

with ether. The ether was taken off and the residue distilled giving 14.5 g. (65.6%) of distillate, b.p. 76–78° (10 mm.), n_D^{25} 1.4649. The infrared spectrum of the product showed strong absorption at 1625 cm^{-1} .

Anal. Calcd. for $\text{C}_8\text{H}_{13}\text{O}_2\text{Br}$: C, 43.5; H, 5.88; Br, 36.2. Found: C, 43.81; H, 6.04; Br, 36.58.

Ethyl β -Phenylpropiolate (XVII).—Triethyl phosphonoacetate (11.2 g., 0.05 mole) was added at 25° dropwise to a slurry of 50% sodium hydride (2.4 g., 0.05 mole) in 100 cc. of dry 1,2-dimethoxyethane. The solution was stirred for 1 hour until hydrogen gas evolution ceased. To the homogeneous solution was added dropwise iodine (12.7 g., 0.05 mole) dissolved in a minimum of solvent. After the addition, the solution was stirred at room temperature for 1 hour and cooled to 10°; 50% sodium hydride (4.8 g., 0.10 mole) was added to the chilled solution all at once. The mixture was allowed to come to room temperature gradually during which time rapid gas evolution took place. Benzaldehyde (5.3 g., 0.05 mole) was added dropwise keeping the temperature at 25°. After the addition the solution was heated slowly to 40° at which temperature rapid gas evolution took place. After gas evolution had ceased, the solution was cooled and a large excess of water added. The aqueous solution was extracted with two 100-ml. portions of ether, and the ether extract dried over magnesium sulfate and evaporated. The residue now was distilled giving 5.1 g. (59% yield) of distillate, b.p. 78–80° (0.1 mm.), n_D^{25} 1.5800. The product absorbed at 2220 cm^{-1} and its infrared spectrum was identical with that of an authentic sample.

1-Carboethoxy-3-ethyl-3-phenylallene (XVIII).—Triethyl phosphonoacetate (11.2 g., 0.05 mole) was added dropwise at 25° to a slurry of 50% sodium hydride (2.5 g., 0.05 mole) in 100 cc. of dry 1,2-dimethoxyethane. The solution was

stirred for 1 hour until gas evolution had ceased. Phenyl ethyl ketene (7.3 g., 0.05 mole) was added dropwise keeping the temperature below 30°. After the addition, which was exothermic, the solution was heated briefly to 50°, cooled to room temperature and taken up in a large excess of water. The aqueous solution was extracted with two 100-ml. portions of ether, the ether extract dried over magnesium sulfate and evaporated. The residue was distilled giving 3.5 g. (32% yield) of liquid, b.p. 89–90° (0.1 mm.), n_D^{25} 1.5490. The product was unstable, becoming viscous on standing. The infrared spectrum of the product showed strong absorption at 1940 cm^{-1} .

Anal. Calcd. for $\text{C}_{14}\text{H}_{16}\text{O}_2$: C, 77.82; H, 7.46. Found: C, 77.62; H, 7.74.

1-Carboethoxy-2-phenylcyclopropane (XIX).—Triethyl phosphonoacetate (22.4 g., 0.1 mole) was added dropwise with stirring to a slurry of 50% sodium hydride (5.0 g., 0.014 mole) in 100 cc. of dry 1,2-dimethoxyethane at 25°. After the addition the solution was stirred for 1 hour until gas evolution had ceased. Styrene oxide (12.0 g., 0.1 mole) was added. The solution was refluxed for 4 hours at 85°, cooled to room temperature and taken up in a large excess of water. The aqueous solution was extracted with two 100-ml. portions of ether. The ether extract was dried over magnesium sulfate, evaporated and the residue distilled giving 8.0 g. (42% yield) of distillate, b.p. 100° (0.5 mm.). The distillate crystallized on standing, m.p. 37–38°. The product showed the expected infrared spectrum with the characteristic cyclopropane band at about 1020 cm^{-1} .¹⁹

Anal. Calcd. for $\text{C}_{12}\text{H}_{14}\text{O}_2$: C, 75.51; H, 7.36. Found: C, 75.38; H, 7.39.

(19) V. A. Stabey, *J. Am. Chem. Soc.*, **76**, 3604 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN 1, N. Y.]

