Reaction of Fatty Acids with 3,3'-Iminobis-propylamine to Produce Soil Hydrophobic Agents

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The reaction between two moles of fatty acid and one of 3,3'-iminobis-propylamine (DPTA) is somewhat analogous to the reaction between fatty acid and diethylenetriamine (DETA) that we had reported previously, but there are significant differences. Conversion to the diamide $HN(CH_2CH_2CH_2NHCOR)_2$ proceeds much more rapidly but less efficiently than does the reaction of fatty acid with DETA. The former diamide is obtained in only about a 70% yield and byproducts are obtained, whereas the reaction with DETA yields the diamide almost quantitatively. Cyclization to the pyrimidine

$$RCONHCH_2CH_2CH_2\ NCH_2CH_2CH_2N = CR$$

is extremely slow and incomplete. The analogous cyclization of α,ω-diamides of DETA produces high yields of imidazolines. The AOCS wet method for amine titration gave erroneous structural information when the test was applied to the diamides of DPTA, as was the case for the DETA-diamide. The water repellency of soils treated with a homologous series of fatty iminobis-propylamine (DPTA)-diamides was studied, and the following observations were made: 1) the fatty DPTA-diamides were slightly more hydrophobic than the fatty DETA-diamides, which we ascribe to the additional methylene groups of the former; 2) hydrophobicity intensified with increasing molecular weight of the saturated fatty acids; and 3) unsaturation, as in the oleic derivative, enhanced hydrophilicity.

This study represents a continuation of research (1,2) on organic compounds which, when applied to soils, would make the soils hydrophobic and thus facilitate water harvesting. Water harvesting is the process of collecting water from plots that have been made water-repellent, so that the runoff from these plots may be employed in agriculture. This technique would be particularly useful in arid and semiarid areas.

The purpose of this research is to find relatively inexpensive, easily applied surfactants that would increase runoff by reducing water infiltration of the soil. A variety of compounds, including metallic soaps, dialkyl quaternary ammonium chlorides, fatty amine acetates and sodium methyl silanolate, have been tried with varying degrees of success (3). Investigations with cationic surfactants showed that these were strongly absorbed by clay surfaces through ionic bonding, which was not readily broken by washing. The cationic surfactants created a layer of increased hydrophobic character beneath the soil's surface (4,5). These results suggested that an investigation of various cationic structures on soil properties would be fruitful.

For a study of chemical structure vs physical properties, the cationics selected had to be available over a wide range of molecular weight, such as the fatty acid derivatives of diethylenetriamine (DETA) and 3,3'-iminobis-propylamine (DPTA). These compounds are used industrially as textile softening agents and in plastics and polymers as antistatic agents. Clay soils are prevented from crusting by addition of a liquid dispersion of fatty DETA-diamides or fatty DPTA-diamides (6). Although the fatty DETA-diamides were evaluated previously (1,2), a similar characterization of the fatty DPTA-diamides has not appeared in the chemical literature.

The objectives of this investigation were a) to prepare diamides and pyrimidines from the C_9-C_{18} saturated fatty acid, methyl oleate and tallow fatty acids and DPTA through a study of reaction parameters such as temperature, time and reduced pressure; and b) to measure their physical and chemical properties for a comparison with the properties obtained previously for the fatty DETA-diamides. This comparison would bring into focus the relative effectiveness of soil hydrophobic agents.

MATERIALS AND METHODS

Materials. The following chemicals were used: 3,3'-iminobis-propylamine and nonanoic (C_9) (pelargonic) acid from Aldrich Chemical Co. (Milwaukee, Wisconsin); C_{12}, C_{14}, C_{16} and C_{18} saturated fatty acids from Armak Industrial Chemical Division (Chicago, Illinois); tallow fatty acids T-11 and T-22 from Procter & Gamble, Industrial Chemical Division (Cincinnati, Ohio); and methyl oleate (laboratory preparation).

Instrumentation. The following instruments were used: Model 1610 infrared spectrophotometer from Perkin-Elmer Corp. (Norwalk, Connecticut); a Fisher-Johns melting point apparatus from Fisher Scientific Co. (Pittsburgh, Pennsylvania); contact angles, Gaertner goniometer from Gaertner Scientific Corp. (Chicago, Illinois); a Jeol JNM-GX 400 FT NMR spectrometer (Peabody, Massachusetts); and a Finnigan MAT-331A mass spectrometer from Finnigan Corp. (Sunnyvale, California).

