[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Some Reactivity Ratios of Esters of Acrylic Acid

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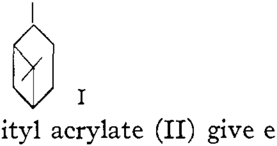
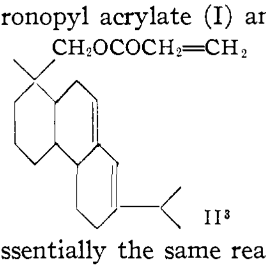
Reactivity ratios for hydronopyl acrylate with styrene, vinyl chloride and acrylonitrile and for abityl acrylate with vinyl chloride have been determined. These values are essentially the same as values determined with methyl acrylate.

Reactivity ratios for copolymerizing monomers have become important in the prediction of types of monomers which will combine to give polymers and in determining the regularity of such polymeric materials. These values depend to a large extent on the stability of the intermediates produced during the polymerization processes and, of course, vary with the type of initiator used for the polymerization. Resonance stabilization and polarity effects are important in determining reactivity ratios of vinyl monomers and steric effects are also significant.

Recent experiments have continued to emphasize that the alkyl group in an ester of an α,β-unsaturated acid and the acyl group in a vinyl ester do not greatly influence the reactivity ratios of such esters with many vinyl monomers.[2] We have now found further evidence of this in that the two new esters of acrylic acid, hydronopyl acrylate (I) and abityl acrylate (II) give essentially the same reactivity ratios with styrene, vinyl chloride and acrylonitrile as have been determined for methyl acrylate.



I



II[3]

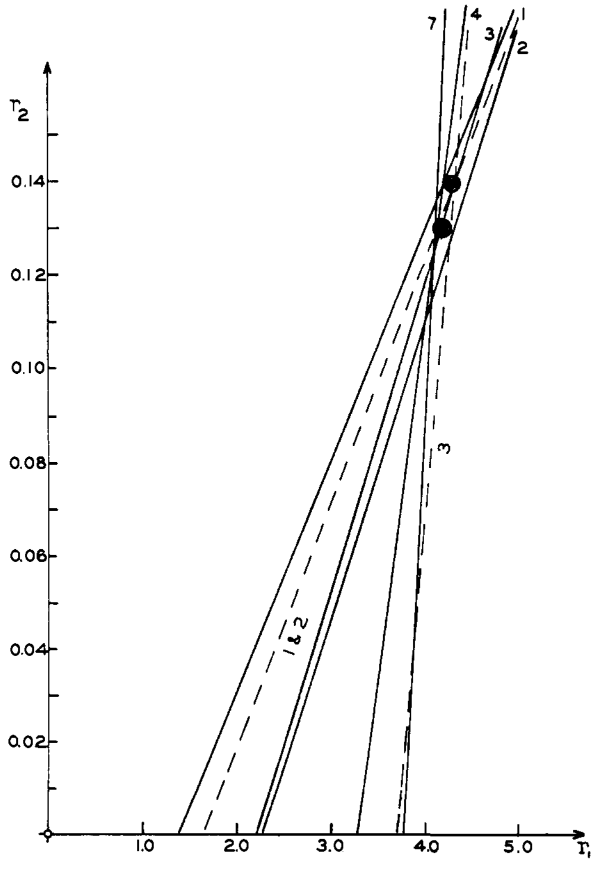


Fig. 1.—Copolymerization of vinyl chloride with hydronopyl acrylate (- - - -) and abityl acrylate (——).

