ions, whereas those with meta nitro groups were least sensitive.

3. 4,4′-Dinitrodiphenylthiocarbazone may be used to advantage for a test for mercurous mercury in concentrations as great as 1/1,000,000.

ATHENS, GA. RECEIVED[7] OCTOBER 29, 1945

---

[7] Original manuscript received November 24, 1944.

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY, PHILADELPHIA 18, PENNSYLVANIA[1]]

Pyrolytic Preparation of α-Carbalkoxyalkyl Acrylates and Methacrylates[1a]

BY E. M. FILACHIONE, J. H. LENGEL AND C. H. FISHER

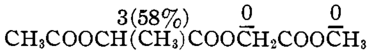
α-Carbalkoxyalkyl acrylates and methacrylates have been prepared by treating alkyl lactates with acrylyl chloride, methacrylyl chloride or methacrylic anhydride[2,3] and by heating potassium acrylate or methacrylate with methyl chloroacetate[3] or methyl α-bromobutyrate.[3] The acrylates and methacrylates of this type thus far prepared polymerize readily, and in this respect resemble the unsubstituted alkyl esters[4,5] of acrylic and methacrylic acid. The purpose of the present work was to devise an alternative method for making certain carbalkoxyalkyl acrylates (II) and methacrylates (IV) and to determine the relative thermal stabilities of the three ester groups present in the α-acetoxypropionates (I) and α-acetoxyisobutyrates (III) of hydroxy esters such as methyl lactate.

$$\underset{\text{I}}{CH_3COOCH(CH_3)COOCH(CH_3)COOCH_3} \xrightarrow[550°]{500\text{ to}} \underset{\text{II}}{CH_2{=}CHCOOCH(CH_3)COOCH_3} + CH_3COOH$$

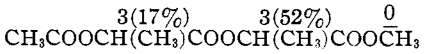
$$\underset{\text{III}}{CH_3COOC(CH_3)_2COOCH(CH_3)COOR} \xrightarrow[550°]{450\text{ to}} \underset{\text{IV}}{CH_2{=}C(CH_3)COOCH(CH_3)COOR} + CH_3COOH$$

The α-acetoxypropionates (I) and α-acetoxyisobutyrates (III) used in the pyrolysis experiments were made conveniently and in high yields by acylating methyl glycolate or alkyl lactate with acetoxypropionyl chloride or acetoxyisobutyryl chloride. One of the compounds (acetoxypropionate of methyl lactate, I) prepared in this manner and used in the present work had been made previously by treating methyl lactyllactate with acetic anhydride.[6]

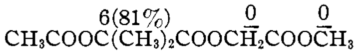
The acetoxy esters (I and III) were decomposed by passage through a Pyrex glass tube heated at temperatures ranging from 450 to 550°. Although each of the compounds pyrolyzed contained three esterified carboxyl groups, decomposition occurred preferentially at the carboxyl group esterified with the hydroxy acid having the largest number of hydrogen atoms on its beta-carbons. This relation between thermal stability and number of beta-hydrogen atoms was in agreement with previous observations,[7] and the acetoxy esters subjected to pyrolysis were selected (with the exception of α-carbomethoxyethyl α-acetoxypropionate, (I)) so that one ester group would have more beta-hydrogens than either of the other two. The number of β-hydrogen atoms and extent of cleavage for each ester group are shown below (per cent. yield of corresponding unsaturated ester or olefin used as measure of cleavage)


(V)

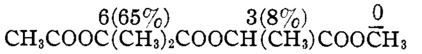
$$CH_3COO\overset{3(58\%)}{CH(CH_3)}COO\overset{0}{CH_2}COO\overset{0}{CH_3} \quad \text{(V)}$$


(I)

$$CH_3COO\overset{3(17\%)}{CH(CH_3)}COO\overset{3(52\%)}{CH(CH_3)}COO\overset{0}{CH_3} \quad \text{(I)}$$


