centrated hydrochloric acid was distilled in a 5-liter flask attached to a Vigreux column and stillhead. A high reflux ratio was maintained. The azeotropic mixture (b. p. 71.8°) of 46% of ethyl alcohol and 54% of ethyl acetate was first removed and this was followed by ethyl acetate of b. p. 77.1°. The distillation of the residue under diminished pressure gave 600 cc. of the glycol, which was practically the same yield as in the foregoing run.

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The Bromination of 4-Phenylphenyl Bromoacetate

BY LEE C. HENSLEY AND STEWART E. HAZLET

This report contains additional experimental data obtained in this Laboratory in connection with substitution reactions in esters containing diphenyl groups.[1] 4-Phenylphenyl bromoacetate was selected because of its similarity to 4-phenylphenyl chloroacetate, the bromination of which was studied recently,[2] and because it contained the larger bromine atom in place of chlorine.

Preparation of the Bromoacetates of the Bromophenylphenols.—These esters were prepared by treating the appropriate phenol, in the presence of 1,4-dioxane as a diluent, with one and one-half molecular proportions of bromoacetyl bromide in an equivalent quantity of dry pyridine. The colorless esters were extracted from the reaction mixtures with boiling benzene and recrystallized from suitable solvents, *cf.* Table I.

TABLE I

BROMOACETATES OF THE BROMOPHENYLPHENOLS

Phenol used	Yield, %[d]	Solvent	Crystal form	M. p., °C.	Formula	Analyses, % Br Calcd.	Analyses, % Br Found
2-Bromo-4-phenyl-[a]	15.4	Ligroin (70–90°)	Irregular platelets	55–56	$C_{14}H_{10}O_2Br_2$	43.24	43.69
2,6-Dibromo-4-phenyl-[a]	20	Ligroin (70–90°)	Prisms	78–79	$C_{14}H_9O_2Br_3$	53.45	53.75
2,6-Dibromo-4-(4-bromophenyl)-[b]	45.5	Ligroin (70–90°) or ethanol	Long prisms	148–149	$C_{14}H_8O_2Br_4$	60.60	60.06
4-(4-Bromophenyl)-[c]	34.4	Ethanol	Long prisms	141.5–142	$C_{14}H_{10}O_2Br_2$	43.24	43.20

[a] Ref. 3. [b] Bell and Robinson, *J. Chem. Soc.*, 1127 (1927). [c] Hazlet, THIS JOURNAL, **59**, 1087 (1937); *cf.* also [b]. [d] Purified products.

Bromination of 4-Phenylphenyl Bromoacetate. (A) In Glacial Acetic Acid ("Analytical Reagent").—To a solution of 15 g. of 4-phenylphenyl bromoacetate[2] in 100 ml. of hot glacial acetic acid ("analytical reagent"), a trace of iron powder was added, 3.4 ml. of bromine dissolved in 30 ml. of glacial acetic acid was introduced dropwise over a period of twenty minutes, and the subsequent steps were much the same as in the procedure described previously.[2]

From what corresponded to *Fraction A-I* in the anaolgous study,[2] 2.1 g. of 4-phenylphenyl acetate (m. p. 84–86°) was obtained. From what corresponded to *Fraction A-II*,[2] approximately 0.1 g. of each of the following was obtained by fractional crystallization: 4-phenylphenol (m. p. 160°), 2,6-dibromo-4-phenylphenol (m. p. 89–93°), and 2,6-dibromo-4-(4-bromophenyl)-phenol (m. p. 154–157°). Identification by means of a mixed melting point determination with an authentic sample was made in each case.

(B) In Specially Treated Glacial Acetic Acid.—The method was similar to that used for the chloroacetate,[2] and separations were effected as in (A) above. From 10 g. of 4-phenylphenyl bromoacetate, 7.5 g. of starting material (m. p. 111.5–112°) and 0.4 g. of 4-phenylphenol (m. p. 160–164°) were obtained and identified by the mixed melting point method.

(C) In Carbon Tetrachloride.—Ten grams of the bromoacetate was treated in carbon tetrachloride in much the same manner as that reported previously for the chloroacetate.[2] After one crystallization from ethanol, 5 g. of product resulted; several recrystallizations gave a product which melted at 140–140.5°, and no depression in melting point was observed when a sample of this product was mixed with a sample of 4-(4-bromophenyl)-phenyl bromoacetate prepared as described above and listed in Table I.

The ester was hydrolyzed; the resulting phenol melted at 163–164°. A mixture of it and 4-(4-bromophenyl)-phenol, obtained by the hydrolysis of 4-(4-bromophenyl)-phenyl benzoate,[3] melted at 163–164°. This further justified the characterization of the substitution product as 4-(4-bromophenyl)-phenyl bromoacetate.

The bromination of 4-phenylphenyl bromoacetate proceeds in a manner which is essentially analogous to the bromination of the chloroacetate studied previously, *viz.*, in glacial acetic acid ("analytical reagent") several products were obtained: 4-phenylphenol, 2,6-dibromo-4-phenylphenol, 2,6-dibromo-4-(4-bromophenyl)-phenol, and 4-phenylphenyl acetate. These results differ from those obtained with 4-phenylphenyl acetate[4]; in that case, 2-bromo-4-phenylphenyl acetate was formed.

In specially treated glacial acetic acid, no substitution was effected, and starting material and some 4-phenylphenol were obtained.

When carbon tetrachloride was the solvent used, bromination of 4-phenylphenyl bromoacetate yielded 4-(4-bromophenyl)-phenyl bromoacetate; under similar condi-

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[1] For the last report *cf.* Hazlet and Van Orden, THIS JOURNAL, **64**, 2505 (1942).

