

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY¹]

Polymerizable Derivatives of Long-Chain Fatty Acids. VI. Preparation and Applicability of Urea Complexes of Vinyl Esters²

BY DANIEL SWERN AND WILLIAM S. PORT

It has been shown that vinyl esters of long-chain fatty acids, such as vinyl pelargonate, laurate, palmitate and stearate, form urea complexes in good to excellent yield (56 to 99%). Advantage has been taken of the technique of urea complex formation to separate vinyl pelargonate from cross-linking contaminants and to recover monomeric vinyl palmitate from mixtures containing monomer, polymer, inhibitor and other unknown impurities. The technique of urea complex formation should be useful in a variety of polymerization and preparation investigations involving monomers which contain long chains.

The recently discovered characteristic of urea of forming well-defined, crystalline complexes readily with straight-chain aliphatic compounds but not with most branched-chain or cyclic compounds,³⁻⁵ has tremendous potential value in a wide variety of isolation and purification problems. In studying the polymerization of vinyl esters of long-chain fatty acids,⁶ it was believed that urea complex formation would aid considerably in the solution of two problems, provided that urea formed complexes readily in high yield with long-chain vinyl esters. These problems were (1) the separation of vinyl pelargonate from minor quantities (probably less than 1%) of cross-linking contaminants and (2) the recovery of vinyl palmitate from mixtures which also contained polymer, inhibitor, and other (unknown) impurities.

It was quickly determined that pure vinyl pelargonate, laurate, palmitate and stearate⁷ readily formed urea complexes in yields ranging from 56 to 99%. The complexes were typical, well-defined, easily filtered crystals, usually needles and, from all indications, were similar in every way to the complexes obtained from other classes of straight-chain aliphatic compounds.

Purification of Vinyl Pelargonate.—Commercial pelargonic acid (80–90% pelargonic acid) is prepared by oxidative cleavage of oleic acid, and it is contaminated with mono- and dibasic materials. Multiple fractional distillation yields pelargonic acid having the correct physical and chemical characteristics, but it is undoubtedly still contaminated with small quantities of polyfunctional impurities because vinyl pelargonate prepared from it⁷ forms cross-linked, insoluble polymers under conditions which yield soluble polymers from pure vinyl caprylate, laurate, myristate, palmitate and stearate.⁶ These impurities are not removed even by repeated fractional distillation of the vinyl pelargonate, and it was concluded that they probably consisted of divinyl esters of dibasic acids, such as adipic and glutaric acids.

Since ease of formation and stability of urea complexes decrease as the chain length of the straight-chain compounds decreases, it was anticipated that the cross-linking contaminants, particularly if their chain length was less than that

of vinyl pelargonate, would remain in the filtrate from which the urea complex of vinyl pelargonate had been precipitated. The vinyl pelargonate isolated from the complex should then yield soluble thermoplastic polymers rather than cross-linked gels.

Vinyl pelargonate was precipitated in three steps as urea complex, and each portion isolated from the complex yielded a soluble polymer. Total recovery of vinyl pelargonate was 99%, thus confirming the premise that cross-linking contaminants were present in minor amounts. In addition to yielding a suitable grade of monomer, the technique was relatively simple and rapid.

Recovery of Vinyl Palmitate from Mixtures Containing Polymers and Other Impurities.—In studying the fundamental properties of polyvinyl palmitate, and other polyvinyl esters of long-chain acids,⁶ it is necessary to purify the polymers by multiple solvent precipitation to ensure freedom from unpolymerized monomer, inhibitors which have been added to minimize subsequent polymerization, and other impurities. When only a low conversion to polymer has been effected, large amounts of residual monomer have to be separated and these are usually discarded because of the difficulty in isolating the monomer from the complex mixture in which it is present. Consideration of the nature of the mixture indicated that only unpolymerized vinyl palmitate should be able to form a urea complex. This was confirmed and it was shown that vinyl palmitate could be readily isolated from such mixtures by precipitation as urea complex. The recovered vinyl palmitate was suitable for use in polymerizations.

The technique just described should be applicable to the isolation of vinyl esters of other long-chain acids from similar mixtures and of various other monomers containing long straight chains.

Experimental

Materials Used.—The vinyl esters were prepared as described previously.⁷ Urea was reagent grade.

