The linearity may result from a two phase system under these conditions, and so suggests that a solution of 22% NH_4OAc in NH_3 has a low solubility in soybean oil. Other runs with a lower catalyst concentration and 10 times greater NH_3/oil ratio apparently were homogeneous, a condition which indicates good solubility of soybean oil in liquid NH_3 containing up to 15% catalyst.

The commonly accepted mechanism for ester ammonolysis involves a general acid base catalysis by NH_3 (26) wherein either positive or negative ions, or both, in the environment can facilitate the conversion of the cyclic six-member transition state to products:



Many of the ionic catalysts tested in this work (e.g., the zwitterion form of the amino acids) may function by facilitating the reaction as drawn. Ammonium ions probably further accelerate this reaction by assisting protonation of the leaving R'O group and also may promote the reaction by way of noncyclic intermediates (13).

This facile synthesis of unsaturated amides from vegetable oils under mild thermal conditions provides a route to aldehyde amides and amino amides of potential interest for polyamides. This route facilitated our current research program on making nylon-9 from soybean oil. The surfactant and corrosion-inhibiting activity observed for soybean amides may also be of potential value (6).

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