[2] Hazlet, Hensley and Jass, *ibid.*, **64**, 2449 (1942).

[3] Hazlet, Alliger and Tiede, *ibid.*, **61**, 1447 (1939).

[4] Hazlet and Kornberg, *ibid.*, **61**, 3037 (1939).

tions, 4-phenylphenyl chloroacetate gave rise to the analogous bromination product.[2]

DEPARTMENT OF CHEMISTRY
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Evidence of Deuterium Exchange in the System $DCl–CH_3OH$[1]

BY A. G. GASSMANN,[2] C. J. HOCHANADEL AND R. J. HARTMAN[3]

Following the procedure of Hartman and Borders[4] the esterification of a number of organic acids in methanol at 25°, to which deuterium chloride was added, was carefully measured and found to follow the Goldschmidt equation[5] with the same fidelity as corresponding esterifications catalyzed by hydrochloric acid; and the velocity constants for a series of nine organic acids at 25° in solutions to which deuterium chloride had been added, were found to be identical within the accuracy of the experiments with velocity constants obtained by Hartman and Borders[4] and Hartman and Gassmann[6] for these same acids under corresponding conditions when hydrochloric acid was present.

This is shown by the results listed in the table.

TABLE I

VELOCITY CONSTANTS FOR ESTERIFICATION OF AROMATIC ACIDS WITH METHANOL AT 25°

Acid	10^5k	
	DCl	HCl[4,6]
o-Toluic	6.61	6.41
m-Nitrobenzoic	7.29	7.28
p-Nitrobenzoic	8.04	8.67
p-Chlorobenzoic	10.5	11.4
m-Chlorobenzoic	11.6	12.4
m-Iodobenzoic	13.6	13.7
p-Toluic	18.5	19.7
Benzoic	19.1	19.2
m-Toluic	21.8	21.7

This identity was of course to be expected in view of the known rapid exchange reaction in the system, $DCl–CH_3OH$. It was found that the rate at which 0.1000 *N* and 0.0200 *N* DCl reacts with methanol at 25, 40, 50, and 60° was approximately the same as that previously reported for hydrogen chloride and methanol.[7]

DEPARTMENT OF CHEMISTRY
INDIANA UNIVERSITY
BLOOMINGTON, INDIANA RECEIVED JANUARY 27, 1943

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[1] This paper represents a brief abstract of a part of a thesis presented by Albert George Gassmann to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Present address: University of Detroit, Detroit, Michigan.

[3] Present address: The Dow Chemical Company, Midland, Michigan.

[4] Hartman and Borders, THIS JOURNAL, **59**, 2107 (1937).

[5] Goldschmidt and Udby, *Z. physik. Chem.*, **60**, 728 (1907).

[6] Hartman and Gassmann, THIS JOURNAL, **62**, 1559 (1940).

[7] Smith, *ibid.*, **62**, 1136 (1940); see also Hinshelwood, *J. Chem. Soc.*, 599 (1935).

Reactions of Nickel(II), Nickel(II,III), and Iron(III) Oxides in Liquid Ammonia[1]

BY ROLAND B. HOLT AND GEORGE W. WATT

Subsequent to the work of Moore and Watt[2] on reactions of certain oxides of iron and cobalt in liquid ammonia, analogous studies have been made on nickel(II), nickel(II,III), and iron (III) oxides. Since the experimental methods were essentially identical with those described previously,[2] only the conclusions arising from these latter experiments are included here.[3]

Experimental

Materials.—The commercial reagent grade oxides were dried at 110° before use and had the following compositions: *Nickel(II) oxide.* Calcd. for NiO: Ni, 78.57. Found: Ni, 78.55. *Nickel(II,III) oxide.*[4,6] Calcd. for Ni_3O_4: Ni, 73.35. Found: Ni, 73.85. *Iron(III) oxide.* Calcd. for Fe_2O_3: Fe, 69.94. Found: Fe, 70.03.

Reactions with Liquid Ammonia.—Nickel(II), nickel(II,III), and iron(III) oxides were found to be insoluble in and unreactive toward liquid ammonia at 25°. The oxides were recovered unchanged after agitation with ammonia over a period of twenty-four hours.

Reactions with Ammonium Salts.—Iron(III) oxide was recovered unchanged after treatment with liquid ammonia solutions containing a large excess of ammonium chloride or ammonium nitrate for twenty-six hours at 100°. Under the same conditions, 11.2% of a sample of nickel(II) oxide was dissolved by a liquid ammonia solution of ammonium chloride while less than 1% of the sample was dissolved when ammonium nitrate was employed. When treated similarly for a period of forty-eight hours, nickel(II,III) oxide reacted with ammonium nitrate solutions to form small quantities of nickel(II) oxide together with high yields of blue crystalline nickel(II) nitrate 6-ammonate.[6]

Anal. Calcd. for $Ni(NH_3)_6(NO_3)_2$: Ni, 20.5; NH_3, 35.7. Found: Ni, 20.1; NH_3, 35.5.

The analogous reaction with ammonium chloride solu-

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[1] Original manuscript received November 9, 1942.

[2] Moore and Watt, THIS JOURNAL, **64**, 2772 (1942).

[3] Attention is called to the fact that the experimental data and qualitative observations which led to the conclusions reported herein, and which were included in the original manuscript, may be obtained from the M.A. thesis (The University of Texas, June, 1942) of Roland B. Holt.

[4] Clark, Asburg and Wick, THIS JOURNAL, **47**, 2665 (1925).

[5] Howell, *J. Chem. Soc.*, **123**, 669 (1923); *cf.* Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green, and Co., New York, N. Y., 1937, Vol. XIII, p. 396.

[6] Ephraim, *Ber.*, **46**, 3106 (1913).