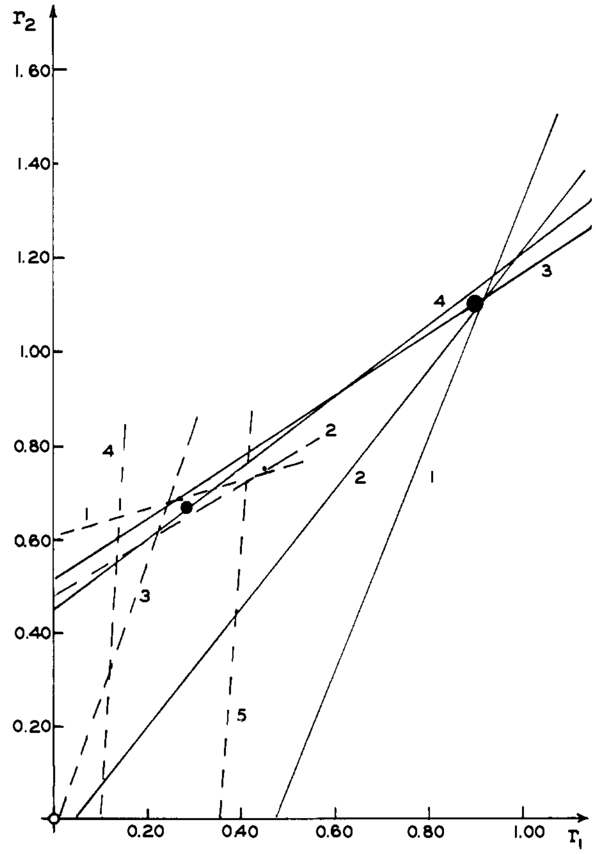


Fig. 2.—Copolymerization of hydronopyl acrylate with styrene (- - - -) and acrylonitrile (——).

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[1] This is a partial report of work done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act. The contract was supervised by Dr. J. C. Cowan of the Northern Utilization Research and Development Division of the Agricultural Research Service.

[2] P. Agron, T. Alfrey, J. Bohrer, H. Haas and H. Wechsler, *J. Polymer Sci.*, **3**, 157 (1945); W. S. Port, E. F. Jordan, J. E. Hansen and D. Swern, *ibid.*, **9**, 493 (1952); M. F. Margaritova and V. A. Raĭskaya, *C. A.*, **49**, 14372 (1955); C. S. Marvel, J. W. Johnson, J. Economy, G. P. Scott, W. K. Taft and B. G. Labbe, *J. Polymer Sci.*, **20**, 437 (1956); C. S. Marvel and W. G. DePierri, *ibid.*, in press.

[3] This ester is really a mixture prepared from the commercial Abitol of Hercules Powder Co. Abitol contains 15% of dehydro, 40% of dihydro and 45% of tetrahydro of the abietic acid structure.

TABLE I

COPOLYMERIZATION OF ALKYL ACRYLATES WITH VINYL MONOMERS

No.	M_1, g.	M_2, g.	Polymer, %	Mole fraction Γ_1 of M_1	Mole fraction Γ_2 of M_2	Microanalyses, %		Calcd. mole fraction γ_1 of M_1 in high polymer	Calcd. mole fraction γ_2 of M_2 in high polymer
	Methyl[a] acrylate	Styrene				C	H		
1	9.89	1.65	5.2	0.8788	0.1212	68.75	7.19	0.6877	0.3129
2	5.74	5.50	10.4	.5580	.4420	78.49	7.37	.4233	.5767
3	4.49	6.71	8.2	.4473	.5527	80.16	7.51	.3753	.6247
4	2.81	8.35	9.6	.2893	.7107	83.50	7.36	.2767	.7233
5	1.73	9.44	5.6	.1815	.8185	85.90	7.53	.2036	.7964
	Methyl[b] acrylate	Vinyl chloride				Cl			
1	0.82	8.55	8.8	0.0651	0.9349	34.38		0.3207	0.6793
2	1.41	10.28	6.8	.0906	.9094	29.54		.4007	.5993
3	1.99	9.13	8.2	.1366	.8634	24.43		.4898	.5102
4	2.78	8.35	10.6	.1946	.8054	19.88		.5738	.4262
	Methyl[b] acrylate	Acrylonitrile				N			
1	4.12	6.03	0.7	0.2963	0.7037	17.90		0.2264	0.7736
2	5.99	3.38	3.1	.5221	.4779	11.54		.4425	.5575
3	6.93	2.53	6.4	.6280	.3720	8.56		.5623	.4377
4	8.07	1.14	2.9	.8135	.1865	3.89		.7810	.2190
5	8.05	0.72	4.1	.8733	.1267	2.67		.8456	.1543
	Hydronopyl[b] acrylate	Styrene				C			
1	2.94	4.62	5.6	0.2296	0.7704	85.37		0.2489	0.7511
2	3.91	3.62	15.2	.3360	.6640	83.62		.3362	.6638
3	6.83	1.81	8.6	.6387	.3613	80.76		.5122	.4878
4	7.77	0.92	7.7	.7982	.2018	79.84		.5802	.4198
5	6.83	0.47	20	.8719	.1281	77.62		.7751	.2249
	Hydronopyl[a] acrylate	Vinyl chloride				Cl			
1	4.89	5.00	23	0.2157	0.7843	9.22		0.5917	0.4083
2	5.92	6.06	24	.2155	.7845	9.28		.5898	.4102
3	7.83	2.10	6	.5118	.4882	3.11		.8290	.1710
	Hydronopyl[a] acrylate	Acrylonitrile				N			
1	7.69	0.82	11	0.6912	0.3088	2.74		0.6733	0.3267
2	6.82	1.41	9	.5359	.4641	4.88		.5128	.4872
3	5.92	2.36	6	.3745	.6255	8.08		.3511	.6489
4	3.95	2.43	38	.2795	.7205	10.93		.2525	.7475
	Abityl[a] acrylate	Vinyl chloride				Cl			
1	7.69	5.34	12	0.2070	0.7930	6.70		0.5751	0.4249
2	6.10	3.37	10	.2470	.7530	5.37		.6342	.3658
3	6.49	3.25	18	.2657	.7343	5.19		.6429	.3571
4	7.89	2.04	8	.4121	.5879	2.95		.7677	.2323
5	8.62	0.99	10	.6121	.3879	1.46		.8728	.1272

