that the frictional resistance of a particle in a solution is modified in such a manner by its neighbors that the total resistance can be expressed as a power series of concentration, in which the first order term happens to have a coefficient roughly equal to the coefficient of the first order term in the relationship between solution viscosity and concentration. Should subsequent research show that the correlation between solution viscosity and frictional resistance is universal, this latter explanation and all others not postulating a fundamental connection between the two phenomena would lose all appeal.

IV. Summary

The reciprocal of the sedimentation constant, corrected in the usual manner, of tobacco mosaic virus preparations was found to be a linear function of virus concentration. It was shown that when the sedimentation rate is corrected for the viscosity of the virus solution instead of for that of the solvent this dependence upon concentration largely vanishes. There remains a small residual effect in the opposite direction which may be interpreted as being due to non-ideality of the solution. Data from the literature on the sedimentation of various polymers and macromolecules show that this close relationship between the apparent concentration dependence of sedimentation rate and solution viscosity is fairly general. Data from the literature on the diffusion of simple electrolytes also support the conclusion that solution viscosity rather than solvent viscosity should be considered in physical studies of this type.

PRINCETON, N. J. RECEIVED APRIL 21, 1944

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY][1]

Preparation and Pyrolysis of Lactic Acid Derivatives. Production of β-Alkoxyethyl and Tetrahydrofurfuryl Acrylates[2]

BY M. L. FEIN, W. P. RATCHFORD AND C. H. FISHER

The corresponding acrylates or methacrylates have been obtained in moderate or high yields by pyrolyzing tetrahydrofurfuryl α-acetoxypropionate[3] and the β-methoxyethyl[4] and β-phenoxyethyl[4] esters of α-acetoxyisobutyric acid. These results suggested that an ether linkage on the β-carbon of the alkyl group increases the thermal stability of esters; the present work was done to ascertain the correctness of this premise and to determine whether β-alkoxyethyl acrylates can be made satisfactorily by pyrolyzing the corresponding α-acetoxypropionates.[5]

Using equipment previously described,[5,6] the pyrolyses were carried out by passing vapors of the esters through a Pyrex-glass tube heated at temperatures ranging from 475 to 525°. The claim of Claborn[3] that tetrahydrofurfuryl acrylate is the principal product of the pyrolysis of tetrahydrofurfuryl α-acetoxypropionate was confirmed.

Pyrolysis of the β-alkoxyethyl α-acetoxypropionates yielded the corresponding acrylates in yields of 26 to 47% on the basis of the starting material destroyed. Other products of the decomposition were acetic acid, acetaldehyde, carbon monoxide, carbon dioxide and hydrocarbon gases. Methanol was obtained in the pyrolysis of the β-methoxyethyl ester.

Vinyl alkyl ethers might have been formed during the pyrolysis of the alkoxyethyl esters, but these ethers were not found in the reaction products. Possibly the ethers were formed and subsequently decomposed,[7] or perhaps they were present in small quantities but not detected.

The results obtained in a preliminary study of the pyrolysis of β-ethoxyethyl acetate indicate that the β-alkoxyethyl group is relatively unstable to heat. The products identified were acetic acid, acetaldehyde (identified as the 2,4-dinitrophenylhydrazone), carbon monoxide, carbon dioxide and hydrocarbon gases. The production of acetaldehyde from β-ethoxyethyl acetate indicates that this aldehyde can be formed from the ethoxyethyl group as well as from acetoxypropionic acid when ethoxyethyl acetoxypropionate is pyrolyzed.

The considerable difference between the thermal stability of the β-alkoxyethyl and tetrahydrofurfuryl esters shows that the presence of an ether linkage on the β-carbon atom has little stabilizing effect. The ether linkage appears to have some stabilizing effect, however, since the yield of ethyl acrylate obtained by pyrolyzing ethyl α-acetoxypropionate under comparable conditions is only about 20%.[8] The stability of the tetrahydrofurfuryl group, as exemplified by the pyrolysis behavior of its acetoxypropionic ester, may be due to the presence of only one β-hydrogen atom, the

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[1] One of the four Regional Research Laboratories operated by the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] This paper was presented before the Division of Organic Chemistry at the 106th meeting of the American Chemical Society, Pittsburgh, Pa., Sept., 1943. Not copyrighted.

[3] Claborn, U. S. Patent 2,222,363, Nov. 19, 1940; U. S. Patent 2,229,997, Jan. 28, 1941.

[4] Burns, Jones and Ritchie, *J. Chem. Soc.*, 714 (1935).

[5] References to earlier work in this field are given by Filachione and co-workers, THIS JOURNAL, **66**, 494 (1944).

[6] Smith and co-workers, *Ind. Eng. Chem.*, **34**, 473 (1942).

[7] Wang and Winkler, *Can. J. Research*, **21B**, 97 (1943).

[8] Unpublished results from this Laboratory.

