

struct such models of structure as may best explain the observable facts about liquids.

It has been assumed that liquids are systems of two phases at equilibrium. The one, exemplified by the surface, consists of two-dimensional molecular lattice structures; the other occupies the spaces between the former in a truly gaseous condition. The equilibrium is supposed to depend on temperature but not on pressure imposed from outside.

On this basis an equation of the liquid state has

been formulated which contains, besides V , P and T , the dependent variables surface tension and viscosity. The three viscosity functions derived from this equation and representing it in parameter form, *viz.*, that of temperature, pressure and volume, respectively, are in very accurate agreement with measurements on a large number and variety of liquids, and thus confirm the validity of the proposed theory of liquid structure.

SHAWINIGAN FALLS
QUEBEC, CANADA

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMICAL LABORATORY OF LEHIGH UNIVERSITY]

Studies in Ester Hydrolysis Equilibria—Formic Acid Esters

BY RAYMOND F. SCHULTZ

In 1901 Euler¹ studied the hydrolysis equilibrium at 50° for simple formic, acetic and propionic esters, using hydrochloric acid as a catalyst. In 1928 Williams, *et al.*,² in attempting to correlate the hydrolysis equilibrium constants with the dissociation constants of the corresponding acids, investigated the same series of esters at 100° in the absence of a mineral acid catalyst.

The results of Williams agree fairly well with those of Euler and others^{1,3-7} for acetic and propionic esters, but his constants for formic esters are very much higher (see Table I). He believed Euler's results in error due to side reactions between the alcohol and the large amount of hydrochloric acid in his mixtures (0.25 *N* in hydrogen chloride). It is difficult to see why such errors should be confined to the formic esters and not affect the results for the other esters,

because all of Euler's mixtures contained the same high concentration of hydrochloric acid.

In another connection, we attempted to apply the above data to the analysis of various formic ester hydrolysis mixtures, and found inconsistencies. We, therefore, have determined carefully the hydrolysis equilibrium constants for formic esters under a variety of new conditions, and have found a change in the "constants" with varying mole fractions of water present. These effects have not been studied previously in the formic ester series, though they occur to about the same extent as in the acetic ester hydrolyses.³⁻⁷

We also have redetermined constants for ethyl formate in mixtures identical with those of Euler and of Williams.

Experimental

Purification of Materials. Methyl, ethyl and *n*-propyl formate (Eastman Kodak Co.) were purified carefully. Analyses indicated that the final products contained more than 99.5% ester and less than 0.02% formic acid.

Methyl and ethyl alcohols were of absolute c. p. reagent quality, with densities indicating a purity of 99.5% or more. *n*-Propyl alcohol, 99.7% pure by density measurements, was prepared by fractional distillation of an Eastman product.

Formic acid was purified by fractional distillation of a Baker and Adamson 90% product. Analysis by titration of weighed samples showed 99.34% formic acid. In our determinations, a correction was made for the remaining 0.66% as water.

Procedure.—Weighed samples of ester and of 0.005 *N* hydrochloric acid (total volume *ca.* 5 cc.) were sealed into clean Pyrex ampoules of 7-cc. capacity. The mixtures were kept at 100 ± 2° for forty-eight to sixty hours; shorter heating periods gave inconsistent results. Experi-

TABLE I

A COMPARISON OF HYDROLYSIS EQUILIBRIUM CONSTANTS FOR FORMIC ACID ESTERS OBTAINED BY EULER¹ AND WILLIAMS²

	Init. comp. in moles				$K = \frac{[\text{Acid}]^2}{[\text{Ester}][\text{H}_2\text{O}]}$	
	Acid	Alcohol	H ₂ O	HCl	Euler	Williams
Methyl	0.04	0.04	0.95	0.005	0.20	
Methyl	7.10	18.81	1.03
Ethyl	0.04	0.04	0.91	.005	.36	
Ethyl	9.95	9.95	4.00	1.45

(1) Euler, *Z. physik. Chem.*, **36**, 408 (1901).

(2) Williams, *et al.*, *This Journal*, **50**, 1267 (1928).

(3) Jones and Lapworth, *J. Chem. Soc.*, **99**, 1427 (1911).

(4) Schlesinger, *Ber.*, **59**, 1965 (1926); **60**, 1479 (1927); *Acta phys. chim.*, **5**, 93 (1936); **6**, 769 (1937).

(5) Dobrzynski, *Roczniki chemji*, **8**, 369 (1928).