Preparation of Urea Complexes of Vinyl Esters.—The preparation of vinyl palmitate-urea complex is typical: 5 g. of vinyl palmitate, iodine number 87.9, and 15 g. of urea was dissolved in 100 ml. of methanol with gentle warming. Precipitation began while the solution was still warm (about 50°). It was cooled first to room temperature and filtered (weight of complex 10.6 g.) and then cooled to 5° and again filtered (weight of complex 4.3 g.), giving a 75% yield of long needle-like crystals of complex, iodine number 22. The iodine number of the complex is significant since we have shown in studying the preparation of over 50 urea complexes of long-chain fatty acids, methyl esters, and alcohols that the weight ratio of urea to other component is almost invariant at 3:1. In a control experiment no precipitate was obtained when a solution of 5 g. of vinyl palmitate in 100 ml. of methanol (urea absent) was cooled to 5°.

Similar results were obtained in the preparation of complexes from vinyl pelargonate (56% yield), vinyl laurate (61% yield) and vinyl stearate (70% yield). In the preparation of the vinyl stearate complex, about 10–20% isopropyl alcohol was added to the methanol to obtain a homogeneous solution. By employing a urea to vinyl ester ratio of 5:1, yields of complex were usually over 85%.

Purification of Vinyl Pelargonate.—A sample of vinyl pelargonate, iodine number, 136.2 and n_D^{20} 1.4280, yielded cross-linked insoluble gels when polymerized with benzoyl peroxide as initiator under conditions which yielded soluble polymers from other long-chain vinyl esters prepared in an identical manner.^{6,7} The vinyl pelargonate was freed from

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(2) Presented at the Spring Meeting of the American Chemical Society, Buffalo, N. Y., March 24, 1952. For paper V, see *Ind. Eng. Chem.*, **43**, 2105 (1951).

(3) F. Bengen, German Patent Application O.Z. 12438, March 18, 1940; Translation Book 391, Technical Oil Mission Reel 143, Frames 135–139.

(4) W. Schlenk, Jr., *Ann.*, **565**, 204 (1949).

(5) W. J. Zimmerschied, R. A. Dinerstein, A. W. Weitkamp and R. F. Marschner, *Ind. Eng. Chem.*, **42**, 1300 (1950).

(6) W. S. Port, E. F. Jordan, Jr., J. E. Hansen, T. J. Dietz and D. Swern, *J. Polymer Sci.*, **7**, 207 (1951).

(7) D. Swern and E. F. Jordan, Jr., *THIS JOURNAL*, **70**, 2334 (1948).

cross-linking contaminants as follows: 200 g. of vinyl pelargonate and 800 g. of urea were dissolved in 4000 ml. of methanol. The solution was allowed to stand overnight at room temperature (27°) and then filtered, yielding 320 g. of complex. Addition of water to the precipitate dissolved the urea and yielded 80 g. (40% of the original ester) of vinyl pelargonate, n_D^{20} 1.4284, as a water-insoluble colorless oil.

The methanol filtrate from the separation of the first crop of complex was cooled to 2° and an additional 316 g. of complex was obtained. The vinyl pelargonate isolated from it weighed 78 g. (39% yield), n_D^{20} 1.4280.

The second methanol filtrate was concentrated to about one-fourth its volume and cooled to room temperature. The yield of urea complex obtained at this stage was 187 g. from which 41 g. (20% yield) of vinyl pelargonate was isolated.

The total yield of vinyl pelargonate recovered was 99%. A portion of each fraction was polymerized⁶ and soluble polymers were obtained from each.

Recovery of Vinyl Palmitate from Mixtures.—Twenty-six grams of crude vinyl palmitate, also containing polyvinyl palmitate, inhibitors and unknown (colored) components, was added to 500 ml. of methanol. Some polyvinyl palmitate precipitated and was separated by filtration. Seventy-five grams of urea was dissolved in the filtrate and the solution was allowed to stand overnight at room temperature. The quantity of complex which precipitated was 44 g. and it contained about 40% of the vinyl palmitate originally present in the crude mixture. Vinyl palmitate recoveries of as high as 83% have been obtained by increasing the ratio of urea to crude vinyl palmitate to about 5:1.