(VI)

$$CH_3COO\overset{6(81\%)}{C(CH_3)_2}COO\overset{0}{CH_2}COO\overset{0}{CH_3} \quad \text{(VI)}$$


(VII)

$$CH_3COO\overset{6(65\%)}{C(CH_3)_2}COO\overset{3(8\%)}{CH(CH_3)}COO\overset{0}{CH_3} \quad \text{(VII)}$$


(VIII)

$$CH_3COO\overset{6(58\%)}{C(CH_3)_2}COO\overset{3(4\%)}{CH(CH_3)}COO\overset{3(3\%)}{CH_2CH_3} \quad \text{(VIII)}$$

The acetoxypropionate of methyl lactate (I) differed from the other acetoxy esters (V to VIII), in that two of its ester groups had the largest number of β-hydrogen atoms. Since pyrolysis of this ester (I) yielded much more methyl acrylate than carbomethoxyethyl acrylate (II), the acetate group was more stable than the acetoxypropionate group. This observation is in harmony with the fact that ethylene rather than ethyl acrylate is the principal product when ethyl α-acetoxypropionate is thermally decomposed.[8]

Acetone, ethyl acrylate, methacrylic acid and ethyl α-acetoxypropionate were obtained as by-products in the pyrolysis of the acetoxyisobutyrate of ethyl lactate (VIII). Presumably ethyl acrylate and α-acetoxyisobutyric acid (IX) were

---

[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

[1a] Presented at the Meeting in Miniature of the Philadelphia Section, A. C. S., June 13, 1945.

[2] C. E. Rehberg, M. B. Dixon and C. H. Fisher, THIS JOURNAL, **67**, 208 (1945).

[3] D. E. Strain, U. S. Patent 2,141,546, Nov. 27, 1938.

[4] H. T. Neher, *Ind. Eng. Chem.*, **28**, 267 (1936).

[5] C. E. Rehberg, W. A. Faucette and C. H. Fisher, THIS JOURNAL, **66**, 1723 (1944).

[6] H. V. Claborn, U. S. Patent 2,350,388, June 6, 1944.

[7] (a) C. D. Hurd and F. H. Blunck, THIS JOURNAL, **60**, 2419 (1938); (b) C. D. Hurd, "The Pyrolysis of Carbon Compounds," Reinhold Publishing Corp., N. Y., 1929.

[8] R. Burns, D. T. Jones and P. D. Ritchie, *J. Chem. Soc.*, 400 (1935); C. E. Rehberg and C. H. Fisher, THIS JOURNAL, **67**, 56 (1945).

TABLE I

PREPARATION AND PROPERTIES OF ACETYLATED HYDROXY ESTERS

Expt.	Reactants[a]		Yield, % of theoret.	B. p.,		d^{20}_4	n^{20}_D	Mol. ref.		Sapn. equiv.		C, %		H, %	
		Acetoxy-chloride		°C.	Mm.			Calcd.	Obs.	Calcd.	Found	Calcd.	Found	Calcd.	Found
1	Me glycolate	propionyl	88	96	0.6	1.189	1.4273	44.11	44.07	68.06	68.15	47.06	46.76	5.93	5.94
2[b]	Me lactate	propionyl	45	95	.8	....	1.4242	...	...	...	...	...	...	..	..
3	Me glycolate	isobutyryl	89	89	.65	1.1559	1.4291	48.72	48.67	72.73	72.99	49.54	49.61	6.47	6.50
4	Me lactate	isobutyryl	90	82	.3	1.1151	1.4258	53.35	53.34	77.41	77.43	51.72	51.12	6.95	7.19
5	Et lactate,	isobutyryl	92	76	.25	1.0867	1.4247	57.96	57.86	82.08	82.04	53.64	53.49	7.37	7.39