(6) Poznanski, *ibid.*, **8**, 377 (1928); **9**, 369 (1929).

(7) Berthelot and Péan de Saint Gilles, *Ann. chim. phys.*, [3] **65**, 395 (1862); [3] **66**, 5 (1862); [3] **68**, 225 (1863).

TABLE II

Run	Initial composition, mmol.				Equilibrium composition, mmol.				HCl	Ratio [H ₂ O] ^a [HO] + [Ester]	K _{eq.}
	Ester	Water	Acid	Alcohol	Ester	Water	Acid	Alcohol			
METHYL FORMATE											
72	55.43	18.31	0.0	0.0	47.24	10.12	8.186	8.186	0.001	0.248	0.140
73	55.81	16.76	.0	.0	47.77	8.72	8.040	8.040	.001	.231	.155
74	58.12	17.81	.0	.0	49.84	9.52	8.284	8.284	.001	.235	.145
69	50.89	50.68	.0	.0	36.01	35.78	14.88	14.88	.005	.499	.172
70	50.83	50.19	.0	.0	36.01	35.37	14.82	14.82	.005	.497	.173
71	52.51	50.62	.0	.0	37.46	35.57	15.05	15.05	.005	.491	.170
76	33.50	130.00	.0	.0	14.95	11.44	18.55	18.55	.005	.795	.207
77	31.49	125.30	.0	.0	13.79	10.76	17.70	17.70	.005	.799	.211
142	23.98	478.50	.0	.0	3.82	458.3	20.16	20.16	.005	.952	.232
143	25.23	474.00	.0	.0	4.08	452.9	21.15	21.15	.005	.950	.242
111	0.0	6.684	48.56	58.26	35.89	42.57	12.67	22.37	.05	.532	.186 ^b
112	0.0	8.214	48.88	57.44	35.38	43.59	13.50	22.06	.07	.538	.193 ^b
ETHYL FORMATE											
61	42.89	13.71	0.0	0.0	35.90	6.72	6.99	6.99	0.001	.242	.203
62	43.44	13.01	.0	.0	36.59	6.16	6.85	6.85	.001	.231	.208
63	44.41	11.62	.0	.0	37.97	5.18	6.44	6.44	.001	.208	.210
68	45.63	11.10	.0	.0	39.25	4.72	6.38	6.38	.001	.196	.220
58	37.86	38.07	.0	.0	24.90	25.11	12.96	12.96	.004	.501	.269
59	40.74	37.76	.0	.0	27.55	24.55	13.21	13.21	.004	.481	.258
60	40.07	39.89	.0	.0	26.54	26.36	13.53	13.53	.004	.499	.262
64	28.21	112.00	.0	.0	10.53	94.32	17.68	17.68	.010	.799	.315
65	26.86	113.00	.0	.0	9.63	95.77	17.23	17.23	.010	.807	.322
66	27.18	109.90	.0	.0	9.88	92.60	17.30	17.30	.010	.801	.327
67	28.87	112.70	.0	.0	10.84	94.67	18.03	18.03	.010	.796	.317
92	0.0	15.14	40.86	40.59	24.51	39.65	16.35	16.08	.0015	.577	.270 ^c
105	.0	17.59	38.45	40.87	23.55	41.14	14.90	17.32	.0015	.593	.266 ^c
106	.0	17.04	38.79	39.52	23.22	40.26	15.57	16.30	.0015	.590	.265 ^c
93	.0	448.8	21.22	20.94	2.08	450.9	19.14	18.86	2.41	.954	.386 ^d
94	.0	452.2	20.92	20.52	2.01	454.2	18.91	18.51	2.44	.953	.383 ^d
95	.0	448.7	21.47	22.93	2.25	451.0	19.22	20.68	2.44	.952	.392 ^d
PROPYL FORMATE											
17	43.34	11.43	0.0	0.0	37.18	5.27	6.16	6.16	0.001	.209	.193
18	44.49	11.93	.0	.0	38.06	5.51	6.43	6.43	.001	.212	.197
99	42.84	12.15	.0	.0	36.39	5.70	6.46	6.46	.001	.221	.201
23	42.70	42.62	.0	.0	28.51	28.43	14.19	14.19	.004	.500	.249
24	38.53	44.33	.0	.0	24.74	30.54	13.79	13.79	.004	.535	.252
85	42.73	46.11	.0	.0	27.85	31.23	14.88	14.88	.015	.519	.254
86	42.67	45.09	.0	.0	28.01	30.43	14.66	14.66	.015	.513	.252
103	34.60	77.84	.0	.0	17.60	60.84	17.00	17.00	.01	.692	.270
104	33.55	78.72	.0	.0	16.92	62.09	16.63	16.63	.01	.701	.263
96	28.00	112.2	.0	.0	11.16	95.36	16.84	16.84	.01	.800	.267
97	28.17	111.4	.0	.0	11.28	94.51	16.89	16.89	.01	.798	.268
20	28.00	111.7	.0	.0	11.23	94.93	16.77	16.77	.01	.799	.264
42	21.05	112.2	.0	.0	7.12	98.27	13.93	13.93	.01	.842	.277
43	22.08	112.7	.0	.0	7.65	98.27	14.43	14.43	.01	.836	.277
45	14.30	191.0	.0	.0	2.53	179.2	11.77	11.77	.01	.930	.306
101	21.61	392.4	.0	.0	2.88	373.7	18.73	18.73	.02	.948	.325
102	21.12	391.2	.0	.0	2.82	372.9	18.31	18.31	.02	.948	.319
82	0.0	6.15	44.92	39.97	27.09	33.24	17.83	12.88	<.01	.536 ^b	.255
83	.0	6.97	47.67	39.56	27.73	34.70	19.94	11.83	<.01	.540 ^b	.245