Intramolecular Carboxylate Attack on Ester Groups. II. The Effect of Diastereoisomerism in Polymers and their Low Molecular Weight Models¹

BY E. GAETJENS² AND H. MORAWETZ

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The hydrolysis catalyzed by neighboring carboxylate attack on ester groups in copolymers of acrylic acid with small proportions of acrylic or methacrylic esters follows first-order kinetics, but the corresponding reactions of copolymers of methacrylic acid give strongly curved first-order plots and behave as if the copolymers contained two kinds of ester groups with reactivities differing by a factor of about 10. The effect is interpreted as due to steric isomerism of polymer chain sections in the neighborhood of the ester functions and is discussed in terms of present knowledge of conformations of vinyl polymers. To clarify the phenomenon, the hydrolysis rates of monoesters of *meso*- and *rac*- α,β -dialkylsuccinic acids were compared in the pH range where the rate is controlled by neighboring carboxylate attack. The difference in the reactivities of the isomers was very slight with methyl substituents; with isopropyl substituents the derivative of the racemic acid was about twice more reactive. The monoesters of the α,β -dialkylsuccinic acids are much more reactive than monoesters of succinic acid and their hydrolyses have lower activation energies. The data imply that the transition state is closer to a *skew* than to an eclipsed conformation and that the increased reactivity of succinic monoesters on α,β -disubstitution reflects the fact that the energy difference of *trans* and *skew* conformations is less in 1,1',2,2'-tetrasubstituted than in 1,2-disubstituted ethanes.

Introduction

Previous investigations have demonstrated that the hydrolytic rate of carboxylic esters with a free carboxyl attached to the β - or γ -carbon is proportional in the pH range 3–7 to the degree of ionization of the carboxyl group.^{3–9} The mechanism of the

reaction was clarified by Bender and Neveu⁸ and by Bruce and Pandit¹⁰ who showed that the attack of the carboxylic acid anion on the ester group results in formation of an acid anhydride.

Experiments with copolymers of acrylic or methacrylic acid with 1–2 mole % of an acrylic or methacrylic *p*-nitrophenyl ester have revealed an unexpected phenomenon: Whereas ester groups in copolymers of methacrylic esters with acrylic acid hydrolyzed by first-order kinetics, copolymers containing methacrylic esters in a methacrylic acid chain gave first-order plots with a pronounced downward curvature.^{11,12} The polymer behaved as

(1) Financial support of this work by the U. S. Army Office of Ordnance Research is gratefully acknowledged.

(2) Department of Biology, Brookhaven National Laboratory, Upton, L. I.

(3) H. Morawetz and P. E. Zimmering, *J. Phys. Chem.*, **58**, 753 (1954).

(4) P. E. Zimmering, E. W. Westhead, Jr., and H. Morawetz, *Biochem. Biophys. Acta*, **25**, 376 (1957).

(5) E. R. Garrett, *J. Am. Chem. Soc.*, **79**, 3401 (1957).

(6) H. Morawetz and I. Oreskes, *ibid.*, **80**, 2591 (1958).

(7) M. L. Bender, F. Chloupek and M. C. Neveu, *ibid.*, **80**, 5384 (1958).

(8) M. L. Bender and M. C. Neveu, *ibid.*, **80**, 5388 (1958).

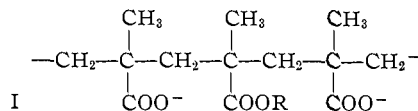
(9) E. Gaetjens and H. Morawetz, *ibid.*, **82**, 5328 (1960).

(10) T. C. Bruce and U. K. Pandit, *ibid.*, **82**, 5858 (1960).

if it contained ester groups of two widely divergent reactivities and the kinetic data could be fitted to an expression of the type

$$X = \alpha \exp(-k_1 t) + (1 - \alpha) \exp(-k_2 t) \quad (1)$$

where X is the fraction of ester groups remaining at time t . The ratio k_1/k_2 of the two rate constants was 10–14 and the fraction α of the more reactive groups about 0.2.¹² This observation was interpreted as follows: A section of the polymer chain in the neighborhood of an ester group is represented by I. Thus both the carbons carrying the ester and



the carboxylate groups are asymmetric. The different reactivity of ester groups may, therefore, reflect a difference in the ease with which a carboxylate may attack the esteric carbon depending on whether the carbons to which the ester and the carboxylate are attached have the same or the opposite steric configuration. If this interpretation is justified, kinetic data such as those described could be utilized to characterize the stereoregularity of vinyl-type polymers.