[a] The reactions, except experiment 2, were carried out in pyridine–benzene solutions. [b] The following constants have been reported (ref. 5) for this compound: b. p. 118° (7 mm.); 81° (0.7 mm.); d^{25}, 1.1400; and n^{20}_D, 1.4244.

formed by the normal thermal cleavage of the middle ester group of VIII; the acetoxyisobutyric acid would be expected[7b] to decompose into acetic acid, acetone, carbon monoxide and methacrylic acid. It is difficult to account for the formation of ethyl acetoxypropionate except by ester interchange reactions.

$$CH_3COOC(CH_3)_2COOCH(CH_3)COOCH_2CH_3 \quad \text{(VIII)}$$

$$\underset{\text{IX}}{CH_3COOC(CH_3)_2COOH} \longrightarrow CH_3COCH_3 + CH_3COOH + CO$$

Relatively high yields of the corresponding acrylates and methacrylates were formed in the pyrolysis of the acetoxy esters V to VIII, indicating that the pyrolysis method can be used satisfactorily to convert certain selected polyesters into carbalkoxyalkyl acrylates and methacrylates. The results obtained with I and VIII suggest that pyrolysis of appropriate acetoxy esters is suitable for preparing various alpha-carbalkoxyethyl methacrylates ($CH_2{=}C(CH_3)COOCH(CH_3)COOR$); the pyrolysis method, however, should not be satisfactory for making α-carbalkoxyethyl acrylates ($CH_2{=}CHCOOCH(CH_3)COOR$). The present work shows again[8] that methacrylates can be made more easily than acrylates by the pyrolysis of α-acetoxy esters.

Polymerization of Carbomethoxymethyl Acrylate and Methacrylate.—The acrylate and methacrylate of methyl glycolate were polymerized, and the polymers were examined briefly. The polymerization of the other acrylate and methacrylates of the present work has been described earlier.[2]

In ease of polymerization and general appearance of the polymers, carbomethoxymethyl acrylate and methacrylate resemble roughly the corresponding unsubstituted esters, methyl acrylate and methyl methacrylate. In agreement with an earlier observation, the effect of substituting the carbomethoxy group for hydrogen in methyl acrylate was to harden the polymer and raise its brittle point (from 3 to 18°). On the other hand, introduction of the carbomethoxy group into methyl methacrylate lowered the brittle point of the polymer from about 90 to 55°.

The polymer of carbomethoxymethyl acrylate was soluble in several solvents, whereas the polymer of the corresponding methacrylate gelled without dissolving. Whether the insolubility of the polymeric methacrylate was due to cross-linkage or to the inherent nature of the linear polymer is not known. Cross-linkage in the methacrylate polymer would not be expected. The polymer was molded, indicating that it was thermoplastic.

Experimental

Acetoxypropionic acid[9] was prepared and converted into α-acetoxypropionyl chloride[10] as previously described. Acetoxyisobutyric acid was made by adding (stirring) 1.1 mole of acetic anhydride dropwise (rate adjusted to maintain temperature at 40 to 60°) to a suspension of 1 mole of α-hydroxyisobutyric acid[11] in 50 ml. of acetic acid and 2 ml. of acetyl chloride. The mixture was then heated on a steam-bath for three hours, and acetic acid was distilled under reduced pressure using a water pump. The acetoxyisobutyric acid was distilled at 90 to 96° (0.5 mm.); n^{20}_D of supercooled liquid was 1.4240. The product crystallized on standing; m. p. 52–56°.

α-Acetoxyisobutyryl Chloride.—This was made from relatively pure acetoxy acid prepared as outlined above, or more conveniently as follows: A mixture of α-hydroxyisobutyric acid (1 mole), 50 ml. of acetic acid and 3 ml. of acetyl chloride was treated with 1.1 moles of acetic anhydride, and then the acetic acid was distilled at 20 to 37 mm. Thionyl chloride (1.2 moles) was added to the residue, and the resulting mixture was warmed on a steam bath to maintain brisk evolution of gases. Acetoxyisobutyryl chloride[12] (73% yield) was distilled at 60–65° (9 mm.): d^{20}_4, 1.1498; n^{20}_D 1.4282; n^{24}_D 1.4264; molecular refraction: calcd., 36.44; obs., 36.70.