^a In the initial mixture. ^b This ratio is [Alcohol] + [H₂O]/[Total Millimoles] in order to correspond to [H₂O]/[H₂O] + [Ester] in a hypothetical initial mixture of ester and water. All quantities in both ratios are millimoles in the initial mixture. ^c Similar to Williams.² ^d Similar to Euler.¹

ments starting with alcohol and acid gave the same constants, showing that equilibrium had been attained in the time allowed.

After equilibrium had been reached, the tubes were cooled to -80° , opened, and the contents dissolved in 50 cc. of acetone. This solution was then cooled to -80° and

titrated rapidly with 0.5 *N* methyl alcoholic sodium methylate, using 1 cc. of a 0.1% solution of brom cresol purple in acetone as an indicator. At the end of the titration, the temperature was still below -50° .

This procedure was arrived at after many preliminary experiments with known formic acid-formic ester mixtures. When the analyses were carried out at 0° with aqueous alkali, inconsistent results were obtained, due to the hydrolysis of as much as 5% of the ester. With methyl alcoholic sodium methylate at 0° , the end-point was obscured by a voluminous precipitate of sodium formate. At temperatures below -50° , the sodium formate failed to precipitate, probably due to supersaturation, and very good end-points were obtained. Phenolphthalein was unsatisfactory as an indicator, as the esters saponified rather rapidly at the *pH* of the end-point (8.3–11.0), and gave high, erratic titers. The validity of brom cresol purple (alkaline end-point at *pH* 6.8–7.2) as an indicator for these analyses was demonstrated by determining the *pH* of neutral sodium formate (7.2 in a 0.5 *N* solution), and by potentiometric titration of formic acid using the glass electrode.

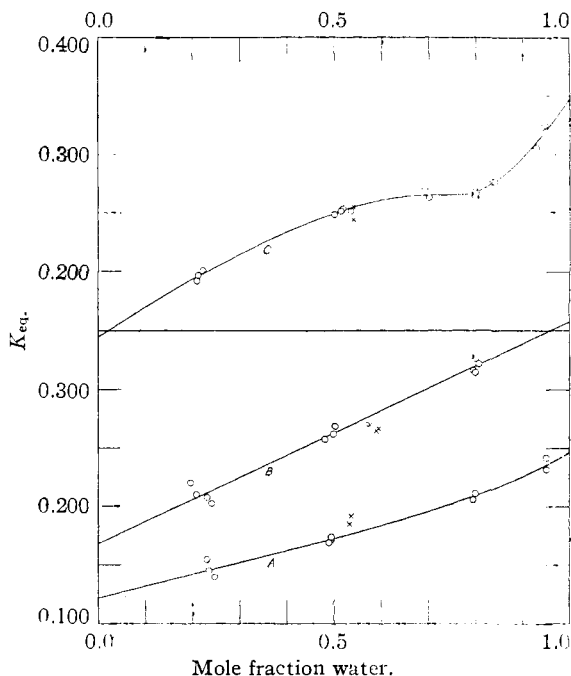


Fig. 1.—Effect of varying water concentrations on hydrolysis equilibrium constant: A, methyl formate; B, ethyl formate; C, propyl formate; *o*, from ester-water mixtures; *x*, from check runs on acid-alcohol mixtures.