Soils. Granite Reef soil is a sandy loam soil, supplied by the U.S. Water Conservation Laboratory (USDA, Phoenix, Arizona). Walla Walla soil contains 30% clay and organic matter and was supplied by the Columbia Plateau Conservation Research Center (USDA, Pendleton, Oregon).

Synthetic procedure: preparation of diamide derivatives. A 26.7-g volume of DPTA (0.20 mol) was added

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rapidly increased to over 200 C, and the theoretical amount of water was obtained in a short period of time. The resultant product, however, contained considerable amounts of the triamide. An experiment was carried out, similar to that described, in which no attempt was made to control temperature. Samples were removed periodically for analysis (Fig. 2). The temperature rapidly increased to 210 C, and the reaction was completed in 90 min. The crude reaction product, recrystallized from isopropanol, was a yellow powder and contained 1.09 meq/g total amine (1.64 theoretical), indicating the product to be a mixture of 66% diamide and 34% triamide. The difference in reactivities of primary and secondary amines, the steric differences between these amines in DPTA, the limited concentration of the carboxylic reagent for product formation and the requirement of relatively higher temperature for triamide formation suggest the formation of diamide is kinetically favored.

Physical properties. The melting points of the DPTA-diamides are reported in Table 1. Melting points ranged from 101-118 C, and decomposition occurred when the diamides were heated above 240 C. To determine the solubility of the DPTA-diamides, 100 ml solvent was added to 10 g palmitic DPTA-diamide and heated with agitation on a hot plate; temperature of clarification was noted. The diamide was insoluble in boiling acetone, carbon tetrachloride and hexane. In ethanol, isopropanol and toluene, the solution became clear at 60-64 C. The diamide in kerosene did not become clear until heated to 76-80 C.

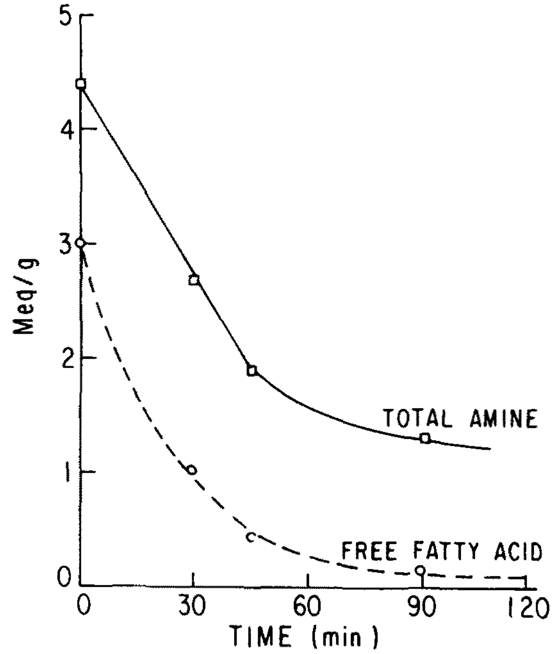

FIG. 2. Reaction rate study: effect of temperature on reaction rate and subsequent triamide formation. 2 mol palmitic acid + 1 mol 3,3'-Iminobis-propylamine, 200–210 C.

TABLE 1

Analytical and Physical Properties of Diamides

RCOOH	Total amine (meq/g) Theoretical	Total amine (meq/g) Found	Melting point	Contact angle (°)
Diethylenetriamine				
C_8H_{17}	2.61	2.60	91–92	94
$C_{11}H_{23}$	2.14	1.85	110–111	99
$C_{13}H_{27}$	1.96	1.69	112–113	99
$C_{15}H_{31}$	1.72	1.70	116–117	96
$C_{17}H_{35}$	1.57	1.50	118–119	98
Δ^9-$C_{17}H_{33}$*cis*	1.57	1.57	52–53	50
Δ^9-$C_{17}H_{33}$*trans*	1.57	1.58	91–92	62
Tallow fatty acid[a]	1.59	1.62	45–55	63
Tallow fatty acid [b]	1.59	1.60	55–65	97
Iminobis-propylamine				
C_8H_{17}	2.43	2.47	101–102	88
$C_{11}H_{23}$	2.02	1.95	106–107	90
$C_{13}H_{27}$	1.81	1.78	109–110	94
$C_{15}H_{31}$	1.64	1.62	114–115	95
$C_{17}H_{35}$	1.51	1.48	117–118	96
Δ^9-$C_{17}H_{33}$*cis*	1.51	1.58	69–70	55
Tallow fatty acid[a]	1.53	1.58	50–55	47
Tallow fatty acid[b]	1.53	1.58	62–68	66