Acylation of Alkyl Glycolate and Lactates.—The hydroxy esters were acylated with acetoxypropionyl chloride or acetoxyisobutyryl chloride in the presence of pyridine, the following being typical: To a solution of ethyl lactate (0.943 mole), 1 mole of anhydrous pyridine, and 150 ml. of benzene, 0.943 mole of acetoxyisobutyryl chloride was added slowly (with cooling and stirring), the reaction temperature being maintained at 18 to 23°. After it had stood overnight, dilute hydrochloric acid was added. The resulting organic layer was washed with aqueous sodium sulfate solution until free of chlorides, and then allowed to stand over anhydrous sodium sulfate. Benzene–water azeotrope was distilled at atmospheric pressure until the vapor temperature was 78°. The distillation was continued in a vacuum, a 92% yield of the acetoxyisobutyrate of ethyl lactate (Table I) being obtained. It boiled at 80–82° (0.3 mm.).

The acylation was less satisfactory in the absence of pyridine (Table I); the acetoxypropionate of methyl lactate was obtained in 45% yield by treating 0.5 mole methyl lactate with 0.5 mole acetoxypropionyl chloride, and fractionally distilling the resulting mixture under reduced pressure.

---

(9) E. M. Filachione and C. H. Fisher, *Ind. Eng. Chem.*, **36**, 472 (1944).

(10) E. M. Filachione, J. H. Lengel and C. H. Fisher, THIS JOURNAL, **66**, 494 (1944).

(11) From the hydrolysis of methyl hydroxyisobutyrate, which was kindly supplied by The Rohm and Haas Company, Philadelphia, Pa.

(12) E. E. Blaise and Herzog, *Compt. rend.*, **184**, 1332 (1927).

TABLE II

PYROLYSIS OF ACYLATED HYDROXY ESTERS

Expt.	Ester pyrolyzed, g.	Temp., °C.	Feed rate, g./min.	Contact time, sec.	Ester dec., %	Unsatd. ester[a]	Yields, moles per mole of ester destroyed: Acetic acid		Acetaldehyde	Methyl acrylate	CO	CO_2	H_2	Hydrocarbons	
							Titr.	Distn.						Unsatd.	Satd.
	Acetoxypropionate of,														
1A	Me glycolate, 100	500	2.96	8	48	0.58	0.97	0.71	..	..	0.4	0.04	0.002	0.14	0.08
1B,	Me glycolate, 101	552	3.05	7.3	86	.54	.91	.72	..	..	.53	.07	.005	.22	.08
2A	Me lactate, 100	500	4.1	6.2	47	.14	1.02	..	0.19	..	.62	.03	.07	.03	.09
2B	Me lactate, 100	497	4.13	6.2	32	..	1.07	..	..	..	.48	.04	..	.02	.12
2C	Me lactate, 100	546	4.87	5	73	.17	1.14	.84	.27	0.52	.81	.05	.007	.05	.08
2D	Me lactate, 101	548	4.1	5.8	79	.10	1.0	.79	.11	.37	..	..	..	..	..
	Acetoxyisobutyrate of														
3A	Me glycolate, 102	501	2.88	8.8	100	.81	.98	..	..	..	.04	.01	.01	.04	0
3B	Me glycolate, 95	551	2.58	9.2	100	.74	1.0	.93	..	..	.15	.02	..	.1	0.01
4A[b]	Me lactate, 100	451	3.77	7.6	85	.65	.87	.61	..	..	.06	..	..	.002	..
4B[b]	Me lactate, 100	500	4.3	6.4	100	.56	1.07	.45	..	.08	.1	..	..	.004	..
5A[b]	Et lactate, 100	450	8.37	9.1	89	.57	.88	.58	.10[c]	..	.14	..	..	.04	..
5B[b,d]	Et lactate, 59	502	3.03	9.4	100	.26	1.16	.60	..	.10[e,f]	.24	..	.004	.15	.005
5C	Et lactate, 280	450	2.44	8.0	70	.58	.86	.61[g]	.09[c]	.04[e,f]	.07	.01	..	.03	..