To assist in the interpretation of the phenomenon described above it was desirable to study the hydrolysis of copolymers of *p*-nitrophenyl acrylate with acrylic or methacrylic acid and compare the results with those for the methacrylic ester copolymers. In addition, the rate was determined for the neighboring carboxylate-catalyzed hydrolysis of monoesters of the *meso* and racemic forms of α,β -dimethylsuccinic acid and α,β -diisopropylsuccinic acid, so as to assess the role of diastereoisomerism in this type of reaction on well characterized model compounds.

Results

The kinetics of the hydrolysis of *p*-nitrophenyl groups attached to three polycarboxylic acids is represented in Fig. 1. There is a striking difference between the behavior of the acrylic acid-acrylic ester copolymer whose hydrolysis follows strictly first-order kinetics and the hydrolysis of the copolymers of methacrylic acid with the acrylic or methacrylic ester, which give both strongly curved first-order plots. The reactions of the last two copolymers follow closely eq. 1 and Table I

TABLE I
RATE CONSTANTS FOR THE HYDROLYSIS OF *p*-NITROPHENYL ESTER GROUPS IN ACID-ESTER COPOLYESTERS AT 25°

Acid	Ester	pH	$10^4 k_1$ (sec. ⁻¹)	$10^4 k_2$ (sec. ⁻¹)	k_1/k_2	α
Methacrylic	Methacrylic	3.5	5.7	0.55	10.4	0.25
Methacrylic	Acrylic	3.5	34	3.1	11	0.20
Acrylic	Acrylic	3.5	31.6

lists the pertinent observed rate constants. It can be seen that for the acrylic and methacrylic ester copolymers of methacrylic acid the k_1/k_2 ratio is very similar and that the fraction α of the more reactive ester groups is also in the same range.

(11) P. E. Zimmering, Ph.D. Thesis, Polytechnic Inst. of Brooklyn, 1955.

(12) H. Morawetz and E. Gaetjens, *J. Polymer Sci.*, **32**, 526 (1958).

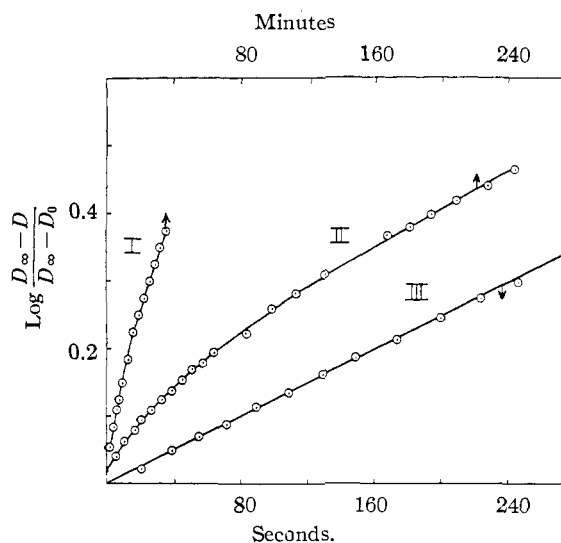


Fig. 1.—Hydrolysis of acid-ester copolymers at 25° and pH 3.5: I, *p*-nitrophenyl acrylate-methacrylic acid copolymer; II, *p*-nitrophenyl methacrylate-methacrylic acid copolymer; III, *p*-nitrophenyl acrylate-acrylic acid copolymer.

The results obtained with the monoesters of α,β -disubstituted succinic acids are listed in Table II. The difference in the reactivity of the fully ionized *p*-acetamidophenyl monoesters of α,β -dimethylsuccinic acid (AP-DMS) at pH 7.0 is only 6%; at lower pH values the reactivities are within experimental error of one another, indicating that a slightly higher degree of ionization of the racemic compound compensates for the lower reactivity of the ionized species.