[a] Polymerizations were carried out at 60°. [b] Polymerizations were carried out at 50°.

The reactivity ratios for methyl acrylate and styrene have been determined by Lewis, Walling, Cummings, Briggs and Mayo[4] and by Alfrey, Merz and Mark[5]; for methyl acrylate and vinyl chloride by Mayo, Lewis and Walling[6] and by Chapin, Ham and Fordyce[7]; for methyl acrylate and acrylonitrile by Okamura and Yamashita.[8] We have determined all of these values again under the same conditions used for the new acrylate esters and report our results below.

Acrylates	r_1		r_2
Methyl	0.15 ± 0.05	Styrene	0.72 ± 0.1
Hydronopyl	0.29 ± .1	Styrene	0.66 ± .1
Methyl	4.4 ± .5	Vinyl chloride	0.12 ± .01
Hydronopyl	4.3 ± .2	Vinyl chloride	0.14 ± .01
Abityl	4.2 ± .2	Vinyl chloride	0.13 ± .01
Methyl	0.84 ± .05	Acrylonitrile	1.5 ± .1
Hydronopyl	0.9 ± .1	Acrylonitrile	1.1 ± .1

Our results for styrene and methyl acrylate are within experimental error of the earlier results.[4,5] Our results for vinyl chloride and methyl acrylate differ slightly from those of Mayo, Lewis and Walling,[6] who found $r_1 = 5$ and $r_2 = 0$. Chapin,

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(4) F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs and F. R. Mayo, THIS JOURNAL, **70**, 1519 (1948).

(5) T. Alfrey, Jr., E. Merz and H. Mark, *J. Polymer Sci.*, **1**, 37 (1946).

(6) F. R. Mayo, F. M. Lewis and C. Walling, THIS JOURNAL, **70**, 1529 (1948).

(7) E. C. Chapin, G. E. Ham and R. G. Fordyce, *ibid.*, **70**, 538 (1948).

(8) S. Okamura and T. Yamashita, *J. Soc. Textile and Cellulose Ind. Japan*, **9**, 444 (1953).

Ham and Fordyce,[7] on the other hand, found $r_1 = 9$ and $r_2 = 0.083$ for this pair. The earlier work[8] on acrylonitrile and methyl acrylate was done in emulsion but our values are quite close to those reported.

These results indicate clearly that the acrylic acid portion of the ester is totally responsible for the reactivity ratio in the case of these esters.

Experimental

Hydronopyl Acrylate.—A mixture of 210 g. (1.25 moles) of hydronopol, 169 g. (1.35 moles) of dimethylaniline and 200 ml. of dry ethyl ether was warmed until the ether was at reflux temperature, the heating source was removed and 129 g. (1.43 moles) of acrylyl chloride was added at a rate sufficient to maintain a gentle reflux. When the amine hydrochloride began to crystallize, it was necessary to cease adding the acid chloride and cool the flask for a short period. When the reaction slowed down, the remaining acid chloride was added, the mixture was refluxed for about two hours and then cooled. About 200 ml. of water was added to dissolve the amine hydrochloride and the ether layer was separated. It was then washed successively with three 50-ml. portions of cold 10% sulfuric acid solution, then with saturated sodium bicarbonate solution and sufficiently with water. A few crystals of hydroquinone were added, the ether was evaporated and the crude product was distilled (b.p. 107–113° (1.5 mm.), 198 g. 72%, yellow oil, $n^{25}\mathrm{D}$ 1.480), then allowed to stand for 24 hours over a small portion of metallic sodium in order to remove the hydroquinone completely and again distilled under reduced pressure. The yield was 74 g. (27% of the theoretical amount) of a product boiling at 73° under 0.05 mm. pressure, $n^{25}\mathrm{D}$ 1.4800. This material polymerized readily when heated with a small portion of benzoyl peroxide.

Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.98. Found: C, 75.74; H, 9.95.