[a] Acrylate or methacrylate of methyl glycolate, methyl lactate or ethyl lactate. [b] Pyrolysis tube swept out with carbon dioxide instead of nitrogen. [c] Acetone, identified as the 2,4-dinitrophenylhydrazone. [d] Distillation residue, possibly polymeric material, amounted to 14%. [e] Ethyl acrylate. [f] Ethyl acetoxypropionate (0.13 mole in 5 B and 0.21 mole in 5C) also obtained. [g] Methacrylic acid (0.06 mole) also obtained.

TABLE III

PROPERTIES OF MONOMERIC CARBALKOXYALKYL ACRYLATES AND METHACRYLATES

	B. p., °C.	Mm.	d^{20}_4	$n^{20}D$	Mol. ref. Calcd.	Found	Sapn. equiv. Calcd.	Found
Acrylate of								
Methyl glycolate	80	9	1.143	1.4357	32.65	32.82	72.06	71.58
Methyl lactate[a]	77–82	11	....	1.4314	...	...	79.07	77.6
Methacrylate of								
Methyl glycolate[a]	68–69	1.5	1.1066	1.4387	37.36	37.57	79.07	79.11
Methyl lactate[a]	89–90	14	1.0618	1.4335	41.98	42.14	...	...
Ethyl lactate[a]	87–88	10	1.0274	1.4312	46.60	46.93	93.10	90.7

[a] These compounds were described previously, references 2 and 3.

Pyrolysis.—The acetoxy esters were pumped[13] into the top of a vertical Pyrex glass tube (25 mm. diameter) heated over a length of 66 cm. by a 3-section electric combustion furnace. The pyrolysis tube was packed with short lengths of Pyrex glass tubing; free space of heated zone was 123 ml. for all experiments except 5C, in which the free space was somewhat less. The thermocouple was in a well and located at a point 1.5 cm. above the bottom of the heated zone. The temperature was controlled automatically. The apparatus was swept out with nitrogen before and after the pyrolysis.

The pyrolyzate was condensed (water-cooled condenser and Dry Ice traps) at the bottom of the pyrolysis tube, and an aliquot was titrated for free acidity (calculated as acetic acid). Hydroquinone was added to minimize polymerization, and the products were distilled in vacuum in an atmosphere of carbon dioxide. Acetic acid and products of equal or greater volatility were collected in a Dry Ice trap and redistilled at atmospheric pressure (Tables II and III). Discrepancies between titratable acidity and acetic acid indicated by distillation data suggest that unidentified acids were in some of the pyrolyzates.

Identification of Products from the Pyrolysis of the Acetoxyisobutyrate of Ethyl Lactate (experiment 5C).—In a preliminary distillation through a Vigreux column (50 cm. long), first at 30–50 mm. and finally at 0.3–0.5 mm., the following fractions resulted: (A) acetic acid and other volatile products, b. p., under 47° at 0.4 mm.; (B) largely methacrylate of ethyl lactate, b. p., 47–83° at 0.3–0.5 mm.; and (C) starting material, b. p., 83° at 0.65 mm.

Acetone was distilled at atmospheric pressure from Fraction A and identified as the 2,4-dinitrophenylhydrazone. Water (20 ml.) was then added to the distillation flask, and ethyl acrylate was distilled azeotropically. The ethyl acrylate layer of the distillate was redistilled and identified by its boiling point, refractive index, and tendency to polymerize when warmed with benzoyl peroxide.