TABLE II
HYDROLYSIS OF *p*-ACETAMIDOPHENYL ACID α,β -DIMETHYL SUCCINATE (AP-DMS) AND PHENYL ACID α,β -DIISOPROPYL SUCCINATE (P-DIS)

Ester	Acid configuration	pH	Temp., °C.	$10^4 k$, sec. ⁻¹
AP-DMS	<i>Meso</i>	3.35	25.3	49.2
AP-DMS	<i>Meso</i>	4.25	25.3	176
AP-DMS	<i>Meso</i>	7.00	25.3	330
AP-DMS	<i>Meso</i>	7.00	15.9	129
AP-DMS	<i>Meso</i>	7.00	8.7	65
AP-DMS	Racemic	3.35	25.3	49.1
AP-DMS	Racemic	4.25	25.3	174
AP-DMS	Racemic	7.00	25.3	312
AP-DMS	Racemic	7.00	15.9	124
AP-DMS	Racemic	7.00	8.4	59.2
P-DIS	<i>Meso</i>	3.50	44.6	177
P-DIS	<i>Meso</i>	3.50	25.3	36
P-DIS	<i>Meso</i>	3.50	17.2	15
P-DIS	Racemic	3.50	25.3	57

It must be concluded that the spatial interference of the methyl groups in dimethylsuccinic acid monoesters is insufficient to render the reaction sensitive to steric isomerism. This is somewhat surprising in view of the report that the two isomeric dimethylsuccinic acids have widely different rates of anhydride formation.¹³ One would

(13) W. A. Bone and C. H. G. Sprankling, *J. Chem. Soc.*, **75**, 839 (1899).

imagine that the carboxylate attack on a neighboring ester group resulting in anhydride formation⁸ would be affected by steric isomerism in the same manner as the anhydride formation from the acid, but the latter reaction may be heterogeneous and thus reflect differences in the solubility of the isomeric reagents. It may also be noted that the reaction rate of the *p*-acetamidophenyl ester of unsubstituted succinic acid³ is lower by a factor of ten.

With the monophenyl ester of the α,β -diisopropylsuccinic acid (P-DIS) the reaction rate at pH 3.5 was higher by a factor of 1.58 for the derivative of the racemic acid. These compounds were, unfortunately, too reactive in the fully ionized state to be studied by our technique. We can estimate the *pK* values of these monoesters in the following way: The *pK* for the monoesters of the *meso*- and *rac*-dimethylsuccinic acid is, from the pH dependence of the rate constant in Table II, 4.15 ± 0.04 and 4.11 ± 0.04 , respectively. Ebersson's potentiometric data for monomethyl esters in 50% ethanol¹⁴ show for the diisopropylsuccinic acid derivatives *pK* values higher by 0.48 and 0.65, respectively. If we assume a similar shift for the phenyl esters in water solution, the rate constants for the fully ionized monoesters of *meso*- and *rac*-diisopropylsuccinic acid would be estimated as 0.052 and 0.11 sec.⁻¹, so that the monoester of the racemic acid would be more than twice as reactive¹⁵ as the monoester of the *meso*-acid and eighty times as reactive as phenyl acid succinate at 25°.

Activation energies of the hydrolyses were found to be 15.8, 16.3 and 16.4 kcal./mole for *meso*-AP-DMS, *rac*-AP-DMS and *meso*-P-DIS, respectively. These values lie significantly below the activation energies of about 19 kcal./mole found to be characteristic for the neighboring carboxylate attack on the ester function in monoesters of unsubstituted succinic acid with various phenols.⁹

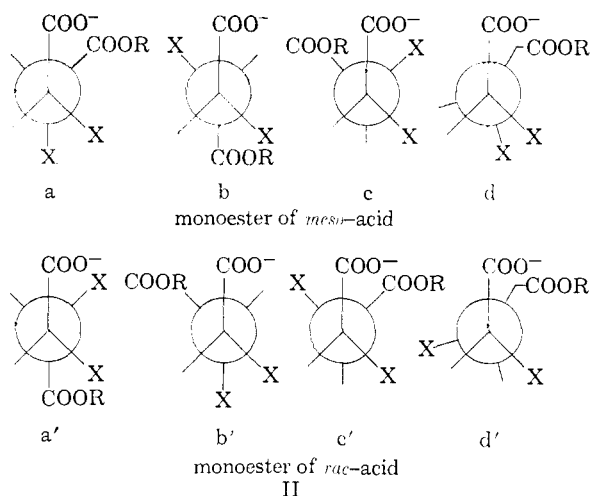
Discussion

Monoesters of α,β -Disubstituted Succinic Acids.—In attempting to interpret the results obtained with the diastereoisomeric monoesters of α,β -disubstituted succinic acids, it is useful to consider the various staggered conformations as well as the eclipsed conformations representing the closest approach of the ester and carboxylate groups as represented in II.