The recovered vinyl palmitate formed thermoplastic soluble polymers when heated with benzoyl peroxide.⁶

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Peculiarity of Dichroism of Aromatic Molecular Compounds. I. The Dichroisms of Quinhydrone, *s*-Trinitrobenzene-*p*-Bromoaniline and Related Compounds

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From the measurements of dichroisms of quinhydrone, chloranil-hexamethylbenzene, *s*-trinitrobenzene-*p*-bromoaniline and picryl chloride-hexamethylbenzene, the crystal structures of which had been determined by X-ray analysis, the following general rule has been derived: "for the first bands which are supposed to consist of absorptions principally due to π -electrons and the substituents of the benzene rings, the absorptions with the electric vectors vibrating perpendicular to the ring plane are always bathochromic and hyperchromic to the absorptions with those vibrating parallel to it." This result is quite reverse to the case of common aromatic compounds, and gives interesting suggestions to the nature of the intermolecular forces in molecular compounds.

Introduction

In order to explain the intense color of molecular compounds, a number of researches have been carried out from various physical and chemical points of view. Recently Michaelis and Granick¹ measured the absorption spectra of molecular compounds of the quinhydrone type in solutions. But in the solution all of them dissociate into their components, although not completely. So it is necessary for us to measure their absorptions in crystalline state. These studies, however, have never been attempted, because of the difficulty in getting large but thin crystals suitable for ordinary measurements of absorption spectra. By making use of the microscopic method,² this difficulty can be easily avoided. In the previous works,^{2,3} the dichroisms of the π -bands in common aromatic compounds have been observed and the following general rule established; "the \parallel -absorption is always bathochromic and hyperchromic to the \perp -absorption." Here, \parallel - or \perp -absorption means the spectrum by the light with the electric vector abundant with the parallel or perpendicular component to the benzene ring. So it seems very interesting to investigate whether the above rule holds also for the molecular compounds. A few compounds whose crystal structures had been determined by X-ray analysis were selected and their dichroisms in the visible and ultraviolet region were quantitatively measured.

(1) L. Michaelis and S. Granick, *THIS JOURNAL*, **66**, 1023 (1944).

(2) K. Nakamoto, *ibid.*, **74**, 390 (1952).

(3) K. Nakamoto, *ibid.*, **74**, 392 (1952).

Experimental

Materials (1) **Quinhydrone.**—Microcrystals by Merck and Co., Inc., were used, monoclinic system, m.p. 169°. Thick crystals are violet-black and have metallic luster due to their surface reflections; straight extinction, when observed from the *c*-axis. Thin crystals are dichroic; violet red, with polarized light parallel to the needle axis (*a*-axis) and red, with polarized light perpendicular to it.

(2) **Chloranil-Hexamethylbenzene.**—Blood red solution is obtained at once, when the dilute alcoholic solutions of both the components are mixed in the molar ratio of 1:1. By natural evaporation of the solvent red acicular crystals are produced, m.p. 198°; rhombic system; straight extinction; strongly dichroic; deep violet, parallel to the needle axis (*a*-axis) and reddish-yellow, perpendicular to it.

(3) ***s*-Trinitrobenzene-*p*-Bromoaniline.**—Orange acicular crystals are produced when the dilute alcoholic solutions of both the components are mixed in the molar ratio of 1:1 and the mixed solution is evaporated, m.p. 109°; monoclinic system; straight extinction; orange, parallel to the needle axis (*a*-axis) and bright yellow, perpendicular to it (*b*-axis).

(4) **Picryl Chloride-Hexamethylbenzene.**—Deep yellow acicular crystals are prepared by mixing the chloroform solutions of both the components at the molar ratio of 1:1, and allowing the solution to evaporate at room temperature, m.p. 148°; rhombic system; straight extinction; deep yellow, parallel to the needle axis (*a*-axis), and light yellow, perpendicular to it.

Results and Discussion

Part I. Molecular Compounds of the Quinhydrone Type. (1) **Quinhydrone.**—In 1935, Palacios and Foz⁴ studied the crystal structure of quinhydrone, but their result was not perfect. Recently Osaki and Matsuda⁵ succeeded in its

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(5) K. Osaki and H. Matsuda, *Acta. Cryst.*, in press.