Table I

Physical Properties of Lactic, Acetoxypropionic and Acrylic Esters

Compound	Boiling point, °C.	Pressure, mm.	$n^{20}D$	d^{20}_4	Molecular refraction Calcd.	Molecular refraction Found
Methoxyethyl lactate	81- 82	6	1.4293	1.0990	34.75	34.73
Ethoxyethyl lactate	86- 87	5	1.4290	1.0591	39.35	39.41
Butoxyethyl lactate	109-110	6	1.4321	1.0125	48.58	48.68
Tetrahydrofurfuryl lactate	114-115	5	1.4555[a]			
Tetrahydrofurfuryl lactate[b]	132	12.3	1.4555[a]	1.1359[c]		
Tetrahydrofurfuryl lactate[b]	96	1.9				
Methoxyethyl acetoxypropionate	100-101	7	1.4218	1.0946	44.09	44.10
Ethoxyethyl acetoxypropionate	105-106	6	1.4220	1.0619	48.81	48.71
Butoxyethyl acetoxypropionate	120-121	5	1.4259	1.0284	57.95	57.80
Tetrahydrofurfuryl acetoxypropionate	132-133	7	1.4440[a]			
Tetrahydrofurfuryl acetoxypropionate[b]	139	10	1.4440[a]			
Tetrahydrofurfuryl acetoxypropionate[b]	129	6		1.245[c]		
Methoxyethyl acrylate	76- 79	31	1.4258			
Methoxyethyl acrylate[d]	56	12	1.4272	1.0131		
Ethoxyethyl acrylate	80- 86	27	1.4252			
Ethoxyethyl acrylate[d]	77	19	1.4270	0.9813		
Butoxyethyl acrylate[d]	80	6	1.4310	0.9491		
Tetrahydrofurfuryl acrylate	75	2	1.4585			
Tetrahydrofurfuryl acrylate[d]	87	9	1.4580	1.0643		

[a] Index of refraction at 25°. [b] Reference 3. [c] d^{25}_{25}. [d] Constants supplied by Dr. C. E. Rehberg of this Laboratory, who prepared these acrylic esters by the alcoholysis of methyl acrylate.[9]

Table II

Pyrolysis of Esters of α-Acetoxypropionic Acid

Acetoxypropionate	pyrolyzed, g.	Temp., °C.	Contact time, sec.	Total liquid products, %	Starting material recovered, %	Conversion Into acrylic ester, %	Conversion Into acetic acid, %	Moles of product per mole of acetoxypropionate destroyed: Acrylic ester	Acetic acid	Acetaldehyde[a]	MeOH[b]
Methoxyethyl	95.1	496	8.5	93	54	21.9	35.9[c]	0.475	0.78[c]		
	34.2	503	18	79	10	23.3[d]	85.6[c]	.26	.88[c]	0.2	0.3
	90.1[e]	515	98	77	26.7	18	59.2	.24	.81		
Ethoxyethyl	154.1	490	7.5	91	58	16.8	37.5	.40	.89		
	73	500	27	80	13	18	71[c]	.21	.81[c]	.5	
	36.6	500	13	83	41	17.5	33.3	.29	.57	.5	
	105.5	515	24	81	33.2	25	54	.37	.81	.2	
	29.9	500	19	79	22	10.2[d]	69.3[c]	.13[d]	.89[c]	.4	
	104.7[f]	520	3.2	80		[g]	50.1[c]	[g]			
Butoxyethyl	136.9	490	8.3	88	47.7	17.6	60.8[c]	.34	1.16[c]		
Tetrahydrofurfuryl	159.1	495	9.9	91	44.3	21.6	51.6[c]	.39	0.92[c]		
	97.4	475	7	96	67.8	21.6	32.2	.67	1.0		
	87.4	525	7	91	25.1	52.5	69.6	.70	0.92		

[a] Identified as the 2,4-dinitrophenylhydrazone. [b] Identified as the 3,5-dinitrobenzoate. [c] Determined by titration. [d] In this experiment 18% of the pyrolysis products was obtained as distillation residue. [e] An empty Pyrex glass tube was used in this experiment. [f] The pyrolysis was carried out under a pressure of 100 mm. of mercury. [g] The acrylic ester polymerized in the distilling flask.

cyclic structure, or the fact that the one β-hydrogen atom is protected or suitably influenced by the ring.

Experimental

Preparation of Lactic Esters.—The methoxyethyl, ethoxyethyl, butoxyethyl and tetrahydrofurfuryl esters were prepared by direct esterification of an almost colorless edible grade of 81.8% lactic acid in 56, 60, 81, and 79% yields, respectively, using approximately the procedure given below for β-butoxyethyl lactate. No catalyst was used in the esterification of lactic acid with tetrahydrofurfuryl alcohol.

The yields of the methoxyethyl, ethoxyethyl, butoxyethyl and tetrahydrofurfuryl esters prepared by alcoholysis of ethyl lactate were 70, 72, 71 and 84%, respectively.