As long as the spatial requirements of the carboxylate groups and the X substituents are comparable, one would expect the energy of the ground states to be very similar for the two diastereoisomers. However, the eclipsed conformation d of the monoester of the *meso*-acid represents obviously a higher potential energy than the corresponding conformation d' of the racemic acid monoester, since d involves a close approach of the

(14) L. Ebersson, *Acta Chem. Scand.*, **13**, 211 (1959).

(15) This estimate may not be very reliable since Ebersson¹⁴ found for monoesters of dimethylsuccinic acid in 50% ethanol the *pK* of the racemic acid derivative to be higher by 0.06, while our kinetic data in water show a *pK* value lower by 0.04. If we had assumed, alternatively, that the difference in the *pK* of the monoesters of the two diisopropylsuccinic acids in water is 0.23 as reported by Ebersson for 50% ethanol solution, the ratio of the rate constants for the fully ionized monoesters of the racemic and *meso*-acid would have been 2.7.



X substituents. It would then be expected that racemic monoester derivatives should react appreciably more rapidly if the transition state is approximated by the eclipsed conformation, and the fact that the two diastereoisomeric α,β -dimethylsuccinic monoesters react at comparable rates indicates that the reagent does not have to pass through conformations d and d' to react. (We may note that in the debromination of 2,3-dibromobutane which involves an eclipsed transition state,¹⁶ the rate constants for the two diastereoisomers differ by a factor of 1.9^{16,17}.) On the other hand, if the transition state is more closely approximated by a staggered conformation in which the carboxylate group is close to the ester group, we have to consider the energies of conformations a, c, b' and c'. It may be seen that in the monoester of the *meso*-acid the two pertinent conformations are both *skew*, while in the monoester of the racemic acid the transition state could be approximated by the *trans* conformation b'. Although *trans* conformations of 1,1',2,2'-tetrasubstituted ethylenes should have lower energies than the corresponding *skew* conformations, the energy difference has been shown to be less than 200 cal./mole in *sym*-tetrachloroethane and in 2,3-dimethylbutane.¹⁸ We would then expect on this basis that the diastereoisomeric esters would not differ appreciably in their reactivity if the X substituent is the relatively small methyl groups, while with larger X substituents the derivative of the racemic acid should be somewhat more reactive. This agrees with the observed reactivity pattern.

The monoesters of the racemic dimethyl- and diisopropylsuccinic acids were found to be 10 and 80 times, respectively, more reactive than the corresponding monoesters of unsubstituted succinic acid. Bruce and Pandit¹⁰ found a similar acceleration of the intramolecular reaction with *gem*-dimethyl substituted succinic or glutaric acid monoesters and ascribed this "*gem*-dimethyl ef-

(16) W. G. Dauben and K. S. Pitzer, in "Steric Effects in Organic Chemistry," ed. M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 9-10.

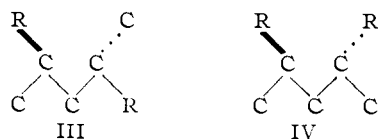
(17) S. Winstein, D. Pressman and W. G. Young, *J. Am. Chem. Soc.*, **61**, 1645 (1939).

(18) Reference 15, p. 53.