In the first series of experiments (Fig. 1, Table II), the mole fraction of water was varied from 0.2 to 0.95. About 0.002 mole per cent. of hydrochloric acid was used as a catalyst. This quantity of acid, as is obvious from Fig. 2, does not affect the constant. In the second series, the ratio of ester to water was held at 1.0, and the hydrochloric acid concentration was varied from 0.45 to 1.9 mole per cent. The data are summarized in Fig. 2.

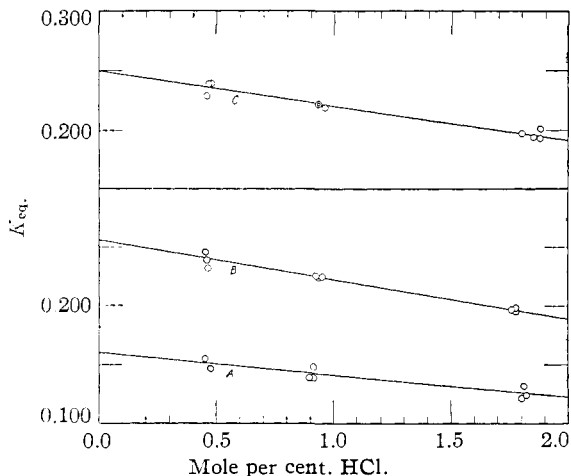


Fig. 2.—Variation of hydrolysis equilibrium constant with hydrochloric acid concentration where $(\text{H}_2\text{O})/(\text{Ester}) = 1$: A, methyl formate; B, ethyl formate; C, *n*-propyl formate.

Greater concentrations of acid were not used in order to avoid side reactions like the formation of alkyl halide. For the same reason the period of heating was kept as low as possible in the second series (15 hours). In none of our experiments was there a detectable loss of hydrochloric acid due to alkyl halide formation.

Discussion of Results

The results of this investigation show that the hydrolysis equilibrium "constants" for formic esters vary with the concentrations of the reactants. Calculations were made from the usual formula

$$K_{\text{eq.}} = \frac{[\text{HCOOH}][\text{ROH}]}{[\text{HCOOR}][\text{HOH}]} = \frac{[\text{HCOOH}]^2}{[\text{HCOOR}][\text{HOH}]}$$

When minute quantities of hydrochloric acid (not more than 0.002 mole per cent.) are employed as a catalyst, the "constant" increases with rising water concentrations (Fig. 1 and Table II). If the initial water-ester ratio is fixed at 1.0, then the "constant" is lowered by relatively large amounts of hydrochloric acid (Fig. 2). The latter effect is well known and has been studied extensively by Jones and Lapworth and others³⁻⁴ in connection with the hydrolysis of acetates; these authors have not studied the formic esters.

The effect of varying water concentrations, either in the absence of hydrochloric acid or in the presence of very small quantities, has not been studied in any detail for either formic esters or acetic esters. The very early work of Berthelot⁷ and that of Poznanski⁶ on the esterification of acetic acid with varying concentrations of alcohol and acid, both indicate some change in the esteri-

fication "constant" with proportions of the reactants.

We repeated the experiments of Euler¹ and Williams² using ethyl alcohol and formic acid. Our results for Euler's mixture check his results fairly well. For mixtures identical with those of Williams in his series "A" determinations (except for the addition of 0.0015 mole per cent. of hydrochloric acid which, according to our work on the effect of hydrochloric acid, should not influence the equilibrium noticeably), we get a much lower value for the constant. Williams obtained a value of 1.45; our value is 0.265.

As pointed out in the experimental section, our work with known mixtures indicates that Williams' twenty-four hour heating period was probably too short for the attainment of equilibrium, and that titration with aqueous alkali at 0° results in considerable hydrolysis of the ester present.

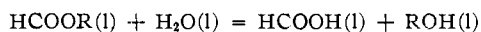
Williams observed a correlation between the hydrolysis equilibrium constants of formic,² acetic²⁻⁷ and propionic esters, and the dissociation constants of the corresponding acids. On the basis of our results such a correlation vanishes, since our values for formic esters are lower than those for acetic and propionic esters, rather than higher as Williams found.