[a] T-22 fatty acids, C_{18}*cis* = 36%, C_{18}*trans* = 7%.
[b] T-11 fatty acids, C_{18}*cis* = 6%, C_{18}*trans* = 24%.

Analyses. The fatty DPTA-reaction product, although predominantly diamide, contained significant amounts of the triamide. The compounds after purification were examined by ^{13}C NMR and MS for structural identification.

^{13}C NMR data were obtained for the DPTA derivatives prepared from pelargonic, lauric, myristic and oleic acids (Table 3). In all cases the spectra confirm the structures as symmetrical diamides, with shifts in general agreement with those reported by Butler et al. (8) for stearic DETA-diamides. There were no new resonances in the spectra of DPTA derivatives when compared to DETA derivatives. Consequently, the central methylene carbon in the propyl group was assigned to the 29 ppm region, where there is some resonance multiplicity. The spectrum of the oleic derivative was similar to that of the saturated acids. As expected, it possessed two downfield resonances (129.7 and 130.0 ppm) for the C_9 and C_{10} olefinic carbons. In addition, there were two additional upfield lines at 27.20 and 27.23 ppm, which were assigned to the C_8 and C_{11} allylic carbons (9).

MS was investigated as a means for determining purity of the fatty DPTA-diamides. The major impurity was the fatty DPTA-triamide. According to the AOCS official method for total amine, low values were obtained, indicating that some of the DPTA reaction products might contain as much as 25% of the triamide. The pelargonic DPTA-triamide was analyzed by electron impact (EI) and desorption chemical ionization (DCI) MS. Neither technique produced a useful spectrum of this compound. Therefore, it is concluded that MS cannot be used to confirm the presence of high molecular weight triamide impurities in the fatty DPTA-diamides.

Physical properties. The melting points and contact angles of the fatty DPTA-diamides are compared with the fatty DETA-diamides in Table 1. Most melting points of the diamides of both series were above 100 C; this is typical of high molecular weight amides. The high molecular weight of the diamides resulted in low solubility in most organic solvents. To overcome this deficiency, DPTA-diamides were prepared from T-22 fatty acids, as obtained from tallow, and T-11 fatty acids, tallow fatty acids that have been previously isomerized.

It was planned to establish the hydrophilic or hydrophobic nature of the diamides by contact angle determination. The angles for the lauric acid diamides and higher saturated homologs were 90° and above. Thus, the contact angle measurements cannot discriminate between members of a homologous series, as was also found previously (2). The oleic DPTA-diamide had a contact angle of 55° and was, therefore, more hydrophilic. Since contact angle measurements appeared fairly insensitive to structural differences, it was necessary to determine the actual performance on soil treated with the diamides. The results of the soil infiltration test are recorded in Table 2.

Soil structure is an important factor in the ease with which it can be modified to repel water. For example, small-particle-sized clay soil is more readily made hydrophobic than the larger-particle-sized sandy loam soil. Whereas water penetrated the lauric acid DPTA-diamide-treated Granite Reef soil in 5 hr, similar to the control, a week or longer was required for the higher molecular weight saturated DPTA-diamides. Water passed through the oleic DPTA-diamide in 3 hr and the tallow fatty acid DPTA-diamides within 8 hr, showing the hydrophilic nature of these compounds.

On clay-containing Walla Walla soil, a period of one week or longer was required for all the DPTA-diamide-treated soils, except for the oleic DPTA-derivative. The fatty DPTA-diamides were slightly more hydrophobic than the fatty DETA-diamides, perhaps because of the additional methylene group in the DPTA-diamides. However, since the fatty acid DPTA-reaction is less specific and generates more byproduct, it would be a less desirable source of hydrophobic agents than the fatty acid DETA reaction products.

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