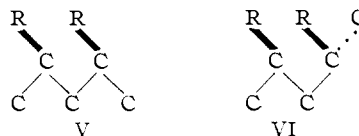
fect"¹⁹ to a "decrease in unprofitable rotamer distribution." It is, in this context, highly significant that the reactions of the α,β -disubstituted succinic acid monoesters have activation energies around 16 kcal./mole, as against an activation energy of 19 kcal./mole for the corresponding reaction of unsubstituted succinic monoesters. This difference may be due, at least in part, to the fact that in the unsubstituted succinic monoesters the *trans* conformation has a considerably lower energy than the *skew* conformation, so that the energy required for the transition between these two conformations makes an appreciable contribution to the activation energy. Thus, we may say that *gem*-dialkyl or α,β -dialkyl substitutions both eliminate a major part of the repulsion which otherwise tends to force the carboxyl and ester groups to be *trans* to each other.²⁰

On the other hand, it has been shown previously that carboxylate attack on phenyl esters can either pass through a tetrahedrally bonded reaction intermediate (as in acetate attack on phenyl acetates) or may take place by a direct displacement mechanism in which the leaving of the phenoxide is synchronized with the approach of the carboxylate to the ester carbon (as in the intramolecular reaction of succinic or glutaric monoesters).⁹ The latter mechanism is characterized by a higher activation energy and a much higher sensitivity to electron-withdrawing *para* substituents. It is possible that the choice between the two mechanisms is rather sensitive to steric factors and that the mechanism is not the same in unsubstituted and in α,β -disubstituted succinic esters. Unfortunately, it proved impossible to check this interpretation by a determination of the reactivity of *p*-nitrophenyl acid α,β -dialkylsuccinates, since these esters were too unstable to be isolated.

Acid-Ester Copolymers.—In chain polymers the conformations of successive C—C bonds in the polymer backbone are not independent of one another but are governed by correlations imposing severe restrictions. This subject has been discussed by Fordham²¹ and subjected to a detailed analysis by Volkenshtein, Ptitsyn and their collaborators, whose results recently have been summarized by Flory.²² For isotactic vinyl polymers the most stable conformation contains an alternating *trans-skew* sequence (III) while the most stable conformation of syndiotactic chains is all *trans* (IV). If the R groups represent an ester function



and a neighboring carboxylate attacking the carbonyl carbon of the ester, the transition state preceding the formation of the six-membered cyclic anhydride should require the two C—R bonds to be parallel, so that the isotactic chain conformation would now have the *trans-trans* sequence V, while the syndiotactic chain would be represented by the *trans-skew* conformation VI.



The passage from III to V would seem to entail a smaller change in energy than that from IV to VI and the intramolecular reaction would, therefore, be expected to be more rapid with isotactic chains. However, the experimental observation that in acrylic acid-acrylic ester copolymers all ester groups are equally reactive shows that this steric effect must be too small to be detectable by observations of reaction kinetics.

In chains of the $(-\text{CH}_2\text{CR}_1\text{R}_2-)_n$ type such as poly-(methacrylic acid), steric interference of the chain substituents is so severe that the C—C—C bond angle in the chain backbone may be distorted considerably from its normal value²³ and the familiar *skew* and *trans* conformations become energetically unfavorable. The crystal structure of isotactic poly-(methyl methacrylate)²⁴ indicates that the *skew* conformations in this polymer are distorted to correspond to a rotation by about 144° from the *trans* position and a similar situation would be expected for poly-(methacrylic acid). Our observation that in methacrylic acid copolymers with methacrylic or acrylic esters the ester groups have two widely different reactivities suggests strongly that in this case with its heavy steric restrictions the ease of approach of the substituents to their nearest neighbor is quite different for the isotactic and the syndiotactic case. Bovey and Tiers have concluded from nuclear spin resonance data that poly-(methyl methacrylate) prepared by radical polymerization has about 8% of asymmetric centers flanked by nearest neighbors with the same configuration (isotactic triads), about 56% with nearest neighbors of the opposite configuration (syndiotactic triads), and a balance of 36% with one nearest neighbor having the same and one the opposite configuration (heterotactic triads).²⁵ It may be noted that Table I gives the fraction of "fast" ester groups as 0.20 and 0.25, which seems too high if they represent isotactic triads alone and too low if they represent the sum of isotactic and heterotactic triads.²⁶

(23) A. M. Liquori, *Acta Cryst.*, **8**, 345 (1955).

(24) J. D. Stroupe and R. E. Hughes, *J. Am. Chem. Soc.*, **80**, 2341 (1958).

(25) F. A. Bovey and G. V. D. Tiers, *J. Polymer Sci.*, **44**, 173 (1960). The corresponding figures for poly-(methacrylic acid) prepared in solvating or precipitating media were reported to us by Dr. Bovey as 12% isotactic, 55% syndiotactic and 33% heterotactic.