Abityl acrylate was not obtained in satisfactory yield from Abitol and acrylyl chloride but was obtained by direct esterification.

Into a 100-ml. 4.6 *M* toluene solution of acrylic acid, 117 g. of Abitol (0.40 mole), 15 g. of hydroquinone and 0.5 g. of *p*-toluenesulfonic acid was suspended a piece of copper wire to help inhibit polymerization, and this solution was heated under a reflux condenser for 22 hours. The condensate was put through a separator to remove water before the toluene was returned to the reaction flask. During this time 7.3 ml. of water was collected. The toluene solution was cooled and most of the hydroquinone crystallized and was removed by filtration. The toluene solution was then washed successively with portions of water until a test portion of the washings no longer gave a yellow color when potassium hydroxide was added. The toluene was removed by distillation (in the presence of copper wire) and the residual ester was distilled twice under reduced pressure. The yield was 80 g. (58%) of a product, b.p. 157–161° (0.5 mm.), $n^{24}\mathrm{D}$ 1.5145. This material polymerized to a colorless polymer when heated at 120° for ten minutes with a little benzoyl peroxide.

Anal. Calcd. for the acrylate ester of a mixture of 15% $C_{20}H_{30}O$, 40% $C_{20}H_{34}O$ and 45% $C_{20}H_{36}O$: C, 80.11; H, 10.61. Found: C, 80.27; H, 10.77.

Other Monomers.—The other monomers which were used in the copolymerization experiments were distilled once to remove inhibitor.

Polymerization.—All polymerizations were carried out in benzene solution with benzoyl peroxide as the initiator. Some were done at 60° and some at 50° as noted in the table. Conversions varied from 1 to 24% and the polymers were purified by reprecipitation with methanol (with abityl acrylate polymers acetone was used) and use of the frozen benzene technique of Lewis and Mayo.[9]

The copolymerization data are presented in Table I and Figs. 1 and 2.

Acknowledgment.—We wish to acknowledge the aid of Mr. Jozsef Nemeth of the University of Illinois, and the Micro-Tech Laboratories, Skokie, Ill., for analytical results reported. We are indebted to Mr. E. L. Patton of the Southern Utilization Research and Development Division of the Agricultural Research Service, Olustee, Florida, for the hydronopol and Abitol used in these experiments.

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[9] F. M. Lewis and F. R. Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17** 134 (1945).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, THE FACULTY OF ENGINEERING, KYOTO UNIVERSITY]

The Preparation of Terephthalic Acid from Phthalic or Benzoic Acid

BY YOSHIRO OGATA, MASARU TSUCHIDA AND AKIHIKO MURAMOTO

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The preparation of terephthalic acid by heating potassium salts of phthalic or benzoic acid has been investigated. It was found that cadmium was the best catalyst cation, zinc the second, and some of the other metals had but inferior catalytic effect. The order of the catalytic efficiency of the anions of cadmium seems to be $\mathrm{I}^- > \mathrm{Br}^- > \mathrm{Cl}^- > \mathrm{CO}_3^{=}$. Dipotassium isophthalate gave the terephthalate more slowly than the phthalate. Several lines of evidence imply an intramolecular mechanism for the rearrangement, but the reaction of dipotassium phthalate catalyzed by radioactive $\mathrm{CdC^{14}O_3}$ gave radioactive terephthalic acid, probably *via* carbon isotope exchange between activated reactant and the catalyst. On the other hand, the reaction between potassium benzoate and $\mathrm{CdC^{14}O_3}$ gave terephthalic acid with very little radioactivity, suggesting a disproportionation mechanism for the reaction.

A recent patent to Henkel[1] describes a preparation of dipotassium terephthalate in high yield by heating at 400–450° dipotassium phthalate with a catalyst including cadmium or zinc salts and also the similar preparation of the terephthalate from potassium benzoate. In the old literature, similar methods for the preparation of terephthalic acid are recorded, *e.g.*, the fusion of dipotassium *p*-sulfobenzoate with sodium formate[2] or the heating of sodium benzoate,[3] but yields were poor.

The present communication summarizes data on the effect of various conditions and catalysts on the yield of the Henkel process for the terephthalic acid synthesis and also our mechanistic investigation using radioactive carbon isotope.

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[1] B. Raecke, *et al.*, to Henkel & Cie, G.m.b.H., German Patents 936,036, Dec. (1955), 945,627 (1956), and additional patents.

[2] I. Remsen, *Ber.*, **5**, 379 (1872).

[3] W. Flight and A. M. Michaelis, *ibid.*, **6**, 1395 (1873).