Butoxyethyl Lactate.—One mole of 81.8% lactic acid (110 g.) was refluxed with 75 ml. benzene under a 200-mm. Vigreux column that supported a moisture trap (Barrett modification of the Dean and Stark tube). After about 20 ml. of water had been removed, 4 moles of β-butoxyethanol (472 g.) and 1 ml. of concentrated sulfuric acid were added. After the refluxing had been continued for about ten hours, a total of 44 ml. of water had been removed. The catalyst was neutralized with 4 g. of anhydrous sodium acetate, and the benzene was distilled at about 30 mm. The excess alcohol was distilled at 51° under a pressure of 4 mm.; the desired product distilled at 107-108° at 4 mm.; $n^{20}D$ 1.4320. The yield was 154 g. or 81% of the theoretical. A high-boiling residue, presumably condensation products of lactic acid, remained in the flask.

Ethoxyethyl Lactate.—The catalyst was prepared by dipping about 4 square inches of aluminum foil in mercury, and rubbing the surface of the foil gently. The aluminum was removed from the mercury before much amalgamation occurred and placed in a flask containing 90 g. of β-ethoxyethanol; the mixture was heated until the foil dissolved. The resulting solution was added, when cool, to a round bottom distillation flask that contained 1 mole (118 g.) of redistilled ethyl lactate and 3 moles (270 g.) of redistilled ethoxyethanol. The mixture was distilled with a high reflux ratio through a Vigreux column 60 cm. high to remove ethanol as it was formed. A small amount of freshly prepared catalyst was added at about eight-hour intervals. After 45 ml. of ethanol had been removed during twenty hours, the vapor temperature rose to that of the excess ethoxyethanol, which was distilled. The desired ester was collected at 87–90° (5 mm.); $n^{20}\text{D}$ 1.4284. The yield was 117 g. or 72% of the theoretical.

Acetylation.—The lactic esters were acetylated with a 10% excess of acetic anhydride, using substantially previously described procedures.[6] The yields were 90 to 95%.

Physical constants of the esters and details of the pyrolysis experiments are given in Tables I and II, respectively. The fractions of the alkoxyethyl acrylates were small, and the physical constants observed for these samples are not considered to be as reliable as those (Table I) determined with larger samples prepared in connection with another investigation.[9] Soft polymers were obtained by heating the acrylic ester fractions in the presence of benzoyl peroxide.

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[9] Rehberg and Fisher, "Preparation of Higher Acrylic Esters by the Alcoholysis of Methyl Acrylate," presented before the Division of Organic Chemistry at the 106th meeting of the American Chemical Society, Pittsburgh, Pa., Sept., 1943.

Summary

The β-methoxyethyl, β-ethoxyethyl, β-butoxyethyl and tetrahydrofurfuryl esters of lactic acid were prepared by direct esterification and by alcoholysis of ethyl lactate. Acetylation with acetic anhydride yielded the corresponding α-acetoxypropionates.

Thermal decomposition of the β-alkoxyethyl α-acetoxypropionates yielded the corresponding alkoxyethyl acrylates in yields of 26 to 47%, along with acetic acid, acetaldehyde, carbon monoxide, carbon dioxide and hydrocarbon gases. A 70% yield of tetrahydrofurfuryl acrylate was obtained by the pyrolysis of tetrahydrofurfuryl acetoxypropionate.

PHILADELPHIA, PA. RECEIVED JANUARY 17, 1944

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY, PHILADELPHIA, PENNSYLVANIA][1]

Preparation and Properties of the *n*-Alkyl Acrylates

BY C. E. REHBERG AND C. H. FISHER

Although acrylic acid is the simplest unsaturated carboxylic acid and its ester spolymerize readily, yielding useful resins,[1a] no adequate study of the preparation and physical properties of the alkyl acrylates has been published. The commercially important methyl and ethyl esters are manufactured by treating ethylene cyanohydrin with the appropriate alcohol in the presence of sulfuric acid, a method which appears to be less suitable for production of higher alkyl acrylates.[1a] Although methyl acrylate can be made satisfactorily by pyrolysis of the acetyl derivative of methyl lactate, pyrolysis of higher *n*-alkyl α-acetoxypropionates produces low yields of *n*-alkyl acrylates.[2,3,4] Most of the published information on acrylic esters has appeared in the patent literature. The purpose of the present work was to prepare the *n*-alkyl acrylates by a generally applicable method[5] and determine their common physical properties. In addition, the esters were polymerized and examined briefly for a preliminary determination of the relation between the structure of the monomer and properties of the polymer.

The higher acrylic esters were made in the present work by alcoholysis,[6,7] a method recommended by Neher[1a] and used previously to prepare ethyl,[5] *n*-propyl,[5] *n*-butyl[5] and cetyl acrylates.[8]

Several of the *n*-alkyl methacrylates, including the *n*-propyl,[9] *n*-butyl,[7] *n*-hexyl[7,10] lauryl[11] and stearyl[11] esters, have been produced similarly by alcoholysis of methyl methacrylate. The ethyl, *n*-propyl, *n*-butyl, and dodecyl esters of acrylic acid have been prepared also by direct esterification,[12] dehalogenation of alkyl α,β-dibromopropionates with zinc,[13,14,15] dehydrohalogenation of β-halopropionic esters,[12a,16,17] acylation of the alcohol with acrylyl chloride,[8,18] dehydration of

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[1] This is one of four Regional Research Laboratories operated by the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

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