(26) In a previous communication (H. Morawetz and E. Gaetjens, *ibid.*, **32**, 526 (1958)) the data for methacrylic acid-methacrylic ester copolymers were interpreted assuming a random sequence of the configuration of the asymmetric centers. This assumption is now known to be erroneous for the polymer used.

(19) R. F. Brown and N. M. vanGulick, *J. Org. Chem.*, **21**, 1046 (1956).

(20) For instance, by analogy, the barrier to a rotation around the C—C bond is reduced from 1140 cal./mole in 1,2-dichloroethane to only 200 cal./mole in 1,1',2,2'-tetrachloroethane.¹⁷

(21) J. W. L. Fordham, *J. Polymer Sci.*, **39**, 321 (1959).

(22) P. J. Flory, Paper presented at 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960; *J. Polymer Sci.*, in press.

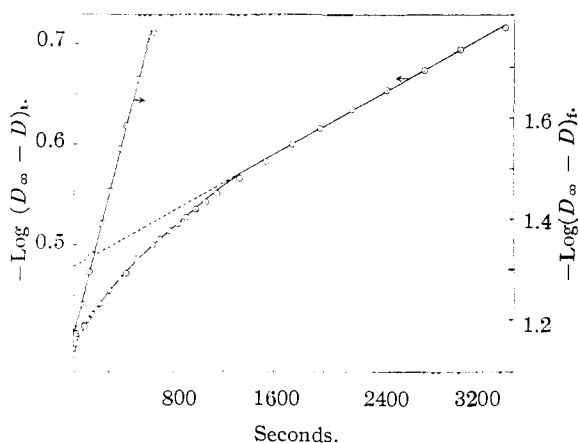
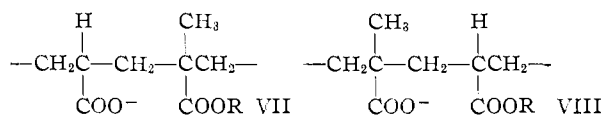


Fig. 2.—Analysis of kinetic data for the hydrolysis of the *p*-nitrophenyl methacrylate-methacrylic acid copolymer at 25° and pH 4.1.

On the other hand, the conclusion that the carboxylate residue is more easily able to approach the ester group on the neighboring chain segment if the asymmetric carbons to which these functions are attached have the same configuration is supported qualitatively by the observation that ionized isotactic poly-(methacrylic acid) has a higher affinity for both hydrogen ions and cupric ions than poly-(methacrylic acid) which is not stereoregulated.²⁷

It is worth noting that in the copolymer of acrylic acid with methacrylic ester all ester groups had the same reactivity,³ while copolymers of methacrylic acid with acrylic ester had ester groups of two widely differing reactivities. Sections of the two chains with the ester group and one neighboring carboxylate are represented by VII and VIII. An inspection of these chain segments would not explain why the diastereoisomers of VIII should



differ from each other in reactivity more than the diastereoisomers of VII. We must conclude that the differences in the behavior of the two copolymers are not due to the single methyl group carried by the carbon to which either the ester on the attacking carboxylate are attached but rather to the conformational difference between the methacrylic and acrylic chain as a whole.

Experimental

Monomers.—*p*-Nitrophenyl methacrylate (m.p. 94.5–95°) was prepared as described previously³; *p*-nitrophenyl acrylate (m.p. 65–65.5°) was made by adding dropwise 10 g. of acrylyl chloride to 5 g. of potassium hydroxide and 7 g. of *p*-nitrophenol in 500 ml. of water solution at 0°. Glacial acrylic and methacrylic acids were received from Rohm and Haas Co. and vacuum distilled before use.

Polymerizations of the mixed monomers (98 mole % acid and 2 mole % ester) were carried out in freshly distilled butanone. The total monomer concentration was 10–20 vol. %, the concentration of azo-bis-isobutyronitrile initiator 0.3–0.7 mg./ml. and the polymerizations were carried out

for 1–2 hours at 60°. The polymer which precipitated in the polymerization medium was filtered off, washed with ether and vacuum dried.