The change in value of the hydrolysis "constants" with conditions, *i. e.*, water-ester ratio and change in hydrochloric acid concentration, shows definitely that the activities are not proportional to the mole fractions. As in the acetic ester series,^{3,4} no more satisfactory explanation can be offered at this time.

If we take a value of K_{eq} , where the mole fraction of water is 0.5 in the starting mixture,⁸ and substitute it in the expression

$$\Delta F^\circ = -RT \ln K$$

we get the free energy change for the reaction



at 373°K. This choice of constant may seem arbitrary, but since the value changes relatively little over the whole range of water concentrations, it will not involve an error of more than about 100 cal.

If we assume that $\Delta H_{298} = 0$, as is indicated by the available combustion data, then K_{eq} is independent of temperature and we can write

$$\Delta F_{298}^\circ = -RT \ln K_{373}$$

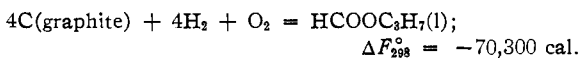
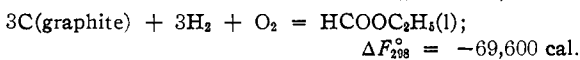
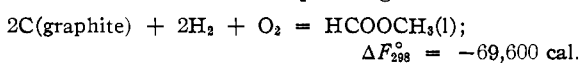
This assumption seems reasonable by comparison

(8) Parks and Huffman, "Free Energies of Organic Compounds," Chemical Catalog Co., New York, 1932, p. 173.

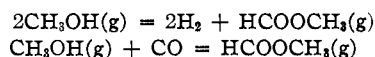
with other esters. Combustion data give $\Delta H_{298} = 0$ for the liquid phase esterification of acetic acid with the lower alcohols, and this has been confirmed experimentally for ethyl acetate.⁹ The conversion of butyric, benzoic, and several other acids to ethyl esters, seems also to be independent of temperature,⁷ hence here too $\Delta H = 0$.

Substituting values for K_{373} in the above expression, we get $\Delta F_{298}^\circ = +1040$ cal. for the methyl formate hydrolysis, +790 cal. for that of ethyl formate, and +1030 cal. for that of *n*-propyl formate.

By combining the above free energy values with those for the free energies of formation of water, formic acid, methyl alcohol, ethyl alcohol and *n*-propyl alcohol,⁸ we obtain the free energies of formation of the corresponding formic esters



Parks and Huffman,⁸ from data for the equilibria^{10,11}



measured at 180-250°, obtained a value of $\Delta F_{298}^\circ = -71,010$ cal. for liquid methyl formate.

Further experiments are in progress to determine how general this variation of hydrolysis "constant" with water concentration may be, and if possible the value of the true thermodynamic constant in each case.

The author wishes to acknowledge the valuable assistance of his wife, Emma Dietz Schultz, in carrying out some of the experimental work.

Summary

The hydrolysis equilibrium "constants" for methyl, ethyl and *n*-propyl formates have been measured in mixtures of the ester with water. As the mole fraction of water increased from 0.2 to 0.95, the "constant" changed from 0.14 to 0.232 for methyl formate, 0.203 to 0.307 for ethyl formate, and 0.193 to 0.325 for *n*-propyl formate.

The "constants" were measured also in ester-water mixtures (1:1) containing relatively large quantities of hydrochloric acid. As the con-

(9) H. S. Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1931, p. 459.

(10) Christiansen, *J. Chem. Soc.*, 413 (1926).

(11) Lacy, Dunning and Storch, *THIS JOURNAL*, **52**, 927 (1930).

centration of hydrochloric acid increased from 0.47 to 1.9 mole per cent., the hydrolysis "constants" decreased as follows: methyl formate 0.155 to 0.122; ethyl formate 0.246 to 0.195; *n*-propyl formate 0.239 to 0.193.

The free energies of formation of the esters at 298°K., as calculated from our data, are: -69,000 cal. for methyl, -69,000 cal. for ethyl, and -70,300 cal. for *n*-propyl formate.