Methylene chloride was added to the aqueous solution in the distillation flask, and water was distilled azeotropically. Acetic acid was then distilled and identified by its boiling point, melting point and refractive index.

Fraction B (containing hydroquinone) was redistilled in an atmosphere of carbon dioxide through an efficient column packed with copper screening. The following main fractions were obtained: B1, b. r., 56–67° at 6.2 mm. (acidic); and B2, the methacrylate of ethyl lactate, b. r., 79–82° at 6.2 mm., $n^{20}D$ 1.4310, saponification equiv., 91.3 (theoretical, 93.1).

Redistillation of B1 gave two fractions boiling at (a) 54–59° at 7.7 mm. and (b) 68–70° at 8.2 mm.

The 54–59° fraction (B1a) was neutralized with sodium bicarbonate solution and steam distilled. The aqueous solution remaining in the distillation flask was neutralized with sulfuric acid and then steam distilled. The distillate was saturated with sodium sulfate and extracted with chloroform. Methacrylic acid (b. r. 75–76° at 22 mm., $n^{20}D$ 1.4305, m. p., 13°, neut. equiv., 87.1 (theoretical, 86.1)) was distilled from the chloroform fraction. These data agree with those previously reported[14] for methacrylic acid. The β-anilino-isobutyranilide, reported[15] to

---

(13) B. B. Corson and W. J. Cerveny, *Ind. Eng. Chem., Anal. Ed.*, **14**, 899 (1942).

(14) W. P. Ratchford, C. E. Rehberg and C. H. Fisher, THIS JOURNAL, **66**, 1864 (1944).

(15) W. Autenrieth and C. Pretzell, *Ber.*, **36**, 1262 (1903).

melt at 122°, was prepared from the sample of methacrylic acid and found to melt at 120–121°.

Fraction B1b (b. r., 68–70° at 8.2 mm.) was neutralized with sodium hydroxide and distilled (86° at 22 mm., n^{20}_D, 1.4087, d^{20}_4, 1.0450, and saponification equiv., 80.2). These constants for ethyl α-acetoxypropionate are, respectively: 86° at 22 mm., 1.4085, 1.0441 and 80.1. Further reasons for concluding that this sample was ethyl α-acetoxypropionate are: saponification yielded ethanol, identified as the 3,5-dinitrobenzoate (m. p., 94–95°); acetanilide (m. p., 115°) was obtained by refluxing the sample with aniline; and the temperature at which a 50-50 solution by volume of the sample and n-heptane separated into 2 layers was 3° (50-50 solutions of n-heptane-ethyl α-acetoxypropionate and n-heptane-ethyl α-acetoxyisobutyrate became immiscible at 3° and −20 to −25°, respectively).

It was assumed that ethylene was the gaseous olefin produced in experiments 5A–5C.

Polymeric Carbomethoxymethyl Acrylate.—When emulsion polymerized as described previously,[3] 10 g. of the acrylate of methyl glycolate yielded 8.5 g. of soft and pliable polymer that became brittle at 15 to 20°. Mass polymerization occurred readily when a sealed tube of the monomer containing 1% benzoyl peroxide was allowed to stand at room temperature.

The polymer (0.25 g. per 5 ml. solvent) was soluble in acetone, ethyl acetate, methyl lactate, dioxane, nitromethane and ethylene chloride; the last two compounds seemed to have highest solvent power. The polymer was insoluble in toluene, β-butoxyethyl acetate, heptane, ethanol and water.

Polymeric Carbomethoxymethyl Methacrylate.—When the emulsion of the polymer was coagulated, the polymer separated as a fine powder that filtered with difficulty. At approximately 65° the polymer agglomerated, yielding a granular product that was easily filtered or decanted. Although only 18.5 g. polymer was obtained from 25 g. monomer, probably the polymerization yield was nearly quantitative, since little or no monomer was volatilized by the distillation of water from the emulsion prior to coagulation.