***p*-Acetamidophenyl Acid α,β -Dimethylsuccinates (AP-DMS).**—The *meso*- and the *rac*- α,β -dimethylsuccinic anhydrides (m.p. 41–43°, lit.¹³ 31°; and 91°, lit.¹³ 91°, respectively) were prepared as described by Bone and Sprankling.¹³ A solution of 3.2 g. of *p*-acetamidophenol in 100 ml. of acetone was mixed with a solution of 1 g. of sodium hydroxide in 2 ml. of water and the mixture was cooled to 0°. After addition of 1.28 g. of the *rac*- or the *meso*- α,β -dimethylsuccinic anhydride, the mixture was stirred for 10 minutes at 0°, acidified with concd. HCl and extracted three times with ether. The extract was dried over anhydrous magnesium sulfate and evaporated to dryness under reduced pressure. The product was recrystallized from acetone-benzene. The monoester of the racemic acid was obtained in 0.5 g. yield (m.p. 118–119°). *Anal.* C, 60.64; H, 6.11; N, 5.34. The monoester of the *meso*-acid was obtained in 0.4 g. yield (m.p. 130–151°). *Anal.* C, 60.56; H, 6.04; N, 5.44. Calcd. for C₁₄H₁₇NO₅: C, 60.20; H, 6.14; N, 5.02.

Sodium Salts of Phenyl Acid α,β -Diisopropylsuccinates (P-DIS).—*meso*- and *rac*- α,β -diisopropylsuccinic acids were prepared as described by Eberson²⁸; m.p. 166–169° (lit. 171°) and 221–223° (lit. 226–228°), respectively. These were converted to the corresponding anhydrides by refluxing for 2 hours with excess acetyl chloride. The acetyl chloride was evaporated under reduced pressure. The colorless, oily anhydrides were found to have the expected infrared spectra.

The sodium salts of the isomeric phenyl acid α,β -diisopropylsuccinates were prepared by adding the *meso* or the racemic form of α,β -diisopropylsuccinic anhydride (1.4 g., 0.01 mole) to a solution of 0.01 mole of sodium phenoxide in anhydrous ether and stirring the mixture for 12 hours at room temperature. The resulting white gelatinous precipitate was collected, washed several times with anhydrous ether, and dried *in vacuo*. About 6 g. of a white solid was obtained which was found to have the expected infrared spectrum. The free, liquid monoesters could not be obtained in an analytically pure form because of their extreme reactivity.

Rate Measurements.—The rate of release of phenol, *p*-acetamidophenol and *p*-nitrophenol from the corresponding esters was followed spectrophotometrically on a Beckman DU spectrophotometer at 270, 280 and 350 μ , respectively. The spectrophotometer was fitted with a special cylindrical cell 10 cm. long with 50-ml. capacity and was manipulated as described in a previous publication.⁹ The hydrolyses were initiated by adding stable stock solutions of the esters to 50 ml. of buffer. The following stock solutions were used: AP-DMS 0.8 mg. in 1 ml. of dioxane; P-DIS 1 mg. of the sodium salt in 0.1 ml. of glacial acetic acid; copolymers, 4–6 mg. in 1 ml. of methanol, containing 0.001 N HCl.

Treatment of Kinetic Data.—Plots of $-\log(D_\infty - D)_t$ ($D_\infty - D_0$) against t (where D_∞ , D and D_0 are optical densities observed after very long reaction times, at time t and time 0) were prepared and where these plots were linear, the first-order rate constant was obtained by multiplying the slope by 2.303. With two of the copolymers non-linear plots were obtained and these were treated as indicated on Fig. 2. Here the curved full line with ordinates designated $-\log(D_\infty - D)_t$ represents the directly observed data, while the dashed line with ordinates designated by $-\log(D_\infty - D)_s$ is an extension of the asymptote. The slope of the dashed line is $2.303k_2$, where k_2 is the rate constant of the "slow" ester groups. The difference between the intercepts of the dashed and the full line, respectively, gives $-\log(1 - \alpha)$ where α is the fraction of "fast" ester groups. A plot of $-\log(D_\infty - D)_f$ against t , where $(D_\infty - D)_f = (D_\infty - D)_t - (D_\infty - D)_s$ is shown as the steep line on the left of Fig. 2 and the slope of this line is $2.303k_1$, where k_1 is the rate constant of the "fast" ester groups.

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