BETHLEHEM, PENNA.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE COLLEGE OF WASHINGTON]

The Bromination of 4-Phenylphenyl Benzoate

BY STEWART E. HAZLET, GLEN ALLIGER¹ AND RALPH TIEDE¹

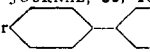
In a previous report² it has been shown that although the bromination of 4-phenylphenol results in substitution at a position ortho to the hydroxyl group, modification of hydroxyl to benzenesulfonyloxy hinders substitution in the ring to which the group is attached and yields 4-(4-bromophenyl)-phenyl benzenesulfonate. In the present work a study has been made of the bromination of 4-phenylphenyl benzoate to determine whether the benzoyloxy group would hinder substitution in the ring to which it is attached as had been noted in the case of benzenesulfonyloxy. The results of the present study indicate that the substitution does proceed in a manner analogous to that in the case of the sulfonyl compound. The reactions and proof of structure are summarized in Chart I.

The structure of III was established by its hydrolysis to V and VI and also by its synthesis from a sample of V obtained by the hydrolysis of IV.² Further, the preparation of VIII from VII showed that III was definitely different from the benzoate of VII.

In general, yields of purified products were not so satisfactory as in the study of the sulfonyl compounds. The bromination of II did not take place readily and the hydrolysis of III was less satisfactory than that of the analogous compound (IV) previously reported. Therefore, the preparation of V from IV is a method superior to its preparation from III here reported.

Slightly differing accounts of the preparation and properties of IX have appeared in the literature.³ This compound and VII have been

(1) Seniors in the Department of Chemistry.

(2) Hazlet, *THIS JOURNAL*, **59**, 1087 (1937). Compound VII, Chart I should be Br--NO₂, as described in the paper.

(3) (a) Raiford and Colbert, *ibid.*, **47**, 1454 (1925); (b) Bell and Robinson, *J. Chem. Soc.*, 1127 (1927). (c) The dibromo compound, m. p., 96°, obtained by Raiford and Colbert [*THIS JOURNAL*, **47**,

prepared, carefully purified and analyzed; the results are recorded in the Experimental Part. Likewise, reported melting points of II differ considerably.^{3a,4} Uniformly, in this work, a product melting at 149-150° was obtained.

Experimental Part⁵

4-Phenylphenyl Benzoate (II).^{3a,4}—This compound was prepared by the treatment of 4-phenylphenol (I), dissolved in pyridine, with 1.1 moles of benzoyl chloride in the usual manner.⁶ The crude product was obtained in almost quantitative yield, but considerable loss was involved in its purification. For recrystallizations toluene, ethanol, glacial acetic acid, and methanol have been used.⁷ The purified product melted between 149 and 150°.

4-(4-Bromophenyl)-phenyl Benzoate (III).—4-Phenylphenyl benzoate (II) (10 g.) was suspended in 150 cc. of glacial acetic acid and heated on a boiling water-bath with vigorous stirring. A trace of iron powder was added and bromine (2.8 cc., approximately 1.5 molecular proportions) was then introduced drop by drop. The heating and stirring were continued for three hours after the last of the bromine had been added; then the mixture was cooled and poured into 300 cc. of cold water. The product, which solidified, was collected by filtration and represented an

1457 (1925)] by bromination of 4-phenylphenol was regarded as the 2,6-dibromo derivative, though analysis for halogen indicated that the product was not quite pure. Nitration of it by the Zincke method gave a nitro compound that melted at 171° and for which halogen analysis indicated that all bromine had been retained.

In a similar way Bell and Robinson [*J. Chem. Soc.*, 1132 (1927)] prepared from the same starting material what they recorded as 2,6-dibromo-4-phenylphenol. Their product showed a melting range of 91-94°, it was not analyzed, and oxidation of it gave some 4-bromobenzoic acid, all of which leaves considerable doubt as to the purity of their product. The formation of 4-bromobenzoic acid indicates the presence of 4-(4-bromophenyl)-phenol or 2-bromo-4-(4-bromophenyl)-phenol. The presence of the latter in Raiford and Colbert's product could have accounted for the nitro-dibromo compound they isolated.

Because of these possibilities, and in the light of the results obtained by Raiford and Miller [*THIS JOURNAL*, **55**, 2125 (1933)] in an extended study of the Zincke nitration, the dibromo compound in question will be investigated further.—L. Chas. Raiford, The State University of Iowa, Iowa City.

(4) Kaiser, *Ann.*, **257**, 101 (1890).

(5) Semi-micro methods were used for all analyses.

(6) Hazlet, *THIS JOURNAL*, **59**, 287 (1937).

(7) One of us (S. E. H.) prefers the use of methanol. Although large volumes of this solvent are required, the character of the crystalline product from this solvent seems superior.