Mass polymerization in a sealed tube at 63° of monomer containing 0.1% benzoyl peroxide yielded a transparent, colorless casting in a few hours. The polymer was hard at room temperature but softened between 52 and 58°. A hard polymer was obtained also by heating monomer in the absence of benzoyl peroxide at 63° overnight.

The polymer (0.25 g. per 5 ml. solvent) gelled without dissolving in acetone, ethyl acetate, methyl lactate, dioxane, nitromethane, ethylene chloride, and β-butoxyethyl acetate. It swelled slightly in toluene, and was insoluble in heptane, ethanol and water.[16]

Summary

Several α-carbalkoxyalkyl acrylates and methacrylates were prepared by pyrolyzing the α-acetoxypropionate of methyl glycolate and methyl lactate and the α-acetoxyisobutyrate of methyl glycolate, methyl lactate and ethyl lactate. The relation between ester structure and thermal stability is discussed.

The acrylate and methacrylate of methyl glycolate were polymerized, and certain properties of the polymers determined.

(16) Strain (ref. 3) polymerized carbomethoxymethyl methacrylate at 100° and obtained a soluble polymer. Possibly the increased solubility of his polymer was due to lower molecular weight.

PHILADELPHIA 18, PA. RECEIVED OCTOBER 26, 1945

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, AUCKLAND UNIVERSITY COLLEGE]

The Osmotic and Activity Coefficients of Zinc Nitrate, Zinc Perchlorate and Magnesium Perchlorate. Transference Numbers in Zinc Perchlorate Solutions

BY R. H. STOKES AND BARBARA J. LEVIEN

Zinc chloride in aqueous solutions exhibits anomalies which may be ascribed to the formation of intermediate or complex ions. The activity coefficient curve plotted against $\sqrt{m}$ does not fall into the regular sequence of other bivalent metal chlorides,[1] and at high concentrations the cationic transference numbers are negative.[2,3] Similar anomalies have been found to occur with zinc bromide with respect to both the activity coefficient[4] and the transference numbers.[5] With zinc iodide these interfering effects appear to be negligible up to about 0.5 M, but at higher concentrations deviations of the same type have been found.[6,7,8]

At low concentrations the activity coefficient of zinc iodide is close to that of magnesium iodide, suggesting that if intermediate and complex ion formation were absent, there would be a parallelism between the activity coefficients of zinc and magnesium salts. This view is supported by the observation that the ionic diameters of these two cations are similar in the crystal state. To test this further, a search has been made for "normal" zinc salts, for which purpose the activity coefficient of zinc nitrate has been determined and compared with the known values for magnesium nitrate,[9] the activity coefficients of zinc and magnesium perchlorates have been measured and compared and transference numbers in zinc perchlorate solutions have been calculated from the e. m. f.'s of cells with transference.

Experimental

Preparation of Solutions.—A weighed quantity of zinc oxide, previously heated to drive off water and carbon dioxide, was dissolved in the calculated amount of a perchloric acid solution whose concentration had been deter-

---

(1) R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 419 (1941).

(2) G. Scatchard and Tefft, THIS JOURNAL, **52**, 2272 (1930).

(3) A. C. Harris and H. N. Parton, *Trans. Faraday Soc.*, **36**, 1139 (1940).

(4) R. H. Stokes, J. M. Stokes and R. A. Robinson, *ibid.*, **40**, 533 (1944).

(5) H. N. Parton and J. W. Mitchell, *ibid.*, **35**, 758 (1939).

(6) R. H. Stokes, *ibid.*, **41**, 12 (1945).

(7) W. Hittorf, *Pogg. Ann.*, **106**, 513 (1859).

(8) R. G. Bates, THIS JOURNAL, **60**, 2983 (1938).

(9) R. A. Robinson, J. M. Wilson and H. S. Ayling, *ibid.*, **64**, 1469 (1942).